Photoionization of Alkylphenothiazines in Vesicles: Effects of the Alkyl Chain Length and the Vesicle Surface Charge

Masato Sakaguchi, Ming Hu, and Larry Kevan*

Department of Chemistry, University of Houston, Houston, Texas 77204-5641 *(Received: May 23, 1989)*

The photoionization of alkylphenothiazine (AP = alkylphenothiazine) in vesicles were observed by electron spin resonance (ESR) and electron spin echo modulation (ESEM) methods. Alkylphenothiazine derivatives including sodium 10-methylphenothiazinesulfonate (C_1PSO_3Na), sodium 10-dodecylphenothiazinesulfonate ($C_{12}PSO_3Na$), sodium 3-(10′-phenothiazinyl)propane-1-sulfonate (PC_3SO_3Na), sodium 6-(10′-phenothiazinyl)hexane-1-sulfonate (PC_6SO_3Na), and sodium 12-(10′-phenothiazinyl)dodecane-1-sulfonate ($PC_{12}SO_3Na$) were synthesized and used to study the effects of the alkyl chain length, the position of the sulfonate group, and the vesicle surface charge on the photoionization. A singlet ESR spectrum due to the alkylphenothiazine cation radicals (AP^+) was observed from rapidly frozen AP in dioctadecyldimethylammonium chloride (DODAC) or dihexadecyl phosphate (DHP) vesicles photoirradiated for 10 min with $\lambda > 300$ nm. In DODAC vesicles with a positive surface charge, the photoionization yield of $PC_{12}SO_3Na$ with a sulfonate group at the dodecyl chain end is higher than that of $C_{12}PSO_3Na$ with a sulfonate group on the phenothiazine ring. The photoionization yields of AP having the sulfonate group at the alkyl chain end in DODAC vesicles increase with decreasing alkyl chain length. The ESEM data support a correlation between the distance of PC_nSO_3Na (n = 3, 6, and 12) from the vesicle surface and the photoionization yield. The highest photoionization yield was obtained from PC_3SO_3Na, which has the shortest alkyl chain in this study and has the sulfonate group at the end of the propyl chain. The photoionization yield of AP in DHP vesicles with a negative surface charge was not changed by added alkyl chains or the position of the sulfonate group in AP. The results are discussed in terms of the alkyl chain length, the position of the sulfonate group, and the vesicle surface charge.

Introduction

Photoionization of molecules in micelle and vesicle assemblies has been used as a model system for light energy storage.[1-4] Such molecular assemblies allow compartmentalization of electron donors and acceptors relative to the solvent, which is usually water. Photoinduced net charge separation can be partially controlled by variation of the structural parameters of the molecular assembly such as surface charge,[5-9] headgroup variation,[5,8] alkyl chain length variation,[5,10] and addition of slightly water soluble molecules like alcohols and cholesterol, which modify the assembly surface.[11-14]

The photoproduced cation is paramagnetic so it can be monitored by electron spin resonance (ESR). This is most generally applicable in rapidly frozen solutions in which electron spin echo modulation (ESEM) spectroscopy[4] can also be applied. ESEM has provided structural information about the molecular nature of the surface modifications of the molecular assemblies. This has led to a general correlation between the net photoionization yield and the strength of the photoproduced-cation interactions with water at the assembly interface as measured by ESEM.[4,5]

In addition to micellar and vesicle surface modification to control the photoionization yield, it is possible to modify the electron donor or acceptor structure to achieve a measure of location control relative to the surfactant assembly interface and thus control the photoionization yield. This is done by adding variable-length alkyl chains to the electron donors and acceptors. ESEM provides a means of directly assessing the changes in interface localization as a function of alkyl chain length. This was first demonstrated with alkylmethylviologen electron acceptors in both vesicles and micelles[15] and that work has been extended.[16,17] Vesicles show stronger effects than micelles.

In the present study, the effects of alkyl chain length on alkylphenothiazine electron donors in vesicles is investigated by ESR and ESEM methods. Localization control by the alkyl chain length is found, but the effects are modified by the vesicle surface charge and the position of a sulfonate group incorporated into the phenothiazine.

Experimental Section

Materials. The following five alkylphenothiazine surfactants were prepared by a modified literature procedure.[18]

Sodium 10-Dodecylphenothiazinesulfonate ($C_{12}PSO_3Na$). Phenothiazine (6.5 g or 0.0177 M) in dry dimethyl sulfoxide (30 mL, dried with $LiAlH_4$) was treated with sodium hydride (0.8 g) under nitrogen atmosphere in the dark for 1 h to produce the N sodium salt. Then 1-bromododecane (5 mL) was added, and the solution was stirred for 24 h at room temperature to give *N*-dodecylphenothiazine, which was extracted with cyclohexane (~15 extractions). The cyclohexane solution was washed with deionized water and dried with $CaCl_2$ for 24 h. The cyclohexane was evaporated, and the solid product was redissolved in hexane/tetrahydrofuran (1:1 v/v) and purified on an active alumina column[19] (50 g, 80–200 mesh, 2-cm diameter) with hexane as the eluant. The eluted fractions were evaporated and the residue analyzed for *N*-dodecylphenothiazine by thin layer chromatography (flexible plates, Baxer Scientific; ethanol/hexane (3:7 v/v) as developer) with luminescent detection (280-nm excitation) and by ultraviolet absorption (λ_{max} = 255 and 310 nm). The total yield of *N*-dodecylphenothiazine was 4.5 g.

The purified *N*-dodecylphenothiazine (4 g) was dissolved in 10 mL of nitrobenzene and treated with chlorosulfonic acid (1 mL) at room temperature for 2 h to generate the sulfonate. Solid NaOH (0.5 g) was added to neutralize the excess acid, and the solution was stirred for 1 h and filtered and the solid washed with hexane several times to remove the nitrobenzene. The solid was recrystallized with 95 wt % ethanol. A pin-shape crystal was obtained. The ^1H NMR data (D_2O) show peaks at 0.85 ppm

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(CH_3), 1.20 ppm ($(CH_2)_{n-3}$), 3.85 ppm (CH_2N) and 6.80–8.00 ppm (phenothiazine proton), which are consistent with the literature data[20] for 10-dodecylphenothiazinesulfonate. The relative NMR peak areas agreed with these assignments. The UV absorption showed λ_{max} at 260 and 315 nm.

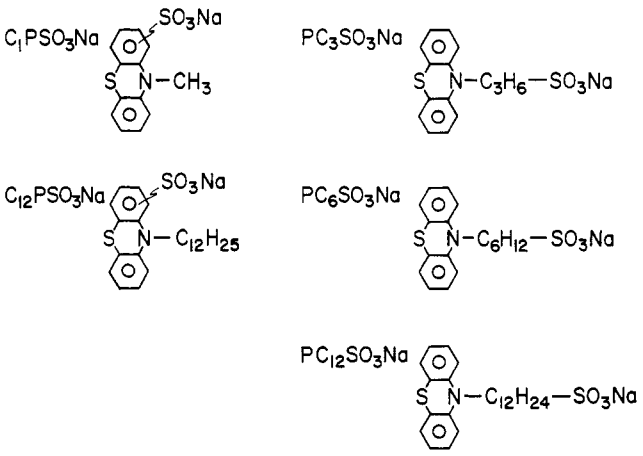
Sodium 10-Methylphenothiazinesulfonate (C_1PSO_3Na). Chlorosulfonic acid (4 g) was added to a solution of methylphenothiazine (5 g) in nitrobenzene (30 mL), and the solution was heated at 100 °C for 1 h for sulfonation. Then, solid NaOH (0.5 g) was added to neutralize the excess acid, and the solution was stirred for 1 h. The solvent was evaporated, and the solid residue was extracted with methanol. The filtrate was evaporated, and the solid product was recrystallized in 50 wt % ethanol. A water-soluble product was obtained. The UV absorption showed λ_{max} at 260 and 315 nm, the same as for $C_{12}PSO_3Na$.

Sodium 12-(10′-Phenothiazinyl)dodecane-1-sulfonate ($PC_{12}SO_3Na$). Sodium hydride (1.5 g) was added into a solution of phenothiazine (7.8 g or 0.034 M) in dry tetrahydrofuran (30 mL dried with $LiAlH_4$) and stirred for 1 h at room temperature to form the phenothiazine N sodium salt. A solution of 1,12-dibromododecane (16.7 g or 0.051 M) in tetrahydrofuran (30 mL) was added to the N sodium salt solution and stirred for 24 h at room temperature to form 12-(10′-phenothiazinyl)dodecyl bromide. This solution was filtered to remove solids, and the solvent was evaporated. A yellow viscous liquid was obtained. The ^1H NMR spectrum with a triplet at 3.90 ppm (CH_2N) and a triplet at 3.30 ppm (CH_2Br) shows that the yellow liquid contains the bromide product. Ethanol (5 mL) and a saturated aqueous solution of Na_2SO_3 (10 mL) were added to the yellow liquid and refluxed for 24 h for sulfonation. Then, the solvent was evaporated, the solid was washed with a mixture of tetrahydrofuran and hexane (1:4 v/v) several times to remove the unreacted bromide and the 12-(10′-phenothiazinyl)dodecyl side product. The solid residue was recrystallized from water. The ^1H NMR data (D_2O) show peaks at 1.10 ppm ($(CH_2)_{n-3}$), 1.32 ppm (CH_2CN), 2.5 ppm ($CH_2SO_3^-$), 3.90 ppm (CH_2N), and 6.80–8.00 ppm (phenothiazine proton), which are consistent with the literature data[20] for 12-(10′-phenothiazinyl)dodecane-1-sulfonate. The relative NMR peak areas agreed with these assignments. The UV absorption showed λ_{max} at 257 and 310 nm.

Sodium 6-(10′-Phenothiazinyl)hexane-1-sulfonate (PC_6SO_3Na). Sodium hydride (1.5 g) was added slowly to a solution of phenothiazine (7.8 g) in 30 mL of dry tetrahydrofuran. The solution was stirred for 1 h at room temperature to form the phenothiazine N sodium salt. A solution of 6.5 mL of 1,6-dibromohexane in 30 mL of dry tetrahydrofuran was added to the phenothiazine N sodium salt solution and stirred for 24 h at room temperature to form 6-(10′-phenothiazinyl)hexyl bromide. This solution was filtered to remove solids, and then the solvent was evaporated. A yellow viscous liquid was obtained that contained crude 6-(10′-phenothiazinyl)hexyl 1-bromide. The ^1H NMR data show triplets at 3.70 ppm (CH_2N) and at 3.10 ppm (CH_2Br). The yellow liquid was dissolved in 5 mL of tetrahydrofuran and 10 mL of saturated sodium sulfite aqueous solution. This solution was refluxed for 10 h for sulfonation. Then, the solvent was evaporated, and the solid was washed with tetrahydrofuran to extract the product. Adding hexane to this tetrahydrofuran solution precipitated the product. This product was further purified by a crystallization from ethanol (95 wt %). The ^1H NMR (D_2O) data show peaks at 1.1 ppm ($(CH_2)_n$), 1.3 ppm (CH_2CN), 2.5 ppm (CH_2N), 3.90 ppm (CH_2N), and 6.8–8.0 ppm (phenothiazine proton). The relative NMR peak areas agreed with these assignments. The UV absorption showed λ_{max} at 255 and 310 nm.

Sodium 3-(10′-Phenothiazinyl)propane-1-sulfonate (PC_3SO_3Na). A solution of 5 g of phenothiazine in 20 mL of dry tetrahydrofuran was added to a suspension of 1.5 g of NaH in 20 mL of dry tetrahydrofuran. The phenothiazine N sodium salt was formed by stirring for 1 h at 50 °C. The solution was cooled to room temperature, and 5 g of 1,3-dibromopropane in 10 mL of dry tetrahydrofuran was added slowly and stirred for 1 h to form 3-(10′-phenothiazinyl)propyl bromide. The resulting solution was filtered to remove solids. The solution was evaporated to remove solvent, and the residue was washed by petroleum ether to remove excess 1,3-dibromopropane. Crude 3-(10′-phenothiazinyl)propyl bromide was obtained. The crude 3-(10′-phenothiazinyl)propyl bromide was dissolved in 5 mL of tetrahydrofuran and added to a saturated aqueous solution of sodium sulfite and refluxed for 1 h to form 3-(10′-phenothiazinyl)-propanesulfonate. The solvent was evaporated from this solution, and the residue was extracted with 95 wt % ethanol. The ethanol solution was evaporated to remove the solvent to leave a crude product with some side product 3-(10′-phenothiazinyl)propylene. The side product was removed by washing the solid with acetone several times. Then, the product was recrystallized in 95 wt % ethanol. The ^1H NMR (D_2O) data show peaks at 2.0 ppm (CH_2CN), 2.5 ppm (CH_2N), 3.95 ppm (CH_2N), and 6.5–7.5 ppm (phenothiazine proton). The UV absorption showed λ_{max} at 254 and 303 nm.

TABLE I: Structures of Alkylphenothiazines



The molecular structures are summarized in Table I.

Vesicles. Dihexadecyl phosphate (DHP) was purchased from Sigma Chemical Co. and was used without further purification. Dioctadecyldimethylammonium bromide (DODAB) was purchased from Eastman Chemicals and purified by recrystallization from acetone. A methanol/chloroform (70:30 v/v) solution of DODAB was passed through an ion exchange resin type AG2X8, 20–50 mesh from Biorad Laboratories. The eluent containing DODAC was evaporated, and the solid residue was recrystallized two times from acetone/water (95:5 v/v). Tris(hydroxymethyl)aminomethane (TRIS) and 2 N hydrochloric acid were purchased from Aldrich (Gold Label, 99.9+%) and Sigma Chemical Co. Water was triply distilled as described elsewhere.[21] Deuterium oxide (D_2O) was obtained from Aldrich (99.8 atom % D).

Apparatus. Sonications of vesicle solutions were carried out by using a Fisher Model 300 sonic dismembrator operated at 35% relative output power with a 4-mm-o.d. microtip under nitrogen atmosphere. DODAC vesicles in triply distilled water and in D_2O were formed by sonication for 15 min at 53 ± 2 °C.[17,22] DHP vesicles in 20 mM TRIS buffer solution adjusted to pH = 7.8 with hydrochloric acid were formed by sonication for 20 min at 71 ± 2 °C.[16,17,23] After sonication, each alkylphenothiazinesulfonate solution was added, and the sample was introduced into 2-mm-i.d. by 3-mm-o.d. Suprasil quartz tubes, allowed to stand for 1 h at room temperature, and then rapidly frozen and stored in liquid nitrogen. These procedures after sonication were carried out within 2 h. The respective concentrations of alkylphenothiazinesulfonate and surfactants were 0.5 and 18 mM.

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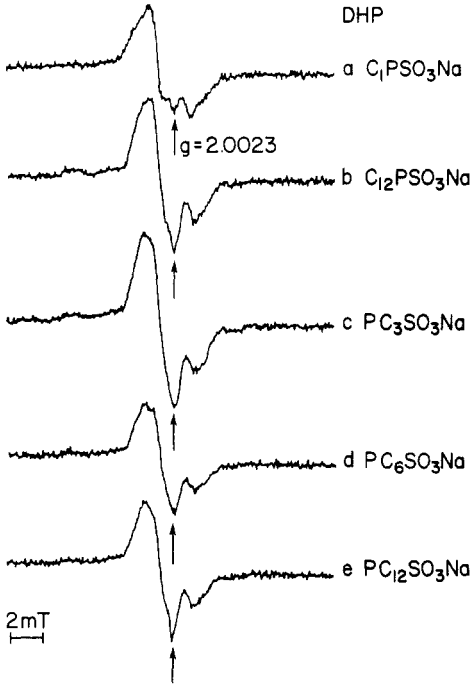

Figure 1. ESR spectrum at 77 K from various alkylphenothiazines in DHP vesicles after 10 min of photoirradiation with a WG320 filter ($\lambda > 300$ nm). The arrows indicate AP^+ radicals.

Photoirradiations were carried out at 77 K with 300-W Cermax xenon lamp (LX 300 UV) with a power supply from ILC Technology. The light passed through a 10-cm water filter and a glass filter (Corion Shott glass filter WG320, $\lambda > 300$ nm; or Corning glass filter no. 7-54, $240 < \lambda < 410$ nm).

ESR spectra were recorded with a Bruker ESP300 spectrometer at X-band with 100-kHz magnetic field modulation at 77 K at 0.2-mW microwave power to avoid power saturation. The magnetic fields were measured with a Varian E-500 nuclear magnetic resonance gaussmeter, and the microwave frequencies in the 9-GHz range were directly measured with a Hewlett-Packard 5350 B microwave frequency counter.

Two-pulse electron spin echo spectra were observed at 4.2 K at 9 GHz and about 330 mT with a home-built spectrometer.[24]

Results and Discussion

No ESR spectrum was observed from the alkylphenothiazines in DHP vesicles before photoirradiation. All of the samples photoirradiated with $\lambda > 300$ nm were pink, which is characteristic of alkylphenothiazine cation radicals (AP^+).[25,26] Each ESR spectrum is similar (Figure 1). The ESR spectrum from PC_3SO_3Na in DHP photoirradiated with $\lambda > 300$ nm is shown in Figure 2a. Since no ESR spectrum was observed from DHP alone irradiated with the WG320 filter ($\lambda > 300$ nm), photoirradiation was carried out with a Corning 7-54 filter ($240 < \lambda < 410$ nm). Then, a broad ESR singlet spectrum ($g_0 = 2.0024$) was observed from DHP alone (Figure 2b). No color was observed. The water solvent for DHP has no absorption band in the range of $240 < \lambda < 410$ nm. Therefore, the broad singlet is assigned to DHP surfactant radicals (DH), but the structure is not determined. The peak position with the arrow in Figure 2b coincides with the peak position with the arrow in Figure 2a and suggests that there is a DH radical contribution in Figure 2a. This was subtracted by adjusting the spectral intensity of Figure 2b and subtracting it from Figure 2a. This gave the spectrum in Figure 2c with $g_0 = 2.0059$, which is assigned to the PC_3SO_3Na cation radical. This is confirmed by the same spectrum found for irradiated (WG320 filter) PC_3SO_3Na in frozen aqueous solution (Figure 2d). This assignment is consistent with the g factors reported for cation radicals of alkylphenothiazine derivatives such as $g = 2.0052$ for 10-ethylphenothiazine,[27] $g = 2.0052$ for 10-methylphenothiazine,[27] $g = 2.0053$ for 10*H*-phenothiazine,[28] and $g = 2.0053$ for 2-methoxy-10*H*-phenothiazine.[29]

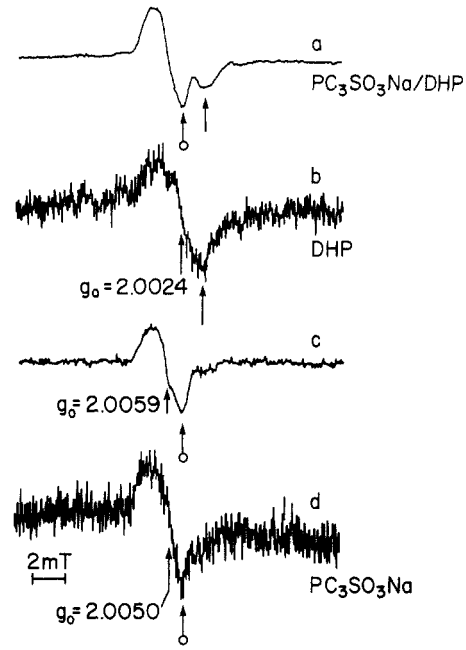

Figure 2. ESR spectra at 77 K from (a) PC_3SO_3Na in DHP vesicles after 10 min of photoirradiation with a WG320 filter ($\lambda > 300$ nm), (b) DHP vesicles only after 10 min of photoirradiation with a Corning 7-54 filter ($240 < \lambda < 410$ nm), (c) the radical cation from PC_3SO_3Na after subtraction of the radical from DHP (see text), and (d) the radical cation from PC_3SO_3Na in frozen aqueous solution photoirradiated for 10 min with a WG320 filter. Arrows with and without circles indicate the peaks due to AP^+ and DH radicals, respectively.

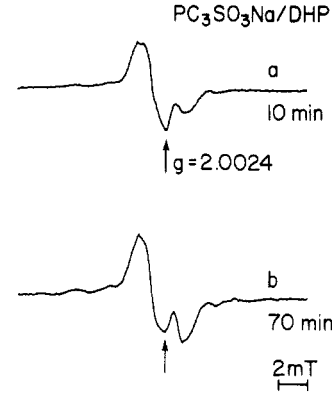

Figure 3. ESR spectra at 77 K from PC_3SO_3Na in DHP vesicles after photoirradiation for 10 and 70 min. Arrows indicate the peaks due to AP^+.

The peak position on each ESR spectrum from alkylphenothiazinesulfonate in DHP (Figure 1) indicated with arrows is assigned to AP^+. Also each sample is pink, which is characteristic of AP^+.[25,26] Therefore, each ESR spectrum shown in Figure 1 is assigned to the superposed spectra of AP^+ and DH radicals.

The ESR spectral changes of PC_3SO_3Na in DHP vesicles photoirradiated with a WG320 filter ($\lambda > 300$ nm) were observed versus irradiation time (Figure 3). The total intensity increased with the irradiation time; however, the intensity of AP^+, indicated

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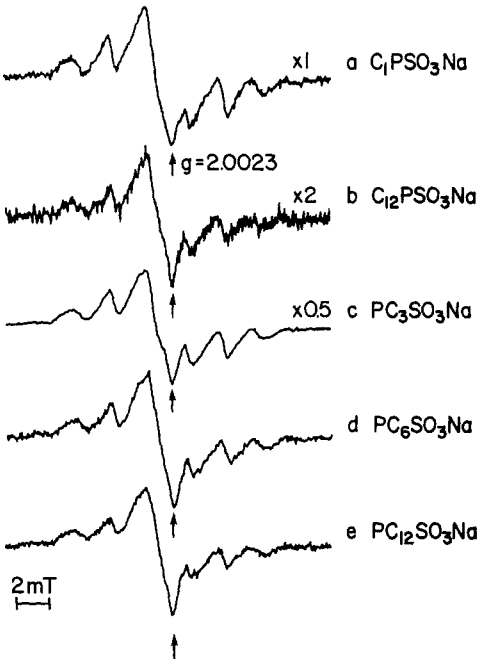

Figure 4. ESR spectra at 77 K from various alkylphenothiazines in DODAC vesicles after 10 min of photoirradiation with a WG320 filter. The arrows indicate AP^+ radicals.

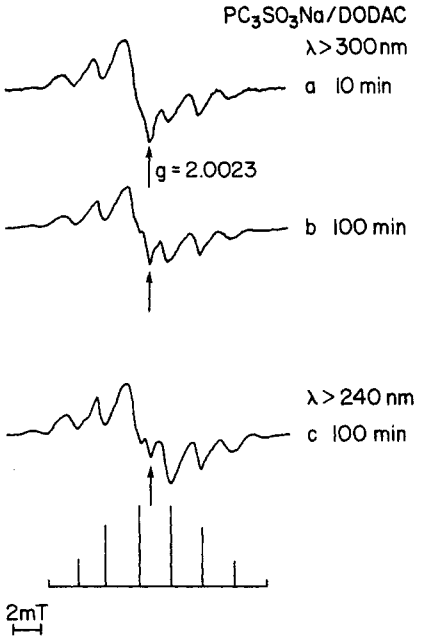

Figure 5. ESR spectra at 77 K from PC_3SO_3Na in DODAC vesicles after photoirradiation for (a) 10 min, (b) 100 min with a WG320 filter, and (c) 100 min with a Corning 7-54 filter. The stick diagram shows an idealized octet spectrum of the surfactant radical. Arrows indicate AP^+ radicals.

by arrows, remained about constant with irradiation time. No ESR spectrum was observed from DHP only irradiated with a WG320 filter. It is suggested that DH radicals are produced by photoinduced radical conversion from AP^+ as found previously.[17]

The ESR spectra observed from various alkylphenothiazines in DODAC vesicles irradiated with a WG320 filter ($\lambda > 300$ nm) for 10 min are shown in Figure 4. All samples are slightly pink. The peak position indicated by arrows in each spectrum indicates AP^+. Before photoirradiation, no ESR spectrum was observed from alkylphenothiazinesulfonates in DODAC vesicles. Also, no ESR spectrum was observed from DODAC vesicles only, even after 70 min of irradiation. Therefore, the peak in each ESR spectrum is assigned to AP^+.

The ESR spectral changes of PC_3SO_3Na in DODAC vesicles photoirradiated with a WG320 filter were also observed versus irradiation time (Figure 5a,b). The total intensity increased with irradiation time; however, the relative intensity of AP^+ decreased as shown by the arrows in Figure 5. After photoirradiation for 100 min with a Corning 7-54 filter ($240 < \lambda < 410$ nm), the peak due to AP^+ almost disappears (Figure 5c), and an octet spectrum that has the intensity ratios 1:5:9:12:13:10:5:1 and hyperfine splitting 2.2 mT is observed. The pink of AP^+ is absent. The octet spectrum is in fairly good agreement with the intensity ratios 1:5:11:15:15:11:5:1 and hyperfine splitting 2.2 mT of DODAC radicals (DAC) produced by radical conversion with alkylviologen cation radicals.[17] Since no ESR spectrum was observed from photoirradiated DODAC vesicles only, the results suggest that the DAC radical is produced by radical conversion from AP^+ *during* the photoirradiation.

Thus, AP^+ is produced by the photoirradiation of alkylphenothiazinesulfonate in DHP or DODAC vesicles with a WG320 filter ($\lambda > 300$ nm), and part of the AP^+ converts to surfactant radicals (DH or DAC) *during* the photoirradiation as in (1). The total ESR intensity therefore indicates the net photoionization yield.

$$AP^+ + RH \xrightarrow{h\nu} AP^+H + R^\bullet \qquad (1)$$

The relative net photoionization yields of alkylphenothiazinesulfonate in DHP or DODAC vesicles after 10 min of irradiation are plotted against the alkyl chain length of AP in Figure 6. These yields correspond to less than 10% of the total phenothiazine being photoionized and are proportional to initial yields. The yields are normalized to the yield of PC_3SO_3Na in DODAC vesicles. The

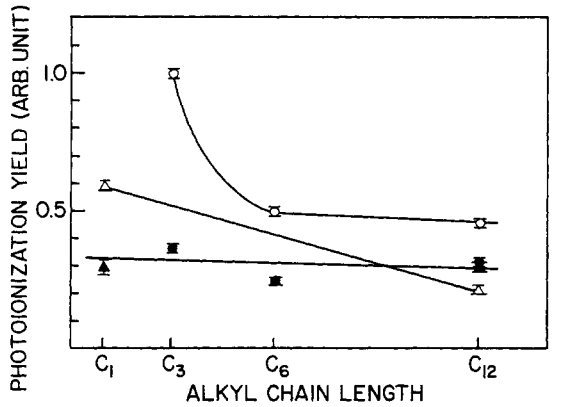

Figure 6. Photoirradiation yield at 77 K from alkylphenothiazines in vesicles for 10 min of irradiation with a WG320 filter versus the alkyl chain length. The symbols (○) and (△) show PC_nSO_3Na (n = 3, 6, 12) and C_mPSO_3Na (m = 1, 12) in DODAC vesicles while (●) and (▲) show PC_nSO_3Na and C_mPSO_3Na in DHP vesicles. The error bars indicate the average deviation of three or more measurements.

photoionization yields of alkylphenothiazinesulfonate in DHP vesicles do not change with alkyl chain length or the position of the sulfonate group in AP. However, in DODAC vesicles, the photoionization yield of $PC_{12}SO_3Na$ is higher than that of $C_{12}PSO_3Na$.

Hidaka et al. have reported[20] that the fluorescence intensity of $C_{12}PSO_3Na$ is 30 times larger than that of $PC_{12}SO_3Na$ generated by laser excitation. This suggests that $C_{12}PSO_3Na$ and $PC_{12}SO_3Na$ are located differently with respect to the vesicle interface as independently indicated by our results.

The low photoionization yield of $C_{12}PSO_3Na$ is likely due to the decrease of electron density on the nitrogen atom by the sulfonate group bonded to the phenothiazine ring.[29] The electron density on the nitrogen atom in $PC_{12}SO_3Na$ is likely unaffected by the sulfonate group bonded at the dodecyl chain end.

The photoionization yield of PC_nSO_3Na (n = 3, 6, 12) increased with a decrease in alkyl chain length. This can be explained by a model in which the alkylphenothiazines are located deeper into the vesicle the longer the alkyl chain. The high yield of PC_3SO_3Na is then due to the shortest distance from PC_3SO_3Na to the positively charged interface of the DODAC vesicles. The photoionized

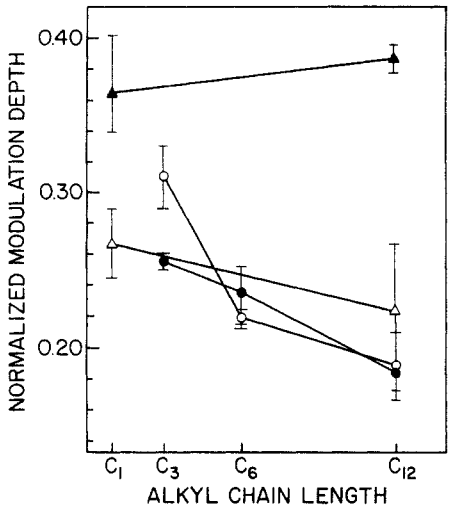

Figure 7. Normalized deuterium modulation depth from alkylphenothiazines in vesicles for 10 min of irradiation with a WG320 filter versus the alkyl chain length. The symbols (○) and (△) show PC_nSO_3Na (n = 3, 6, 12) and C_mPSO_3Na (m = 1, 12) in DODAC vesicles, while (●) and (▲) show PC_nSO_3Na and C_mPSO_3Na in DHP vesicles. The error bars indicate the average deviation of two or more determinations.

electrons from PC_3SO_3Na can more easily escape across the positive vesicle interface than those from longer alkyl chain phenothiazines.

This model is supported by the ESEM data. The normalized modulation depths[30] are plotted against the alkyl chain length of AP in Figure 7. The locations of PC_nSO_3Na (n = 3, 6, and 12) in DODAC vesicles are in a less hydrated region with increasing alkyl chain length consistent with being located deeper into the vesicle relative to the interface. The same trend is shown for C_mPSO_3Na (m = 1, 12) with only two data points.

In the DHP vesicles, the C_mPSO_3Na molecules are located in a more hydrated region than the PC_nSO_3Na molecules. In addition, the hydration of PC_nSO_3Na increases with decreasing alkyl chain length. In spite of these differences in hydration, the photoionization yields are constant. In DHP vesicles with a negative surface charge, the photoionization yields of AP are not affected by the location of the AP or the position of the sulfonate group in the AP. This suggests that the photoionized electrons from AP are impeded from escaping from DHP vesicles by the negative surface charge, and therefore, the back-reaction from AP^+ to AP is promoted. The vesicle surface charge seems to be more effective than the location of the sulfonate moiety for net photoionization.

The effective factors in photoionization of alkylphenothiazinesulfonates in vesicles are the surface charge of the vesicles and the distance of the alkylphenothiazinesulfonates from the vesicle surface. The highest photoionization yield is obtained for the shortest phenothiazine moiety to interface distance and a positive vesicle interface charge.

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Registry No. $C_{12}PSO_3Na$, 106049-51-8; C_1PSO_3Na, 124177-19-1; $PC_{12}SO_3Na$, 74339-97-2; PC_6SO_3Na, 101199-39-7; PC_3SO_3Na, 101199-38-6; $Br(CH_2)_{11}CH_3$, 143-15-7; $Br(CH_2)_{12}Br$, 3344-70-5; $Br(CH_2)_6Br$, 629-03-8; $Br(CH_2)_3Br$, 109-64-8; 10*H*-phenothiazine, 92-84-2; 10-dodecyl-10*H*-phenothiazine, 73487-07-7; 10-methyl-10*H*-phenothiazine, 1207-72-3; 10-(12-bromododecyl)-10*H*-phenothiazine, 80548-36-3; 10-(6-bromohexyl)-10*H*-phenothiazine, 101199-33-1; 10-(3-bromopropyl)-10*H*-phenothiazine, 92357-95-4.

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Photophysics and Photochemistry of Tris(2,2′-bipyridyl)ruthenium(II) within the Layered Inorganic Solid Zirconium Phosphate Sulfophenylphosphonate

Jorge L. Colón, Chao-Yeuh Yang, Abraham Clearfield,* and Charles R. Martin*

Department of Chemistry, Texas A&M University, College Station, Texas 77843 *(Received: May 30, 1989; In Final Form: July 31, 1989)*

The photophysics and photochemistry of tris(2,2′-bipyridyl)ruthenium(II) ($Ru(bpy)_3^{2+}$) adsorbed into the layered solid zirconium phosphate sulfophenylphosphonate are described. The decay kinetics of the metal complex are shown to depart from first-order behavior. Albery's model of dispersed kinetics, which assumes a continuous distribution of rate constants, is used to explain the decay kinetics. The oxidative quencher methylviologen (MV^{2+}) is shown to react with $Ru(bpy)_3^{2+}$ in ZrPS via a combined dynamic and quasi static (sphere of action) quenching mechanism.

Introduction

Much of the effort in solar energy research has focused on the use of electron-transfer reactions to convert and store solar energy. To meet this goal the energy-releasing back reaction has to be suppressed.[1-3] Recently, several strategies for suppressing the back reaction and enhancing the charge separation efficiency have been devised.[1-3] These new strategies make use of interfaces, surfaces, micelles, polyelectrolytes, and other heterogeneous microenvironments to obtain efficient charge separation.

The layered zirconium phosphates[4] are heterogeneous systems which could prove useful as media for solar energy conversion. Zirconium phosphates are acidic, inorganic, ion-exchange materials having a layered structure.[4] These materials have potential applications as catalysts, ion exchangers, solid electrolytes, and hosts for various intercalants.[5-7] Organic derivatives of α-zirconium phosphate (α-ZrP, which has the formula $Zr(HPO_4)_2 \cdot H_2O$) have

* To whom correspondence should be addressed.

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