calculations. The second effect on increasing this resonance integral is to increase the difference between the two carbon spin densities without significantly changing the N spin densities. This can be illustrated by the results of Table II. Comparison of the figures of row 6 with those of row 17 shows that inclusion of Fe–N interaction has changed the ratio of the N spin densities from 1.19 to 1.23 and that of the C spin densities from 1.97 to 2.79. The N spin densities therefore provide a measure of the overall electron-withdrawing or -donating ability of the metal moiety and the C spin densities of the π back-bonding. For the pentacyano complex reasonable agreement is obtained with parameters such as those in row 14 of Table II. These parameters indicate that the pentacyanoferrate group is overall less electron withdrawing than a proton. Presumably this is the result of a balance between σ withdrawal and π donation. The fit for the hydride radical is less satisfactory as illustrated by the final two rows of Table II. Qualitatively, since the N spin densities are very similar, the electron-withdrawing ability of the metal group is quite similar to that of a proton or methyl cation and since the C spin densities are very different the π-donating ability is high. These are reasonable electronic properties for this group.

Conclusion

The *N*-methylpyrazine radical shows considerable promise as a useful spin-labeled ligand. Its ease of preparation and air stability suggest that an extensive coordination chemistry may be developed. It will no doubt reduce metal ions in oxidation states susceptible to easy reduction but there are prospects for forming complexes with a fairly wide variety of metals. The spin density distribution, and hence the ESR spectrum, has been shown to be sensitive to metal complexation. The calculations show that the effects of σ metal–ligand bonding differ from the effects of π metal–ligand bonding. The former is reflected in the change of nitrogen Coulomb integral and the latter in the resonance integral required for the metal–ligand interaction. The ESR spectra obtained are fairly complex but, now that computers are readily available for the rapid simulation of spectra using a range of coupling constants, this is a less serious disadvantage than it was some years ago. Information on metal–ligand bonding can of course be obtained by using a wide variety of spectroscopic techniques but very few allow direct comparison with molecular orbital calculations in the manner made possible by the use of spin-labeled ligands.

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Registry No. Pyrazine radical anion, 34512-20-4; 1,4-dihydropyrazine radical cation, 35862-59-0; 1,4-dihydro-1,4-dimethylpyrazine radical cation, 78147-93-0; 1,4-dihydro-1-methylpyrazine radical cation, 93638-38-1; *N*-methylpyrazine radical, 97613-77-9; (1,4-dihydro-4-methylpyrazin-1-yl)pentacyanoiron(III) free radical, 97570-81-5; (1,4-dihydro-4-methylpyrazin-1-yl)hydridotetracyanoiron(III) free radical, 97570-82-6.

Surfactant and Hydrophobic Derivatives of *trans*-Stilbenes as Probes of Vesicle and Micelle Solubilization Sites. Studies Using Fluorescence and Photoisomerization as Probes[1]

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Abstract: An investigation of the fluorescence and photoisomerization of several surfactant *trans*-stilbene derivatives in aqueous micelles and vesicles is reported. The temperature dependence of ϕ_f was determined for several media over the range 5–70 °C. The results present a picture of similar micellar solubilization sites for the *trans*-stilbene chromophore in every case; the micelle is "seen" by the stilbene as a moderately viscous fluid medium with slightly higher values for ϕ_f and slightly reduced $\phi_{t\rightarrow c}$ compared to nonviscous homogeneous solutions. For vesicles considerably more complex behavior is observed. Generally ϕ_f is considerably higher than in solution and $\phi_{t\rightarrow c}$ is much lower. Several, but not all, of the surfactant and hydrophobic stilbenes show a sharp sensitivity in ϕ_f as a function of T when passing through T_c, the vesicle phase transition temperature. Arrhenius plots for the process competing with fluorescence as a function of temperature show relatively high values for E_a and log A, above T_c, consistent with the high temperature phase providing a microenvironment for the stilbene chromophore like a viscous solvent. Below T_c, the variation of ϕ_f gives much lower values for E_A and log A which suggest escape from the fluorescence state is "order limited" rather than viscosity dominated. These results suggest that the low-temperature phase of vesicles presents an environment for the stilbene chromophore more like an inclusion complex than a fluid medium. The effect of cholesterol addition on DODAC vesicles containing the stilbenes is to increase fluidity below T_c and to effectively increase viscosity above T_c.

The structure of assemblies formed by self-assembly of surfactant or amphiphilic molecules, as well as the reactivity of solutes incorporated into these assemblies, has been the subject of extensive investigations.[3-15] A great deal of work has focused on the structure and properties of micelles; although considerable controversy has centered around both theoretical and experimental

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investigations of micellar structure, there seems to be emerging a clear picture that molecules solubilized in simple detergent micelles experience an environment that is relatively fluid and quite polar.[6,7,10-12] There is considerable evidence that the driving force for solubilization of solutes by micelles is a hydrophobic effect, similar to the micellization process itself, and that most molecules solubilized in detergent micelles are effectively in an interfacial environment.[6,16,17]

In contrast to micelles, bilayer vesicles or liposomes are structurally well characterized in terms of size and shape as well as to the organization of the component lipid or detergent molecules both above and below the phase transition temperature, T_c.[18-24] There has been a great deal of recent interest in vesicles or liposomes as potential reaction media due to their resemblance to the lipid portion of biomembranes as well as their ability to selectively solubilize or entrap a wide variety of dissimilar reagents.[25] A number of applications have been proposed, ranging from drug delivery to selective charge separation. The ability to polymerize vesicles with both hydrophobic and hydrophilic monomers has added still another element of versatility and possible utility for these media.[25-30] Among several questions that remain to be answered concerning the properties of vesicles, one of the most important concerns the "compartmentalization" or solubilization of hydrophobic and hydrophilic reagents within different regions of the bilayer structure. It is already clear that a variety of charged or extremely hydrophilic reagents do not penetrate the vesicle and can be either entrapped within an interior water pool, restricted to the outer, or distributed among both bulk and entrapped water. Other reagents clearly have limited solubility but can penetrate the bilayer structure with reasonable facility and frequency.

The question of solubilization sites within bilayer vesicles is clearly a complicated one if one considers results obtained in a number of recent studies. It is clear, for example, that for a given surfactant vesicle, several different sites can be identified: at the water pool–head group interface of both monolayers there are relatively hydrophilic sites where surface-active molecules frequently are solubilized.[31] For complex surfactants such as phospholipids there exists the possibility of solubilization within the bilayer, but in a region of intermediate hydrophobicity, where polar groups are at least partially "solvated" by water but there is also some of the structural organization associated with the "crystalline" hydrocarbon chains below one phase transition temperature. Finally there should exist within the vesicle solubilization sites of moderate-to-high hydrophobicity and moderate order in both monolayers; clear evidence for residence of various solutes in these sites has been obtained.[1,31,32] Major questions that remain unanswered concern the gradation of sites available and the ability to predict where a given solute will reside. The dynamics of solutes within the vesicle also remain largely undetermined; here a major question concerns the possibilities for interaction of solutes of differing hydrophobicity (or polarity) within the vesicle interior.

In the present paper we report a study of the photophysical behavior of several surfactant and hydrophobic compounds containing the *trans*-stilbene chromophore. Although many fluorescent probes have been used in a number of different ways to probe the properties of micelles and vesicles,[33-47] the *trans*-stilbene chromophore offers some particular advantages. Its photochemistry and photophysics have been well studied and can be regarded as reasonably well-understood.[48-64] The photobehavior of *trans*-stilbene and related molecules is particularly sensitive to environmental effects, especially solvent viscosity.[48,60,65-67] Unlike most fluorescent probes employed thus far, with the notable exception of parinaric acid,[43-47] the stilbene chromophore is elongated and rodlike such that its molecular dimensions do not differ appreciably from those of a polymethylene chain in an extended, all-trans configuration. In fact, studies of some of the stilbenes used in this study in films at the air–water interface indicate that the water-insoluble surfactant stilbenes are remarkably similar

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in their surfactant properties to straight chain fatty acids such as stearic or arachidic acid.[68]

Our studies with the stilbenes show that incorporation into detergent micelles, either cationic or anionic, results in the stilbenes experiencing a moderately viscous fluid environment which appears to differ little for the various stilbenes (as evidenced by fluorescence and isomerization behavior) regardless of structure or location of the stilbene chromophore within the surfactant limit. In contrast we find that in several vesicles there is a wide variation in the photochemical reactivity of the different stilbenes which suggests the presence of a variety of solubilization sites, especially in the "low-temperature" phases below T_c. More importantly, the observation of sharp differences in fluorescence as a function of temperature above and below T_c provides an indicator that the stilbenes are incorporated into "guest sites" similar to inclusion complexes in the gel phase while in the high-temperature phase the microenvironment is that of a viscous but fluid solution.

Experimental Section

Materials. DL-α-Dipalmitoylphosphatidylcholine (DPL), dicetyl phosphate (DCP), and tetrabutylammonium chloride were purchased from Sigma and used without further purification. Lithium chloride was obtained from Fisher and used as received. Sodium dodecyl sulfate (SDS, Biorad, electrophoresis grade) was recrystallized from ethanol. Cetyltrimethylammonium bromide (CTAB, Aldrich) was recrystallized twice from acetone. Cetyltrimethylammonium chloride (CTAC) was made by passing CTAB in methanol through a column filled with anion exchange resin (Biorad, chloride form) twice, then recrystallizing from acetone. Dioctadecyldimethylammonium chloride (DODAC) was made in a similar way from dioctadecyldimethylammonium bromide (DODAB, Eastman) except the recrystallization were from ethyl acetate. Cholesterol was purchased from ICN and used as received. Methylcyclohexane (Baker, Photrex spectrophotometric grade) was used without further purification. Water was triply distilled, once from alkaline permanganate, once from sulfuric acid.

Stilbene Probes. Stilbene was recrystallized and zone refined. Surfactant stilbenes (S4A, S6A, S7A, S10A, S12A, S16A, 6S4A, and 4S6A) were prepared as reported previously.[68,69] The hydrophobic stilbene, 4S4, was prepared from *p*-butylbenzaldehyde (Kodak) via reduction (lithium aluminum hydride), bromination (PBr_3), and Wittig condensation with *p*-butylbenzaldehyde; mp 108–109 °C after recrystallization from ethanol.

Solutions. All solutions were 1.0×10^{-5} M in surfactant stilbene unless otherwise noted. Typically, the appropriate volume of a chloroform (Baker, spectrophotometric grade) solution 1.0×10^{-4} M in surfactant stilbene probe was evaporated under a nitrogen stream and then used to prepare the working solutions.

Micelles. In a flask coated with a surfactant stilbene probe (*vide supra*), the appropriate amount of SDS or CTAC was sonicated (Branson bath-type sonicator) with triply distilled water until a clear solution was obtained. Concentration of surfactant was 0.03 M.

Vesicles. The appropriate amount of stock solution of probe and surfactant were added to a flask. For DPL or DODAC vesicles, triply distilled water was added. For DCP vesicles, 0.85 equiv of NaOH was added in triple distilled water. These suspensions were then sonicated with a Heat Systems Model 220F sonicator microtip at a power setting of 3–4 for 10–15 min above their phase transition temperatures. The vesicle solutions were then centrifuged to remove unsuspended surfactant and titanium particles from the probe. Concentration of surfactant was 0.001 M.

Fluorescence Quantum Yields. Solutions were prepared as described above and then diluted to the same optical density at 310 nm. A reference solution with a known quantum yield of fluorescence was also prepared with the same optical density. For most solutions, the reference was *trans*-stilbene in methylcyclohexane or methylcyclohexane:isohexane 2:1 at 25 °C, which has a quantum yield of 0.05.[50] Because of the higher fluorescence quantum yield for the series MSNA in DPL, the reference used was S10A in DPL at 25 °C, which was calculated to have a quantum yield of fluorescence of 0.46. Fluorescence spectra were measured with excitation at 310 nm. The entire emission band was integrated between 325 and 450 nm to obtain the relative intensities of the solutions. The fluorescence quantum yields were calculated by multiplying the fluorescence quantum yield of the reference by the ratio of the integrated intensities of the sample and the reference. Temperatures were controlled by a Haake A81 temperature bath and monitored by a thermistor probe, accurate to ±0.2 °C.

Isomerization Quantum Yields. Solutions were degassed by three freeze–pump–thaw cycles and then sealed in Pyrex ampules. The samples were irradiated with a medium pressure mercury lamp (Hanovia, 450 W) in a merry-go-round apparatus, using filters to select the 313-nm line. Isomerizations were carried out to 5–10% conversion. Potassium ferrioxalate actinometry was used, and the amounts of isomeric stilbenes formed were determined by UV spectrometry and/or by high-pressure liquid chromatography. A Hewlett-Packard 8450A UV-Vis Diode Array spectrophotometer was used to measure photoisomerization conversions.

Instrumentation. Ultraviolet spectra were recorded either on a Perkin Elmer 576ST, IBM 9430, or Hewlett-Packard 8450A UV–visible spectrophotometers. Fluorescence spectra were recorded either on an SLM 8000 or SPEX 111CM spectrofluorimeter. High-performance liquid chromatography was performed with a Perkin-Elmer Series 1 pump, a Varian Vari-Chrom variable UV–visible detector, and a Whatman Partisil PAC 10/25 normal bonded phase column. Fluorescence lifetime measurements were obtained by single photon counting methods using a PRA Fluorescence Lifetime Instrument, interfaced to a PDP 11/23 microcomputer.

Results

Some of the surfactant and hydrophobic stilbenes used in this study are drawn in extended configurations in Scheme I; to provide a comparison, the surfactants used in this study are also shown. The surfactant stilbenes are designated as *M*S*N*A or S*N*A with *N* and *M* denoting the number of carbons in the chains attached to the 4 or 4,4′ positions of the *trans*-stilbene (S) chromophore. Thus 4S4 is di-*n*-butylstilbene while S4A is *trans*-stilbene butyric acid. From Scheme I it is clear that the *trans*-stilbene chromophore is equivalent to several methylene groups in lengths. Thus S10A is about equivalent in length to DPL or CTAC while S7A is about the same in length as SDS. Other compounds not shown, S16A and S12A, are much longer than the surfactants used in this study while S4A is much shorter. The intrachain derivatives 6S4A, 4S6A, and 4S4 should be comparable in length to S10A and hence to DPL, DCP, and CTAC. With the exception of S4A and, to a lesser extent, S6A, the stilbenes used in this study are of very low solubility in water; however, they are readily incorporated into the aqueous surfactants used by fairly standard techniques as outlined in the Experimental Section.

At the concentration levels used in this study (total [stilbene] $\sim 1 \times 10^{-5}$ M; stilbene/surfactant ratio $\leq 1/100$), all of the stilbenes show "monomeric" absorption spectra very similar to that of *trans*-stilbene in organic solvents. In the temperature studies carried out in both micellar and vesicle solutions the range covering 10–60 °C is wide enough so that some small spectral changes are observed. Figure 1 compares spectra of S10A in DPL vesicles at 60, 45, 35, and 5 °C. At the two upper temperatures no differences are apparent; at the lower temperatures the spectra are slightly less intense, but sharper.

Fluorescence of all of the stilbenes studied in the micellar and vesicle solution shows characteristic monomer fluorescence. However, the intensity, lifetimes, and efficiencies for the fluorescence vary widely with specific stilbene and medium. Table I lists fluorescence efficiencies for the surfactant and hydrophobic stilbenes at 25 °C in several different micelle and vesicle solutions. The efficiencies span the range from a few percent to unit quantum yield; in general, the highest values for each stilbene are measured in neutral DPL vesicles while the efficiencies in micelles are mostly only slightly higher than in homogeneous (methylcyclohexane) solution. The fluorescence in any medium is strongly dependent on temperature; typical plots of ϕ_f vs. T are shown in Figures 2 and 3. For the micelle solutions the plot of ϕ_f vs. T is generally a smooth curve; for several of the stilbenes in vesicles the plots show a sharp discontinuity near the reported phase transition temperature, T_c. For example, the DPL solutions, for which plots are shown in Figure 3, show a sharp decrease whose midpoint is very close to the reported T_c of 41.4 °C.[70] A similar discontinuity is noted for vesicles formed from the cationic surfactant DODAC;

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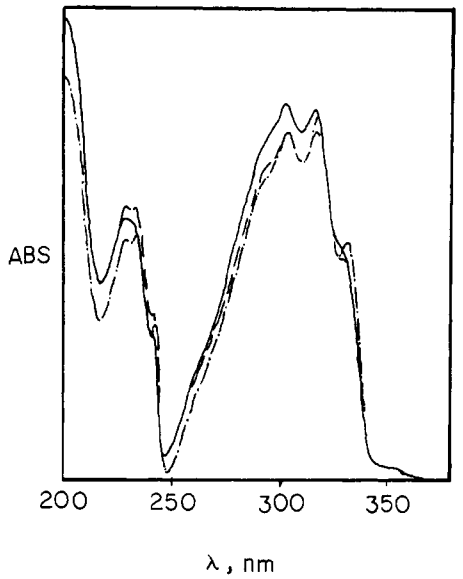

Figure 1. Effect of temperature (°C) on absorption spectrum of S10A in dipalmitoyllecithin vesicles: —, 60 and 45; - - -, 35; - · -, 5.

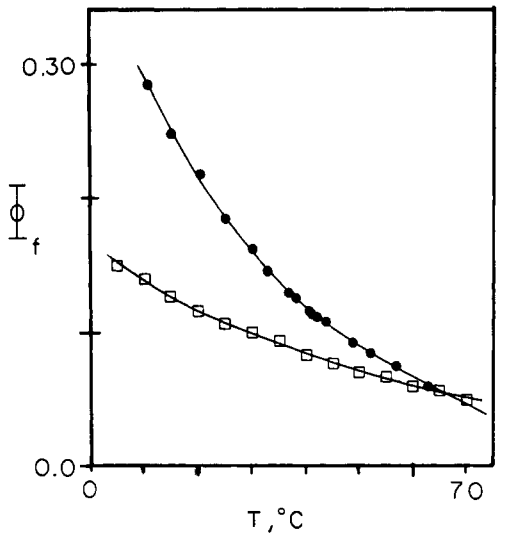

Figure 2. Quantum yield of fluorescence vs. temperature: □, S6A in methylcyclohexane; ●, S16A in CTAC micelles.

Table I. Fluorescence Quantum Yields for Stilbene Derivatives in Different Media at 25 °C[a]

	ϕ_f					
compd	MCH[b]	SDS[c]	CTAC[d]	DCP[e]	1:1 DCP/DPL[e]	DPL[e]
S	0.05[f]	0.07		0.12	0.19	0.19
S4A	0.08	0.12	0.17	0.20	0.20	0.19
S6A	0.09	0.12	0.16	0.43	0.21	0.38
S7A	0.09	0.09	0.16	0.37	0.18	0.42
S10A	0.08	0.12	0.17	0.39	0.24	0.46
S12A		0.14	0.18			0.39
S16A	0.06		0.20		0.26	
6S4A	0.21	0.39		0.66	0.76	0.96
4S6A	0.25	0.38		0.65	0.78	0.91
2S8A	0.21	0.30		0.56	0.62	0.76
4S4	0.20	0.37		0.58	0.70	0.79

[a] Fluorescence quantum yields are the same within experimental error (max, ±0.01) for samples undegassed or deaerated with argon. [b] Methylcyclohexane solution, data from ref 69. [c] 0.03 M sodium dodecyl sulfate in water. [d] 0.03 M CTAC in water. [e] Total surfactant concentration 0.005 M in water. [f] Data from ref 51.

here as shown for S10A in Figure 4 the discontinuity centers near 42 °C, slightly above the reported T_c of 37 °C.[71] Addition of

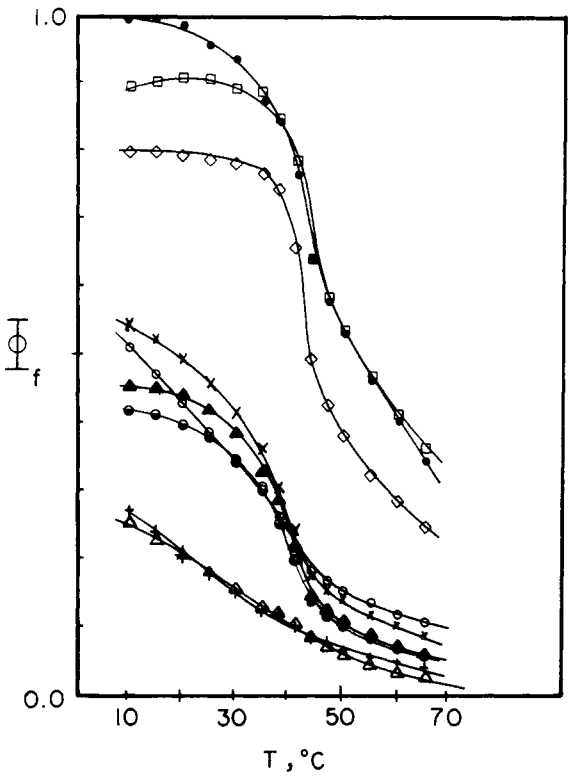

Figure 3. Quantum yield of fluorescence of surfactant stilbenes in dipalmitoyllecithin vesicles vs. temperature: △, *trans*-stilbene; +, S4A; ⊖, S6A; ▲, S7A; ×, S10A; ○, S12A; ◇, 4S4; □, 4S6A; ●, 6S4A.

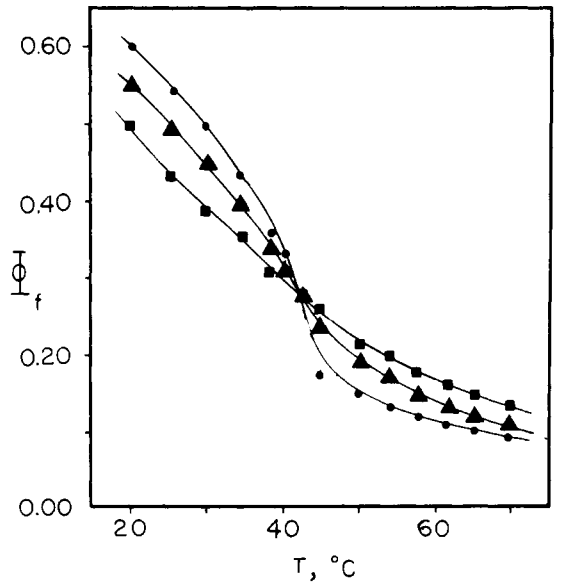

Figure 4. Effect of addition of cholesterol on the plot of quantum yield of fluorescence vs. temperature for S10A in DODAC vesicles.

cholesterol as shown in Figure 4 has the interesting effect of reducing ϕ_f at temperatures below T_c and increasing ϕ_f at higher temperatures.

The fluorescence of the stilbenes in charged vesicles is influenced by addition of salts which contain counterions that can associate with the surfactant headgroups and modify the vesicle–water interface. Table II lists intensity changes observed by adding LiCl and tetra-*n*-butylamonium chloride to solutions of several surfactant stilbenes in DCP vesicles. Increases are observed with both salts, but the effect is much more pronounced with the hydrophobic tetraalkylammonium cation. The effect noted here

(71) Kano, K.; Romero, A.; Djermouni, B.; Ache, H.; Fendler, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 4030.

Scheme I

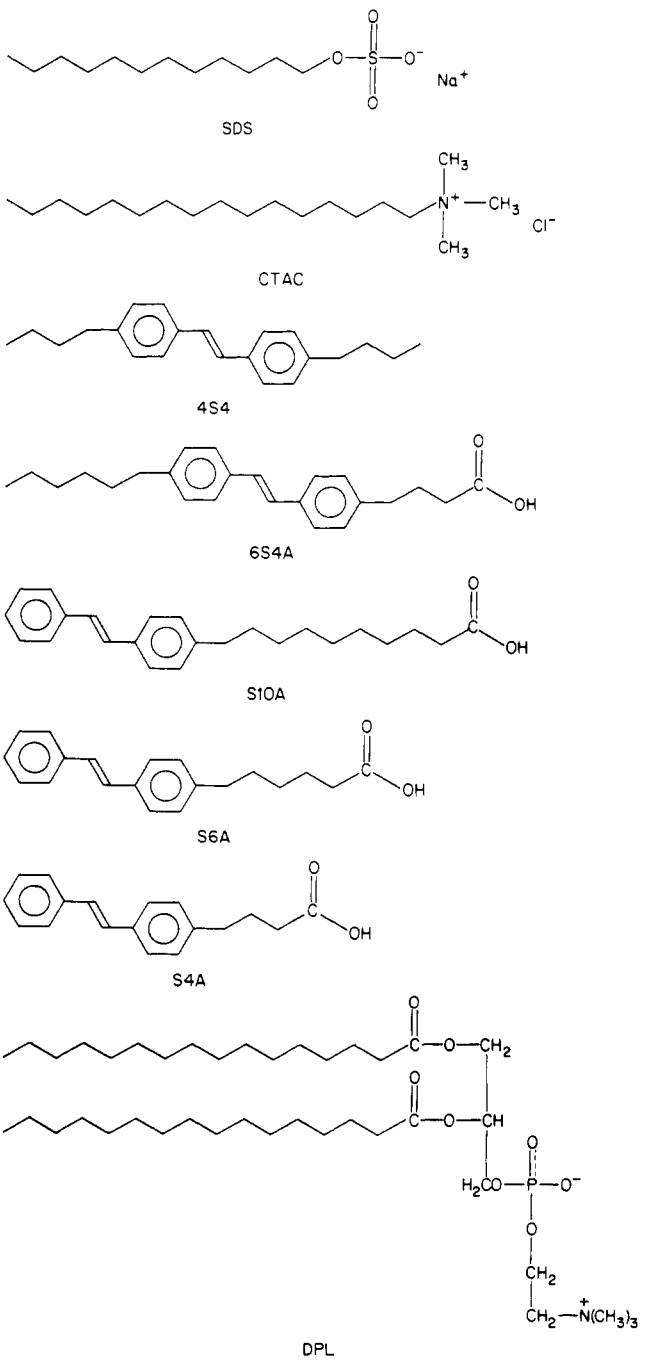

Table II. Relative Fluorescence Intensity of Surfactant Stilbenes in DCP Vesicles in the Presence of Added Salts[a]

		relative fluorescence intensities[b]			
salt	[salt], M	S4A	S10A	6S4A	4S4
LiCl	0.0	1.00	1.00	1.00	1.00
	5.0×10^{-4}	1.03	0.98	1.00	0.99
	1.0×10^{-3}	1.04	0.99	1.04	0.99
	2.0×10^{-3}	1.12	1.02	1.03	0.96
	5.0×10^{-3}	1.77[c]	1.27[c]	1.15[c]	0.97[c]
Bu_4NCl	0.0	1.00	1.00	1.00	1.00
	5.0×10^{-4}	1.52	1.59	1.31	1.03
	1.0×10^{-3}	1.56	1.65	1.30	1.02
	2.0×10^{-3}	1.64	1.66	1.31	1.01
	5.0×10^{-3}	1.73	1.71	1.37	1.04

[a] [Surfactant stilbene] = 1.0×10^{-5} M, [DCP] = 0.005 M, [NaOH] = 0.01 M. Intensities are relative to the intensity without added salt. [b] Intensities are obtained by integrating the entire fluorescence spectrum and then correcting for dilution. [c] Samples became turbid for [LiCl] $\geq 5.0 \times 10^{-3}$ M.

Table III. Fluorescent Lifetimes for Stilbene Derivatives in Different Media at 25 °C[a,b]

	τ_f, ps			
compd	MCH	SDS	DCP	DPL
S4A	210 ± 25	260 ± 80	490 (72%)	570 (35%)
			1,740 (28%)	1,400 (65%)
S10A	210 ± 30		540 (25%	700 (44%)
			1,600 (75%)	1,400 (56%)
6S4A	500	740 ± 30	1,710 ± 200	1,780
4S4	420 ± 40	680	1,700	1,850

[a] Concentrations as in Table I. [b] Data fit best to a single exponential unless two values are listed; numbers in parentheses give weights of the different compounds.

Table IV. Quantum Yields for Trans → Cis Photoisomerization of Substituted Stilbenes in Different Media[a]

	$\phi_{t\rightarrow c}$				
compound	MCH[b]	SDS	DCP	DCP/DPL	DPL
S4A	0.48	0.44	0.38	0.38	0.15
S10A	0.50		0.33	0.34	0.15
S16A	0.50	0.40		0.37	
6S4A	0.37		0.07	0.05	0.014
4S6A	0.36		0.08	0.06	
4S4	0.34		0.09		0.016

[a] Concentrations as in Table I; data are for 25 °C. [b] Data from ref 69.

is reminiscent of the differential binding of inorganic and organic ions observed in an earlier study with anionic micelles and vesicles.[16,17] Not surprisingly, the increase in fluorescence observed is most pronounced with the short-chain S4A and least pronounced with the hydrophobic 4S4.

Fluorescent lifetimes for several of the surfactant stilbenes in a number of different media have been measured by the single photon counting technique. The lifetime of *trans*-stilbene itself is quite short (ca. 80 ps) in fluid solution and below the effective resolution of the facility used; however, the lifetimes of several of the surfactant stilbenes are sufficiently long to be measured in surfactant solution. As listed in Table III single exponential decay is observed for several of the stilbenes in MCH, micellar SDS, and, in most cases, DPL vesicles. The values in the latter medium are close for 6S4A and 4S4 to the limiting lifetime of 1.7 ns calculated for *trans*-stilbene. In contrast, for anionic DCP vesicles, S4A and S10A give a better fit for two-exponential decay; the two components resolved consist of comparable fractions with a short lifetime similar to that obtained in aqueous SDS and a longer lifetime comparable to those obtained in DPL.

The trans → cis photoisomerization of the surfactant stilbenes was studied in several micellar and vesicular media. Quantum yields for the isomerization in aqueous surfactant solutions were determined by absorption spectroscopy by using standard analytical techniques and equations.[69] Quantum yields for isomerization in methylcyclohexane were determined independently by absorption spectral changes and by HPLC separation of cis and trans isomers; the two methods gave good agreement. Table IV gives quantum yields for several stilbenes in a series of micellar and vesicle solutions. The isomerization yields generally follow inversely the changes previously noted in fluorescence; accordingly isomerization yields for all of the stilbenes decrease in the range $\phi_{MCH} > \phi_{SDS} > \phi_{DCP} > \phi_{DPL}$.

The falloff in isomerization in the two vesicle solutions studied is even faster than would be "predicted" by the fluorescence efficiencies. For stilbene it has been determined that the major process competing with fluorescence is conversion to a twisted singlet from which isomerization occurs.[48] This state decays to cis and trans ground states with nearly equal probability; the fraction cis formed is $R = 0.55$.[48,49] R values for the several surfactant stilbenes in different media are listed in Table V. Although these compounds generally give R values close to that for stilbene in MCH and micellar media, there is a pronounced

Table V. Decay Factors, "R", for Surfactant Stilbenes in Different Media at 25 °C[a]

compd	R			
	MCH	SDS	DCP	DPL
S4A	0.52	0.50	0.48	0.19
S10A	0.54		0.54	0.28
S16A	0.53	0.47		
6S4A	0.47		0.21	0.20
4S6A	0.48		0.23	
4S4	0.43		0.21	0.08

[a] Calculated using data from Tables I and IV; R defined as $\phi_{t\rightarrow c}/(1 - \phi_f)$.

decrease in R in vesicles, particularly in DPL.

Discussion

The photochemistry and photophysics of *trans*-stilbene in solution have been extensively studied.[48-64] Despite some earlier disputes,[50-54] there has been general acceptance of a "singlet mechanism" for the direct isomerization.[48] Upon direct excitation of *trans*-stilbene (eq 1) an essentially transoid excited singlet is produced; this state may decay by fluorescence (eq 2, k_f), intersystem crossing (eq 3, k_{is}), or twisting to an approximately perpendicular state, $^1p^*$ (eq 4, k_{tp}), which in homogeneous solutions subsequently decays to trans and cis ground states.[48] For stilbene and some alkyl stilbenes k_{is} is much smaller than k_f (3.86×10^7 s^{-1} vs. 5.89×10^8 s^{-1})[48] such that twisting and fluorescence account for the great majority of excited state decay. While k_f is largely independent of temperature or viscosity, k_{tp} governs an activated

$$^1t \xrightarrow{h\nu} {}^1t^* \quad (1)$$

$$^1t^* \xrightarrow{k_f} {}^1t \quad (2)$$

$$^1t^* \xrightarrow{k_{is}} {}^3t^* \quad (3)$$

$$^1t^* \xrightarrow{k_{tp}} {}^1p^* \quad (4)$$

process which is sensitive to both temperature and medium viscosity.[48,60,65-67] Thus over wide ranges of temperature and viscosity it has been demonstrated that fluorescence and isomerization are coupled in a completely complementary manner.[48,60] Since $k_{is} << k_f$ and k_{tp} is the only activated process, the expression for the quantum yield of fluorescence, eq 5, can be combined with the

$$\phi_f = \frac{k_f}{k_f + k_{is} + k_{tp}} \approx \frac{k_f}{k_f + k_{tp}} \quad (5)$$

Arrhenius equation to yield eq 6.[34,48,60] of $\ln((1/\phi_f) - 1)$ vs. $1/T$;

$$\ln(1/\phi_f - 1) = \ln\left(\frac{A}{k_f}\right) - \frac{E_{tp}}{RT} \quad (6)$$

the value of E_{tp}, the activation energy for twisting, has been measured by Saltiel and co-workers to be 3.53 kcal/mol while the log A_{tp} = 12.6.[48] That the surfactant stilbenes, especially those with only a single alkyl chain, behave similarly to *trans*-stilbene in homogeneous solution has been demonstrated. In the present study we find that ϕ_f for several of these compounds decreases monotonically with temperature increase in nonviscous organic solvents; for S6A in methylcyclohexane a plot of $\ln((1/\phi_f) - 1)$ vs. $1/T$ shows good linearity over the range 5–70 °C and the slope and intercept yield values E_a = 3.47 kcal/mol and log A = 12.2, respectively.

Saltiel and co-workers have studied the viscosity dependence of fluorescence and isomerization; their studies indicate that in viscous solutions the measured activation energy is the sum of the intrinsic barrier E_{tp} and a medium-imposed barrier E_v.[48,72] The rate constant observed for twisting in a viscous or ordered medium, k_{obsd}, is thus a product of intrinsic and medium-dependent terms, and the overall preexponential term is the product of the respective A terms for each process.[72] Saltiel and co-workers have found that both the activation energies and A factors measured for the "composite" process increase with an increase in medium viscosity and that there is an isokinetic relationship between log A and E_v.[48] Since the "expanded" Arrhenius relationship leads to $A_{obsd} = A_t \cdot A_v$ where A_t is the factor associated with twisting and A_v is that associated with viscosity, quite large A_{obsd} values are expected with bulky groups in viscous media; Saltiel[48] has found log A_{obsd} values in the range of 16–18.5 for stilbene and related molecules such as *trans*-1,1′-biindanylidene in glycerol. These values correspond quite closely with those for the surfactant stilbenes in vesicles (vide intra). Given this relatively high and quantitatively definable relationship among stilbene fluorescence, isomerization, and medium viscosity, it would be reasonable to expect that the stilbenes used in this study should furnish a fairly precise picture of the local order viscosity experienced by the *trans*-stilbene chromophore in different sites of the various media.

Table VI. Activation Parameters Extracted from "Arrhenius Plots" of Substituted Stilbene Fluorescence According to Equation 6

compd	medium	temp range, °C	E_A, kcal/mol	log A
S6A	MCH	5–70	3.47 ± 0.13	12.2 ± 0.09
S6A	SDS	10–30	5.93 ± 0.86	13.9 ± 0.64
S16A	CTAC	10–65	6.5 ± 0.11	14.2 ± 0.08
S	DPL	10–30	6.0 ± 0.21	13.8 ± 0.16
S4A		10–30	4.5 ± 0.14	12.7 ± 0.10
S6A		10–35	3.5 ± 1.29	11.6 ± 0.96
S7A		10–35	3.6 ± 1.51	11.6 ± 1.12
S10A		10–35	5.2 ± 0.90	12.7 ± 0.67
S4A		50–65	10.5 ± 0.98	17.1 ± 0.65
S6A		50–65	8.7 ± 0.22	15.6 ± 0.15
S7A		50–65	8.9 ± 0.53	15.7 ± 0.35
S10A		50–65	7.2 ± 0.52	14.5 ± 0.34
S12A		50–65	6.5 ± 0.67	13.9 ± 0.44
S		50–65	7.6 ± 0.66	15.1 ± 0.44
4S4		50–65	8.9 ± 0.70	15.0 ± 0.47
6S4A		50–65	10.8 ± 0.63	16.0 ± 0.42
4S6A		50–65	10.1 ± 0.60	15.6 ± 0.40
S6A	1:1 DCP/DPL	5–35	2.2 ± 0.43	10.8 ± 0.32
S6A	1:1 DCP/DPL	45–70	7.6 ± 0.99	14.7 ± 0.65
S7A	DCP	40–70	13.8 ± 1.14	18.7 ± 0.76
S6A	DODAC	5–30	3.0 ± 0.39	11.4 ± 0.29
S6A	DODAC	45–70	6.3 ± 0.31	13.9 ± 0.21
S10A	DODAC/cholesterol	2:1 20–70	7.5 ± 0.20	14.4 ± 0.14

Micellar Solutions of the Surfactant Stilbenes. As shown in Table I, the surfactant stilbenes used in this study show slightly higher fluorescence efficiencies in anionic (SDS) and cationic (CTAC) aqueous micellar solutions compared to homogeneous nonviscous organic solvents. Comparing the two micellar solutions it can be noted that ϕ_f is slightly higher in each case for CTAC solutions than for SDS. The temperature dependence (see Figure 2) typically shows a monotonic decrease in ϕ_f with increase in T similar to that observed in homogeneous solution. Plots according to eq 6 show good linearity over ranges between 10 and 70 °C. The typical parameters (Table VI) extracted from linear regression analysis according to eq 6 assuming $k_f = 5.89 \times 10^8$ s^{-1} [48] are slightly higher for both E_a and log A than for stilbene or the surfactant stilbenes in homogeneous organic solvents. For example, S6A in SDS gives E_a = 5.93 kcal/mol and log A = 13.9 while for S16A in CTAC we obtain E_a = 6.04 kcal/mol and log A = 13.8. These values are consistent with the findings of Saltiel and D'Agostino[60] in earlier studies of *trans*-stilbene in homogeneous solutions of varying viscosity; the points obtained in our studies for micelles fall close to the isokinetic plot of E_v vs. log A_{tot} developed by these workers. The "picture" one obtains then of SDS and CTAC micelles from investigation of the surfactant stilbene fluorescence is one of a solution having an effective viscosity somewhat greater than for nonviscous homogeneous aqueous or organic solutions. The fact that no important variations in ϕ_f with position of the stilbene chromophore in the surfactant "backbone" together with the lack of an unusual "A" factor in

(72) For other discussions of viscosity and intrinsic barriers to isomerization see ref 65–67.

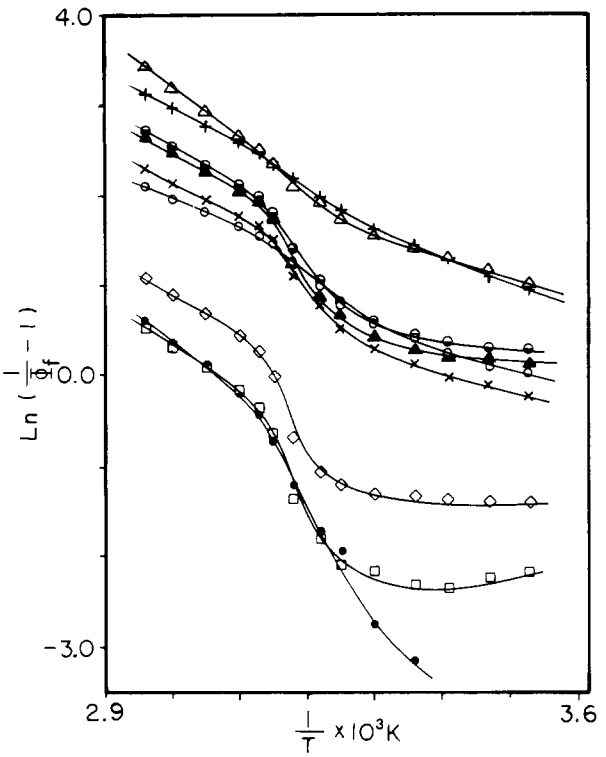

Figure 5. Arrhenius plot according to eq 6. Surfactant stilbenes in DPL; same symbols as Figure 3.

the Arrhenius plot suggests that relatively little order is present in either micelle or at least that any order present is not "experienced" by the stilbene chromophore.

The relatively high quantum efficiencies for $\phi_{t\rightarrow c}$ and nearly "normal" decay ratios (Tables IV and V) for S4A and other surfactant stilbenes reinforce the inferences made above on the basis of fluorescence measurements. These photochemical and photophysical investigations of the surfactant stilbenes say nothing about the location of the stilbene "probe" in the micelle; however, the fact that nearly all of the compounds studied are water insoluble indicates that solubilization is certainly "within" the micelle or at the micelle–water interface and not in the aqueous solution.

Fluorescence and Isomerization of Surfactant Solutions in Vesicles or Liposomes. Although these studies have included investigations of the surfactant stilbenes in the presence of several bilayer assembly-forming surfactants including anionic (DCP), cationic (DODAC), mixed, and neutral (DPL) reagents, the most extensive studies have been made with neutral phospholipid (DPL) vesicles. Other studies have established that the protocol used for preparation of these vesicles gives predominantly small unilamellar vesicles or liposomes.[73] The various surfactant stilbenes show monomeric absorption and fluorescence spectra and, as noted in the Results section, give the highest fluorescence yields in DPL of all of the aqueous surfactants studied. Figure 3 shows clearly the rather pronounced contrast between different stilbene derivatives in DPL. S4A and *trans*-stilbene show a temperature dependence fairly similar to that of micelles; only a slight suggestion of a change in slope near the reported DPL phase transition temperature can be detected. A plot of ln $((1/\phi_f) - 1)$ vs. $1/T$ (Figure 5) shows only a slight bend at the point corresponding to $1/T_c$, and the parameters extracted from the "low-temperature" part of this plot (Table VI) are quite similar to those for the single-chain stilbenes in micelles. Possible explanations for this behavior, especially when contrasted with that of the other stilbenes (vide infra), could be that these compounds either are not solubilized in the ordered hydrocarbon region of the bilayer or that they reside in a hydrocarbon region in which there is considerable disorder or fluidity even below T_c. It is perhaps most consistent to conclude that the *trans*-stilbene chromophores in TS and S4A are "solubilized" in DPL in an interface region which, while of moderate viscosity, lacks the order or crystallinity commonly associated with the low-temperature or gel form of bilayer vesicles.

The fact that S4A gives at least two fluorescence lifetime components (Table III) suggests that solubilization is probably not in a single "site" in the low-temperature form of DPL and DCP. This is of course true for other single-chain stilbenes such as S10A and suggests that some caution must be used in evaluating ϕ_f variations with T since it would appear reasonable that the composite nature of ϕ_f might result in nonsimple relationships according to eq 6. However, for S10A and the other single-chain stilbenes we see behavior, as outlined below, that apparently offers a consistent picture of the solubilization process.

In rather pronounced contrast to TS and S4A, the single-chain stilbenes having 5–15 polymethylene units show substantially higher values for ϕ_f at temperatures below T_c and, perhaps more striking, a sharp discontinuity centered near T_c. Somewhat similar behavior is noted for the intrachain stilbenes 4S4, 4S6A, and 6S4A; these compounds have considerably higher fluorescence efficiencies at all temperatures, but the sharp drop in efficiency occurs at the same point. The discontinuity in ϕ_f for all of these stilbenes is also clearly seen in the "Arrhenius" plot. The similar sensitivity of ϕ_f to the phase transition temperature for the several different stilbenes suggests *generally* similar solubilization sites for the stilbene chromophore in each case. Given the compatibility of the stilbene chromophore in effective size and shape with an all-trans hydrocarbon chain demonstrated in monolayer studies,[68] it seems most consistent to assume that the stilbene chromophore in these compounds is mostly solubilized in an ordered hydrocarbon array with its long axis generally parallel to the extended chains of the host DPL molecules.

Several aspects of the temperature dependence of ϕ_f in DPL for the different stilbenes are noteworthy. First, the Arrhenius plots (Figure 5) for the stilbenes discussed above show the most pronounced change in the apparent intercept or log A factors. Thus for several of the single-chain stilbenes this plot shows two roughly parallel lines with a displacement upward near T_c. For S10A, a compound which nearly matches DPL in length of the "extended" conformation, the slopes above and below T_c give activation energies of 7.4 and 4.6 kcal/mol, respectively. This *increase* in E_a on going above T_c is compensated for by an increase in log A from 12.2 to 14.5. In terms of $\Delta S^{\ddagger}$ this is an approximately 10.6 cal/(mol·K) increase in the overall activation entropy between the two phases. Similar small increases in E_a are measured for other single-chain stilbenes on going from the low- to high-temperature phases with a concomitant increase in log A.

The relatively low values for E_a measured for the single-chain surfactant stilbenes suggest that the effect of solubilization within the semicrystalline gel phase of the vesicle below T_c cannot be simply treated as a viscosity effect analogous to the behavior in micelles or moderately viscous homogeneous solutions. If we assume (the fluorescent lifetime data in DPL (Table III) suggest this to be a reasonable assumption) that these stilbenes reside mostly in a single solubilization site or in a "family" of very similar sites in the low-temperature phase, the tendency of both ϕ_f and the "Arrhenius plot" to level off at low temperatures below T_c is consistent with "locking" of the stilbene chromophore into a site where the probability of twisting is order-limited rather than viscosity controlled. This idea is reinforced by the temperature dependence of fluorescence for 4S4 and 4S6A. For both of these compounds fluorescence reaches an effective limiting value near, but slightly lower than unity at ca. 30 °C. Interestingly 6S4A, which would be anticipated to have the stilbene chromophore somewhat closer to a less ordered interface region, shows high ϕ_f values but these do not level off until lower temperatures are attained. For 6S4A the limiting ϕ_f measured is unity; a unit fluorescence yield for this compound has also been observed when it is incorporated into an amylose inclusion complex.[74] The origin

(73) Mizutani, T.; Whitten, D. G., submitted for publication.

(74) Suddaby, B. R.; Dominey, R. M.; Whitten, D. G. *Can. J. Chem.*, in press.

of the lower-than-unit fluorescence efficiencies for 4S4 and 4S6A is uncertain; since $\phi_{t\rightarrow c}$ yields for these compounds are extremely low in the low-temperature phase of DPL it cannot be assumed that eq 4 is responsible for the measured inefficiencies. It is possible that intersystem crossing (eq 3) could account for the less than unit efficiency but there appears no reason why k_{is} should be higher for these dialkylstilbenes than for 6S4A. The behavior of the various stilbenes studied above T_c is generally similar and appears reasonably straightforward. Plots of ln $((1/\phi_f) - 1)$ vs. $1/T$ (Figure 5) show good linearity for each of the compounds, and the activation parameters extracted from these plots show the high values of log A and E_a (Table VI) anticipated for a moderately viscous homogeneous solution. The values of log A are comparable to those obtained by Saltiel for S in glycerol (vide supra). In fact, a plot of log A_{obsd} vs. $E_a - 3.53$ for S and the single-chain stilbenes shows good linearity with a slope of 0.767 and an intercept of 11.67. These values are within experimental error of those obtained by Saltiel and co-workers[48] for S in viscous homogeneous solvent and thus indicate in the high-temperature domain that the isokinetic correlation exists for solutes "dissolved" in the vesicle. Interestingly the activation energies measured for the single-chain surfactant stilbenes are highest for S4A and decrease as the distance between the charged carboxyl group and the stilbene chromophore increases. The significance of this change should probably be regarded as uncertain, but it appears reasonable that association of the carboxyl group with the polar head group region of the DPL can render the twisting process slightly more difficult. The intrachain stilbenes also show good linearity in the "high-temperature" Arrhenius plots (Figure 5); values for log A and E_a are slightly higher for these compounds, and the points for log A vs. $(E_a - 3.53)$ do not correlate as well with the isokinetic plot discussed above. Nonetheless, the values obtained are in good accord with these stilbenes "experiencing" a viscous but homogeneous solution-like microenvironment in DPL at temperatures above T_c.

Other vesicles which have been investigated include anionic DCP, mixed anionic–neutral DCP:DPL (1:1), and cationic DODAC. For the stilbenes studied in these media somewhat related differences are observed between low and high temperatures. For several single-chain stilbenes in DCP it has been found that plots of ϕ_f vs. T are generally flat or show only slight variations in ϕ_f over the range 5–30 °C; a steady decrease in fluorescence occurs in all cases with increasing temperature from 35–70 °C with no apparent discontinuity. The "Arrhenius" plots of the high-temperature data show good linearity and give similar values for S5A, S6A, S7A, and S10A; the "high-temperature" plot for S7A, for example, gives E_A = 13.8 kcal/mol and log A = 18.7, values similar to those obtained for the single-chain stilbenes above T_c for DPL. S4A shows a plot of ϕ_f vs. T similar to micellar solution or DPL and it appears that here, as with DPL, the short-chain stilbene is not well incorporated into the vesicle interior but is rather in a more open or interfacial site. Other studies have suggested that DCP does not have a well-defined T_c or that it may occur at or near 60 °C.[75] Our results suggest, in contrast, that T_c may be much lower probably in the range 30–35 °C and that no clearcut change occurs near 60 °C. The fact that E_a is higher above 40 °C and that E_a and log A show "normal" values in this region suggests again that in DCP at these temperatures the stilbene is in a microenvironment resembling a viscous homogeneous solution. The small variation of ϕ_f at lower temperatures is consistent with a more rigid environment in which decay away from the requisite geometry for fluorescence is order-limited.

Relatively similar behavior is encountered for S5A, S6A, and S7A in the mixed system 1:1 DCP/DPL. Here there is a monotonic decrease in ϕ_f with increase in T over the range 5–70 °C. However, there is a noticeable change in the slope near 40 °C suggesting that T_c should be in this range. Qualitatively similar behavior to that observed for DPL solution is observed in the plots of ln $((1/\phi_f) - 1)$ vs. $1/T$; for S6A, for example, the "low"-temperature points give E_A = 2.2 kcal/mol and log A = 10.9 while the values of ϕ_f at temperatures above 45 °C give E_A = 7.6 kcal/mol and log A = 14.7.

Cationic DODAC vesicles show behavior consistent with DPL and the mixed DPL/DCP vesicles. For S6A a monotonic decrease in ϕ_f with increase in T is observed with a discontinuity near 35–40 °C. Once again the "Arrhenius plots" give lower values for E_A and log A at temperatures below T_c; for S6A we obtain E_A = 2.95 and 6.34 kcal/mol and log A = 11.4 and 13.9 below and above 40 °C, respectively. As shown in Figure 4, the addition of cholesterol eliminates the discontinuity in ϕ_f near T_c; the Arrhenius plot for S10A in the presence of 33 mol % cholesterol is linear over the range 20–70 °C and gives E_a = 7.53 kcal/mol and log A = 14.4 which are reasonable for a liquid phase of moderate viscosity.

The results obtained in this study suggest that in the low-temperature phase of all vesicle systems studied the stilbene derivatives having alkyl chains of 5 or more carbons are incorporated into the bilayer structure in a manner somewhat similar to an inclusion complex. The "guest" sites occupied by the stilbene chromophores permit some motion during the excited state lifetime as evidenced by the observation of isomerization from trans to cis in each case as recorded in Table IV; however, the evident freedom varies with vesicle type in the apparent order DCP ≈ DCP/DPL > DODAC > DPL. The isomerization studies reveal that in this series there is a decrease in the fraction of those molecules escaping the fluorescent state which isomerize to cis (Table V).

The difference in behavior observed for the surfactant stilbenes between the low- and high-temperature phases appears reasonable on the basis of accepted ideas of vesicle structure. The behavior observed here closely resembles that in polymer systems where the glass–rubber transition separates domains which consist of fairly rigid segments in which components experience low entropy from flexible ones with high entropy.[76-78]

It is interesting to contrast the behavior of the different stilbenes studied in vesicles with each other and with other probes that have been used to investigate vesicles and related assemblies. On the basis of the results obtained in these studies we can conclude that stilbene and the short-chain S4A do not specifically reside in sites within the vesicle interior. An earlier study of *trans*-stilbene fluorescence in DPL under somewhat different conditions by Geiger and Turro[34] shows somewhat different behavior from that observed in the present study. Although this study showed a sensitivity of ϕ_f to the vesicle phase transition, much lower quantum yields were observed and the activation energy was found to be higher at temperatures below T_c. The low values for ϕ_f compared to those for the longer-chain surfactant stilbenes suggest that in both cases studied *trans*-stilbene does not become incorporated into the ordered vesicle interior but rather occupies an interfacial site or disordered region similar to the microenvironment of a micelle but nevertheless close enough to "sense" the sharp phase change of the ordered region occurring at T_c. In contrast, the longer-chain surfactant stilbenes and the double-chain compounds give strong evidence of occupying sites in which the rod-like molecule including the stilbene chromophore is incorporated into the nearly crystalline hydrocarbon lattice with relatively little perturbation of the vesicle. The single-chain stilbenes differ appreciably from the double-chain stilbenes. For the former it seems clear that the low-temperature phase provides a highly constricted site albeit one which does not completely restrict twisting. For the stilbenes in the series S6A–S12A there appears to be relatively little difference "seen" by the chromophore as far as fluorescence above or below T_c is concerned. Since the stilbene chromophore corresponds in length to several methylene groups, it is probably not possible that small differences in order between the alkane chain ends and enterior carbons[79] could be detected.

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The differences between the single- and double-chain stilbenes is probably due to one of two factors. It is reasonable to expect that the anchoring of the chromophore by imbedding both ends into a nearly crystalline lattice should impose severe restrictions on twisting; this could in itself account completely for the limiting ϕ_f values rapidly attained below T_c. Another possibility is that the more effective "anchoring" provided by the second chain restricts the stilbene to an interior site and prevents any migration to or equilibration with the interface region. The observation of only a single component for fluorescence decay with 6S4A and 4S4 supports this as does a study of bromination rates of the stilbenes in DPL which shows extremely slow rates for 6S4A and 4S4 compared to the single-chain stilbenes;[73] since bromination rates are extremely sensitive to the "polarity" of the environment, the slow rate for these compounds supports a view that they are restricted to highly hydrophobic sites, most likely in an ordered hydrocarbon region of the vesicle.

The difference in behavior between 4S4 (di-*n*-butylstilbene) and S is especially striking; the apparent preference of S for an interface site is noteworthy and suggests that structurally related molecules such as 1,4-diphenylbutadiene could occupy similar sites and not the "interior" site often assumed.[40-42] It has been recently demonstrated that the extent of intramolecular excimer formation in 1,1′-dipyrenyl methyl ether can be correlated with T_c for several vesicles; in these studies it has been found that different Arrhenius parameters are obtained above and below T_c as is the case with the stilbenes.[75] However, for the dipyrenyl compound E_a obtained *below* T_c is much larger than that measured at higher temperatures—a finding opposite to those reported above for the stilbenes.[75] The most likely reason for this difference is a difference in the solubilization of the pyrene and stilbene probes. While the stilbene probes are probably very close to passive as far as interrupting the bilayer structure is concerned, it seems reasonable that a larger and non-rodlike molecule such as the dipyrenyl derivative cannot "fit" simply into a crystalline region of the bilayer. Whether this molecule resides at an interface or simply in an interrupted part of the bilayer interior cannot be ascertained; thus although its activation parameters suggest it is in a more solution-like environment as far as microviscosity is concerned, it must be close enough to "normal" areas of the bilayer to be sensitive to the bulk changes occurring near T_c. Along these lines Zachariasse[33] has concluded from a study of 1,3-dipyrenylpropane in vesicles (where similar results are obtained) that the probe must perturb the lipid structure in the ordered phase such that the vesicle is relatively fluid in the vicinity of the probe. It would seem reasonable that a melting or related perturbation probably occurs when other large aromatics, whose fluorescence depolarization behavior readily detects T_c, are "dissolved" in vesicles.

In conclusion, it must be acknowledged that virtually all fluorescent probes or molecules (e.g., spin-label probes)[80,81] having structures very different from the component lipids can produce structural changes in the assembly or occupy sites very different from the host. Knowledge of the microenvironment or solubilization site provided for different kinds of guests is of itself of great importance so studies using different kinds of solute-probes are of importance in any case. The surfactant stilbenes and other probes such as parinaric acid (octadecatetraenoic acid)[43-47] having structures similar to or compatible with the host lipids of vesicles or liposomes appear to offer useful information otherwise not accesible except through techniques involving studies of properties of the lipid hosts themselves; these kinds of probes offer particular use in investigating assembly–solute interactions with solutes which may not themselves serve as probes.

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Dual Fluorescence of 4,4′-Dimethylamino- and 4,4′-Diaminophenyl Sulfone. Consequences of d-Orbital Participation in the Intramolecular Charge Separation Process

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Abstract: 4,4′-Dimethylaminophenyl sulfone (DMAPS) and 4,4′-diaminophenyl sulfone (APS) show multiple fluorescence in polar solvents without the strong diminution of fluorescence efficiency found for similar systems. Based on numerous similarities with the dual fluorescence of dimethylaminobenzonitrile (DMABN), a mechanism involving "twisted intramolecular charge transfer" (TICT) states is proposed. These states are mainly derived from geometries where one anilino or dimethylanilino group is rotated. Fluorescence lifetime and quantum yield data point to the forbidden nature of the radiative TICT transition. The sensitivity of the equilibrium between locally excited (LE) and TICT states to solvent polarity is related to the participation of sulfur d-orbitals which play a significant role in the symmetry reduction process necessary for TICT state formation. Solvatochromic measurements show this state to be of very high polarity, and the LE state of medium polarity. The LE → TICT transition thus involves a strong dipole moment increase accompanied by a directional flip of nearly 90°.

I. Introduction

The observation of dual fluorescence in dimethylaminobenzonitrile (DMABN)[1] stimulated the work of many research groups and eventually led to the notion of "twisted intramolecular charge transfer" (TICT) excited states.[2] These states are possible in

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