

the acetylene becomes bonded to the metal cluster in an unprecedented fashion,⁹ without any major change in the metal atom arrangement. The acetylene is reduced so that the former triple bond is converted into a single C-C bond and the sp carbon atoms become sp³ hybridized (see caption to Figure 2). One of the former acetylenic carbon atoms [C(12)] adopts a μ_2, η^1 -bridging mode, spanning Os(2) and Os(3) (Figure 2), while C(11) is reduced to a methylene group presumably by migration of the two bridging hydrogen atoms of I.¹⁰ [C(12) bridges Os(2) and Os(3) symmetrically and lies 0.19 Å out of the metal plane, while the C-(10)-C(11)-C(12) angle of 109.2 (1.4)^o is almost a perfect tetrahedral value, for distance see caption.]

Unusual structural features of III include a semibringing CO,¹¹ the coordination of an ester O to Os(3) with displacement of CO, and a long Sn-Os(2) bond. The last is not hydrogen bridged (NMR) and may possibly result from a high trans influence of the (sp³) C(12) atom.

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Supplementary Material Available: Elemental analysis, further spectroscopic data, tables of atomic coordinates, temperature factors, and bond lengths and angles for compounds II and III (15 pages). Ordering information is given on any current masthead page.

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Micelle and Vesicle Solubilization Sites. Determination of Micropolarity and Microviscosity Using Photophysics of a Dipolar Olefin¹

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A variety of investigations have shown that properties of molecules solubilized in surfactant aggregates can be modified as a result of the unique microenvironment provided by the assembly of amphiphilic molecules within an aqueous solution.²⁻⁶ Generally such effects are attributable to factors such as pH, polarity, and viscosity being different in the vicinity of the organized assembly (relative to the bulk solvent). While it is intuitively reasonable to expect that different microenvironments

Table I. Lifetime of NMS Triplet State at 27 °C in Homogeneous and Aqueous Micelle Solutions^a

solvent	τ , ns	surfactant ^c	τ , μ s ^d
cyclohexane ^b	77	SDS	9.4
benzene ^b	150		
acetone ^b	263	CTAB	1.5
acetonitrile ^b	385		
methanol ^b	333	Brij-35	1.2
glycerol ^b	6000		
50% MeOH/H ₂ O	4900		

^a In N₂ outgassed solutions. ^b Data taken from ref 11. ^c Surfactant concentrations equal to [CMC] + 0.02 M. ^d All decays fit first-order kinetics with $r > 0.999$.

Table II. Temperature Dependence of NMS Triplet Decay in DPL Vesicles^a

T, °C	C ₁ , ns (weight) ^b	C ₂ , μ s (weight) ^b
28	740 (0.66)	22 (0.34)
35	625 (0.75)	13 (0.25)
40	370 (0.825)	4.5 (0.175)
45	325 (0.90)	1.25 (0.10)
50	290 (0.875)	1.4 (0.125)
55	280 (0.90)	1.25 (0.10)

^a In N₂ degassed solutions. ^b χ^2 -squared for all fits $< 10^{-4}$.

are accessible to molecules solubilized in solutions of surfactant assemblies (micelles, vesicles, reversed micelles, etc.), most experiments indicate that small solubilized molecules "feel" only one environment with respect to polarity and viscosity. Herein we present data which clearly indicate that a single solubilized molecule *can* experience different environments within a synthetic vesicle and that exchange between solubilization sites is slow.

A recent series of papers describing the photochemical and photophysical properties of 4-nitro-4'-methoxystilbene (NMS) indicated this molecule could be useful for examination of microenvironments in surfactant aggregates on the microsecond timescale.⁷⁻¹¹ Pulsed laser photolysis of *trans*-NMS in solution generates a readily monitored transient which has been assigned as the planar trans triplet, ³(*t*-NMS)*.¹⁰ The pertinent feature was the indication that the lifetime of ³(*t*-NMS)* is increased by (1) increased viscosity and (2) increased polarity of the solvent medium; see Table I.^{11,12} In the present paper we report a strong medium dependence of the behavior of ³(*t*-NMS)* in aqueous surfactant solution and its evaluation in terms of microviscosity and micropolarity of solubilization sites in micelles and vesicles.

The triplet lifetime of NMS in various aqueous micellar solutions was measured by laser flash photolysis ($\lambda_{\text{ext}} = 355$ nm, ≈ 5 mJ/pulse); results are presented in Table I. The triplet decays are clearly monoexponential and much longer for NMS in micelles than in most homogeneous solutions, suggesting that the excited molecules experience a single (average) microenvironment of moderate polarity in the micellar solutions. One interesting feature is that $\tau_{\text{SDS}} > \tau_{\text{CTAB}}$ and $\tau_{\text{Brij-35}}$. The increased lifetime in SDS is likely due to a slightly higher effective polarity in this micelle relative to CTAB and Brij-35 micelles.¹³ While NMS is clearly solubilized with the micellar aggregates in aqueous solution,¹⁴ the lifetimes indicate that this dipolar organic molecule experiences a polar environment. This suggests that it is solubilized in an

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(12) Decay of ³(*t*-NMS)* occurs mainly by twisting around C=C yielding the twisted state which subsequently relaxes forming ground-state *t*- and *c*-NMS. The viscosity effect results from an increase in E_a for the twisting process in more viscous solvents. An explanation for the polarity effect upon the lifetime has not been suggested.¹¹

(13) A similar trend has been reported by using the dye indicator $E_T(30)$.⁶

(14) Without added surfactant NMS is insoluble in H₂O ($C < 10^{-7}$ M).

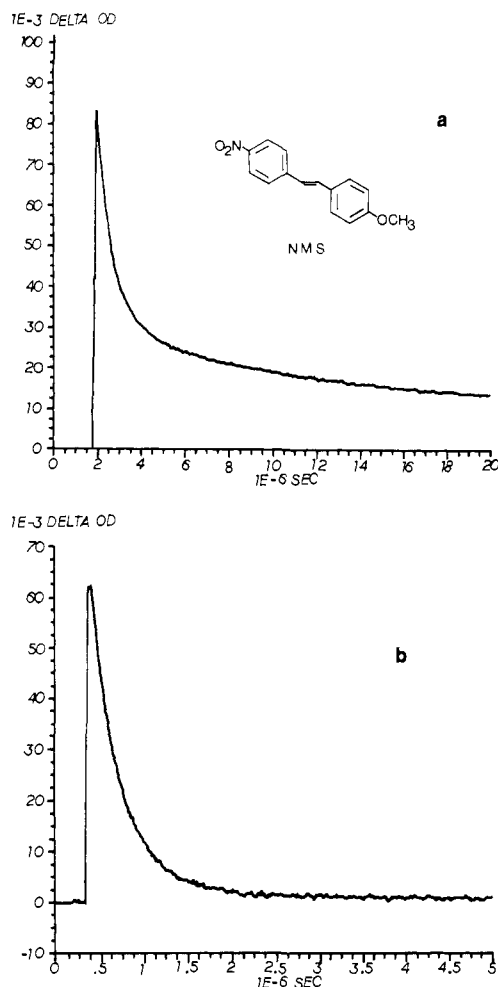


Figure 1. Transient absorbance decay for NMS in DPL vesicles at (a) 28 °C and (b) 50 °C (excitation at $\lambda = 355$ nm, monitor at $\lambda = 600$ nm). Note: (1) Long-lived transient in (a) decays back to base line on longer time scale. (2) Different time base in (a) and (b).

“interfacial” site where it can interact with the surfactant head-groups but be solvated partially by surrounding H_2O molecules.

We have also examined the triplet of NMS in vesicle solutions; qualitatively similar results are obtained in dipalmitoyllecithin (DPL), dioctadecyldimethylammonium chloride (DODAC), and dicetyl phosphate (DCP).¹⁵ Time evolution of the transient in DPL vesicles at 28 °C is shown in Figure 1a. Quite interestingly the transient decay exhibits biphasic kinetics in the vesicle solution:¹⁶ the fast and slow components have lifetimes of 740 ns and 22 μ s, respectively. That both transient components are due to the NMS triplet state is evident by the fact that the transient spectra (Figure 2) taken at 200-ns and 10- μ s delay for the DPL solutions are quite similar to published triplet spectra of NMS in homogeneous solutions.¹⁰

Observation of two decay components for the NMS triplet state in vesicle solutions suggests that photoexcited molecules can reside in solubilization sites within the organized surfactant assembly which provide distinctly different microenvironments.¹⁷ Assignment of the biphasic decay behavior to molecules solubilized in “dissimilar” vesicles present in an inhomogeneous dispersion

(15) Vesicles prepared by sonicating an aqueous suspension of NMS ($C \approx 10^{-5}$ M) and surfactant ($C = 5 \times 10^{-3}$ M) with a probe sonicator for 10 min at 50–60 °C. Solutions were subsequently cooled to room temperature, centrifuged, and filtered through a 0.5- μ m filter prior to measurements.

(16) The transient decay in vesicle solutions can be fitted well by using a double exponential equation, $\Delta A(t) = ae^{-t/\tau_1} + (1-a)e^{-t/\tau_2}$, where $\Delta A(t)$ is the observed transient absorbance, τ_1 and τ_2 are the lifetimes of the fast and slow decay components, respectively, and a is the relative weight of the fast component.

(17) Assignment of the short-lived transient to $^3(NMS)^*$ solubilized in the bulk H_2O can be ruled out as NMS is insoluble in H_2O .

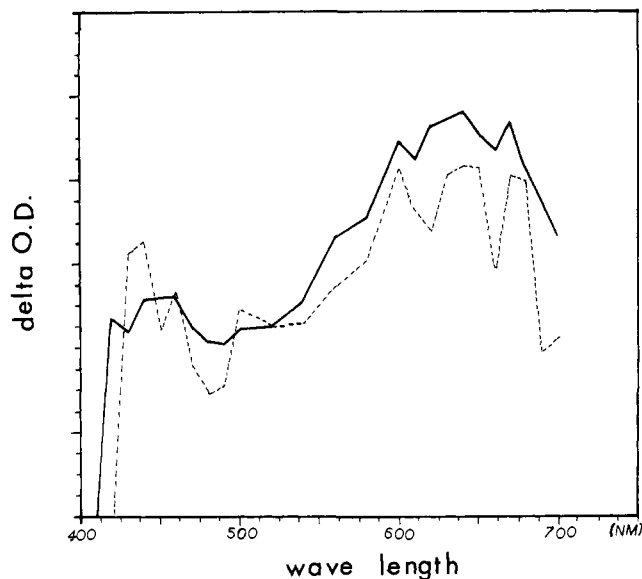


Figure 2. Transient absorption spectrum at different delays following laser flash excitation (—) 200 ns after flash and (---) 8 μ s following the flash.

is ruled out as studies with NMS solubilized in homogeneous vesicle suspensions prepared by ultracentrifugation give the same results.^{18,19} The short-lived transient component suggests that a sizable fraction of the photoexcited molecules are solubilized in a microenvironment much like a polar/nonviscous solvent (MeOH/ H_2O). However, the fact that an appreciable fraction of the transients have a remarkably long lifetime (much longer even than τ in glycerol or aqueous SDS) indicates that many of the photoexcited molecules are in a highly viscous microenvironment where triplet decay via rotation is severely retarded.

Triplet decay has been monitored in DPL vesicle solutions at six temperatures from 28 to 55 °C; Table II shows the results of the double-exponential fits. Several points are noteworthy: (1) the long lifetime component (τ_2) is significantly shortened with increased temperature up to 45 °C and then levels off. (2) The fraction of transients that decay via the short lifetime channel (τ_1) dramatically increases with temperature and levels off for $T > 45$ °C. (The phase transition temperature for DPL is 41.4 °C).²¹ These features are clearly distinguished through comparison of Figure 1, parts a and b; >30% of the triplets decay via the slow channel at 28 °C while only a small fraction (<10%) decays via this pathway at 50 °C.

The biphasic nature and temperature dependence of the triplet decay components support a tenet that photoexcited NMS reside in at least two sites within the vesicle. One possibility is that the two lifetime components reveal different microenvironments for NMS in inner and outer “leaflets” of the bilayer. An alternative explanation could be that NMS is distributed between the vesicle interior and interfacial regions. Both azulene and oxygen (known triplet quenchers) quench the transients with a more pronounced quenching of the “slow” component in each case; however, comparison of $[(\tau^0/\tau) - 1]/\tau^0$ for each quencher suggests relatively little differential quenching rates for oxygen and an effectively slower quenching of the “slow” component for azulene. At the present time we are unable to distinguish conclusively between the above possibilities for the different solubilization sites.

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(19) The small unilamellar vesicles used in this study were also separated from multilamellar vesicles by Sepharose-4B filtration.²⁰ Similar two-component decay was observed in DPL vesicles prepared by a variety of techniques independent of NMS concentration (tenfold range). Concentrations of NMS generally used in these experiments were in a range such that there is less than one NMS molecule/vesicle.

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A key point here is that these results clearly demonstrate that a small nonsurfactant organic molecule can reside in at least two distinctively different environments within the bilayer vesicle and that exchange between these sites *below* the phase transition temperature is slow ($k < 10^{-4} \text{ s}^{-1}$) on the photochemical time scale.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE 8315303) for support of this research.

Registry No. NMS, 1472-68-0; SDS, 151-21-3; CTAB, 57-09-0; Brij-35, 9002-92-0; DPL, 2644-64-6; DODAC, 107-64-2; DCP, 2197-63-9.

Optical Microscopic Study of Helical Superstructures of Chiral Bilayer Membranes

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We describe in the paper the direct observation of helical superstructures produced from bilayer membranes of chiral ammonium amphiphiles.

Recently, we conducted direct observation of aqueous dispersions of synthetic bilayer membranes by using dark-field optical microscopy.¹ Their morphologies were often very different from what we observe by electron microscopy. When bilayer membranes are in the liquid-crystalline (fluid) state, a variety of dynamically changing morphologies such as fibers, tubules, twisted vesicles, etc. are observed. This suggests that shapes of bilayer aggregates are far richer than expected from the electron microscopic (static) observation and clearly points to the advantage of the direct observation. Some amino acid derived amphiphiles produce well-developed bilayer membranes that display remarkable enhancements of circular dichroism^{2,3} and induced circular dichroism.⁴ These results were an indication of the existence of regular superstructures and prompted us to examine these bilayers by optical microscopy.

Double-chain ammonium amphiphiles given in Chart I produce typical bilayer vesicles, when dispersed in water by sonication.⁵ One milligram of these amphiphiles were added to 1 mL of water, allowed to swell by warming, and shaken gently by hand. Transparent dispersions thus obtained were placed on slide glass and were observed by a dark-field light microscope (Olympus BHF, light source; Ushio 200-W high-pressure Hg lamp). When an aqueous dispersion of $2\text{C}_{12}\text{-L-Glu-C}_{11}\text{N}^+$ is maintained at 20 °C for several hours, flexible filaments of lengths of 5–50 μm are formed predominantly (Figure 1a). Spherical vesicles (diameter, 1–10 μm) are present as a minor component. These aggregates show rapid Brownian motions. Upon aging at 15–20 °C for 1 day, the filaments begin to be twisted. It takes several hours for one filament to change completely into a helix such as shown in Figure 1b. The scattering from helices is intensified over a period of 5–6 h (Figure 1c). The helical pitches are similar (ca. 3.2 μm) in Figure 1, parts b and c, and lengths of the helix are 10–100 μm . Some helices are bent. Further shape changes occur more gradually, and after 1 month, rodlike structures become abundant (Figure 1d).

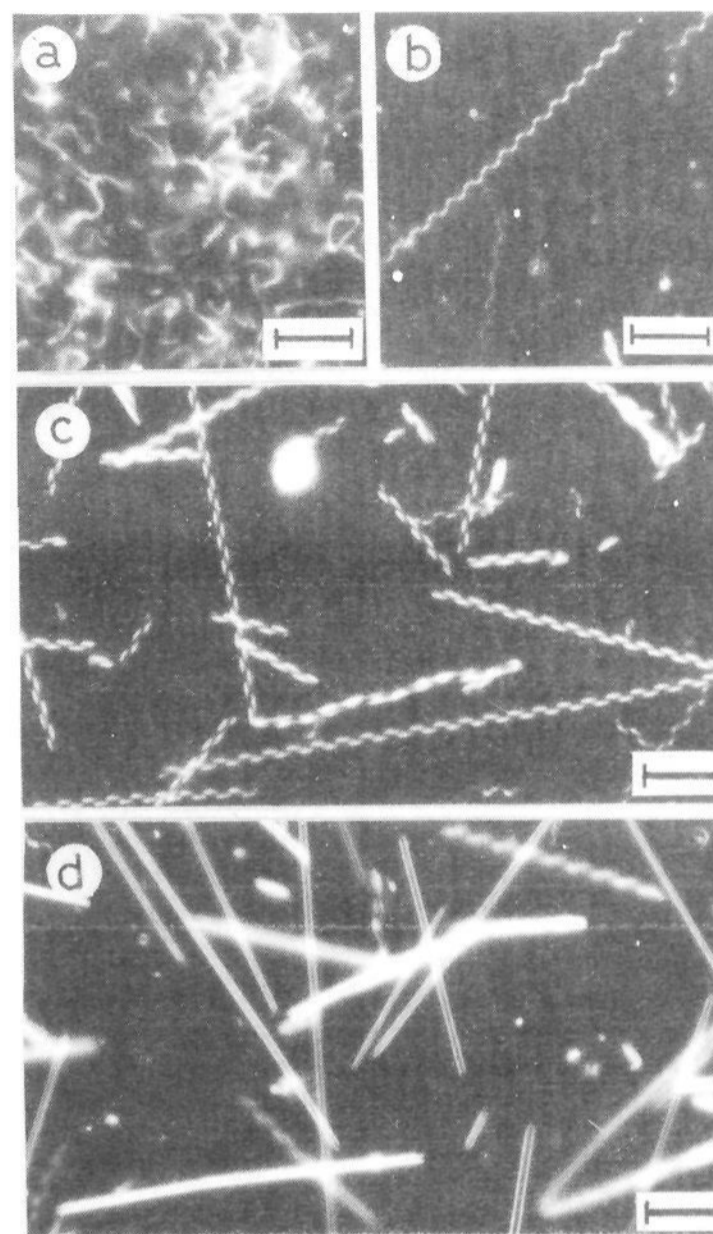


Figure 1. Dark-field optical micrographs of aqueous dispersion of $2\text{C}_{12}\text{-L-Glu-C}_{11}\text{N}^+$ ($1 \times 10^{-3} \text{ M}$). Micrographs (a)–(d) show the growth from fibrous chiral bilayers to helical superstructures. Aging condition: (a) 20 °C, several hours; (b) 15–20 °C, 1 day; (c) 5–6 h after b; (d) 15–20 °C, 1 month. Magnification 1300 times (scale bars, 10 μm).

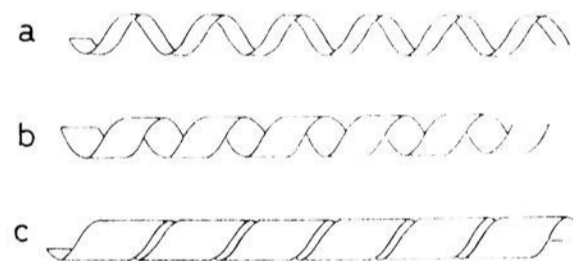
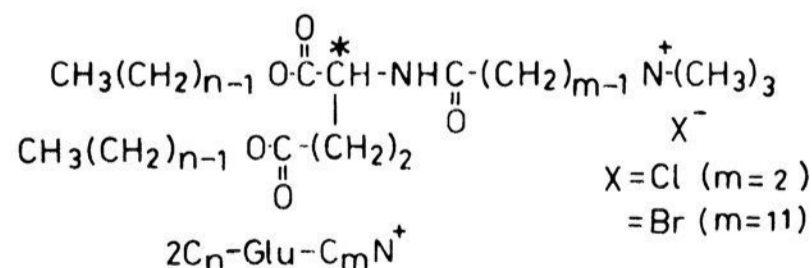


Figure 2. Schematic illustrations of the growing process of a helix. (a), (b), and (c) are illustrations approximately corresponding to Figure 1, parts b, c, and d, respectively.

Chart I



- | | |
|---|--|
| 1, $2\text{C}_{12}\text{-L-Glu-C}_2\text{N}^+$ | 2, $2\text{C}_{12}\text{-L-Glu-C}_{11}\text{N}^+$ |
| 3, $2\text{C}_{12}\text{-D-Glu-C}_{11}\text{N}^+$ | 4, $2\text{C}_{12}\text{-DL-Glu-C}_{11}\text{N}^+$ |
| 5, $2\text{C}_{14}\text{-L-Glu-C}_2\text{N}^+$ | 6, $2\text{C}_{14}\text{-L-Glu-C}_{11}\text{N}^+$ |

The growing processes are schematically illustrated in Figure 2. The pitches of the twisted tapes are identical; therefore, the changes from helices of narrow tapes (Figures 2a and 1b) to rods (Figures 2c and 1d) probably occur via widening of the tape.⁶

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