

mium ions would be transferred with the first layer, an increase of pH would lead to an increased formation of cadmium arachidate rather than to a neutralization of the dye cations by the arachidate anions. If this would happen, the increase of the pH would not lead to a less extensive aggregation of the dye when the subphase pH is increased.

Conclusions

The deposition conditions influence the spectroscopic properties of mixed monolayers of dioctadecyloxycarbocyanine and arachidic acid. The fluorescence is quenched by energy transfer to dimers and higher aggregates formed upon increasing the dye content in the monolayer. In a multilayer where the chromophores are in contact with the cadmium arachidate or arachidic acid groups of another monolayer, an increase of the dye aggregation is observed. This aggregation occurs on a molecular scale as it is not revealed in the surface pressure-area isotherms. At least two different types of aggregates can be distinguished and can be compared to the ones formed in an ethanol matrix at 77 K. The spectroscopic properties of the dye

layer are strongly influenced by the deposition pH.³⁷ An increase of the pH shifts the equilibrium between arachidic acid and arachidate and induces a more efficient mixing between the dye and the matrix (arachidic acid or arachidate). This reduces in turn the extent of the aggregation of the dye molecules. As mixed monolayers are used in microelectronic devices, it will also be important to choose experimental conditions at which the monolayer is deposited very carefully. Upon investigation of such systems, one should always try to determine the organization at the molecular level. If any photochemical or photophysical properties of such systems are investigated, one should always consider eventual intermolecular interactions (aggregation) of the chromophores involved.

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Notes

Cis-Trans Photoisomerization of a Surfactant O-Protonated Stilbazolium Betaine in Micellar Systems

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Introduction

Recently, much attention has been focused on the cis-trans photoisomerization of surfactant derivatives of stilbene and azobenzene when located in assembled surfactant phases, particularly micelles,^{1,2} vesicles (liposomes/bilayers),¹⁻⁴ monolayers spread at the air/water interface,^{5,6} and Langmuir-Blodgett films deposited on optically transparent substrates.⁵⁻⁷ A number of the azobenzene studies were instigated because it is presently thought that some surfactants which can undergo

reversible cis-trans photoisomerization may be able to serve as components in Langmuir-Blodgett thin-film molecular electronic devices.⁷ There have been relatively few studies of other types of molecular cis-trans photoisomers that possess long hydrocarbon chains.

A diverse range of long-chain homologues and analogues of the O-protonated stilbazolium betaine shown in Scheme I can be easily synthesized,⁸⁻¹³ and the stilbazolium betaine chromophore can be covalently attached to polymers.^{14,15} Long-chain homologues of this O-protonated stilbazolium betaine can be spread to form insoluble monolayers at the air/water interface,¹⁶⁻¹⁸ and the preparation of Langmuir-Blodgett thin films based on surfactant derivatives of this O-protonated stilbazolium betaine is reasonably straightforward.¹⁷⁻²⁰ Notably, Langmuir-Blodgett films of the C₂₂ merocyanine (i.e., the C₂₂ deprotonated) form have been found to exhibit very high second-order nonlinear optical susceptibilities, χ^2 .^{19,20} In

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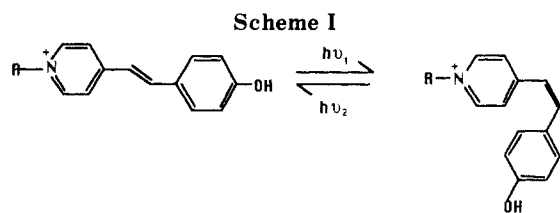
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fact, the χ^2 values for these Langmuir-Blodgett films are significantly higher than those of the inorganic materials currently used in some devices which process optical information.^{20,21}

The methyl homologue ($R = \text{CH}_3$) of the O-protonated stilbazolium betaine depicted in Scheme I undergoes reversible cis-trans photoisomerization in aqueous solution.^{22,23} The primary aim of the present study was to determine whether or not long-chain homologues of this O-protonated stilbazolium betaine are capable of reversible cis-trans photoisomerization in an assembled surfactant phase.

The standard free energy of micellization for a surfactant can depend on the particular orientation of the surfactant head group. For example, for some surfactant stereoisomers²⁴ and some surfactant photoisomers involving heterolytic cleavage,²⁵ the standard free energy of micellization for each of the isomers is distinctly different. It is not yet known if some surfactant cis and trans photoisomers may also display different standard free energies of micellization. Therefore, as an adjunct to the main study, we undertook to determine whether or not long-chain homologues of the chosen O-protonated stilbazolium betaine form micelles.

Experimental Section

Surfactant stilbazolium betaines were synthesized by employing established procedures.^{8,9,13} Brij-35 and octyl β -D-glucopyranoside (OG) were obtained from ICI Australia Operations Pty. Ltd. and Sigma Chemical Co., respectively. Hexadecyltrimethylammonium chloride (CTAC) was supplied by Eastman Kodak Co. Sodium dodecyl sulfate (SDS) was purchased from Sigma Chemical Co. All the surfactants obtained from commercial sources were not further purified. The NaOH, NaCl, and HCl were of analytical reagent grade. Absolute ethanol was acquired from Ajax Chemicals Pty. Ltd. Triply distilled water was used throughout this study. All experiments were performed at 25 °C.

The C_{16} homologue was solubilized in the aqueous micellar solutions by adding a small aliquot (< 0.4 vol %) of an ethanol stock solution. Before the photoisomerization experiments were conducted, the pH was adjusted to greater than 2 pH units above the apparent pK_a of the stilbazolium betaine in the medium of interest.¹³ As well, each solution was left in the dark at this pH for at least 15 h. This procedure was followed because the merocyanine form is considered to exist solely in the trans configuration.^{22,23}

During the photoisomerization experiments, each solution was housed in a water-thermostated vessel which was connected to a cuvette in the spectrophotometer by way of small-bore silicone tubing. The solution was continuously and rapidly circulated between the cuvette and the vessel via a flow-through system which was driven by a peristaltic pump. Prior to irradiation

with select wavelengths of light, the pH of the solution was decreased, so as to be more than 2 pH units below the apparent pK_a of the stilbazolium betaine,¹³ while the solution was kept in the dark and a UV-vis absorption spectrum was recorded. This spectrum was considered to be that of the O-protonated stilbazolium betaine in the trans configuration. The method of Fischer²⁶ was used to calculate both the extent of trans \rightarrow cis conversion after a photostationary state had been reached and the spectrum of the cis form of the O-protonated stilbazolium betaine.

The solutions were irradiated with light from either a combination of a Varian VIX-300 UV 300-W Xenon illuminator and a Bausch and Lomb high-intensity monochromator (set at appropriate wavelengths) or a model UVG-11 UV lamp obtained from UVP Inc. (for the 254-nm light). The photon flux of sample irradiation was determined by using potassium ferrioxalate actinometry.²⁷ For the 254-, 374-, and 394-nm light, the photon flux of sample irradiation ($(I_0 \pm \sigma) \times 10^6$ einstein/min) was 3.2 ± 0.4 , 2.1 ± 0.2 , and 3.1 ± 0.1 , respectively. Spectra were recorded on a Hewlett-Packard HP 8451A diode array UV-vis spectrophotometer. In general, a photostationary state was considered to have been reached when a solution's spectrum did not change significantly over a 5-min period.

Air/aqueous solution surface tension values were obtained by using the du Noüy ring technique.²⁸ The solutions for the surface tension measurements had pH values which ranged between 3.5 and 4.0. Surface tension measurements were made in room-light conditions.

Results and Discussion

The cis-trans photoisomerization of the C_{16} homologue of the O-protonated stilbazolium betaine in aqueous micellar solutions of Brij-35, OG, CTAC, and SDS was investigated. For comparison, the cis-trans photoisomerization of the C_5 homologue in water was also examined. Table I contains the principal data acquired. In all the systems investigated, the long-chain homologue of the O-protonated stilbazolium betaine underwent reversible cis-trans photoisomerization. The extent of trans \rightarrow cis conversion (α) for the C_5 homologue in water is in reasonable accord with the extent of trans \rightarrow cis conversion reported previously for the methyl homologue in water (viz., $\alpha = 0.67$ with 366-nm irradiation and $\alpha = 0.27$ with 254-nm irradiation).²² A typical example of the type of spectral modifications undergone by the C_{16} homologue in aqueous micellar solutions and the C_5 homologue in water is displayed in Figure 1.

There are several interesting aspects to the data presented in Table I. The first is the small but noticeable variation of the extent of trans \rightarrow cis conversion (α) between water and the different micellar systems, at all wavelengths of illumination. This behavior can be qualitatively interpreted in terms of the polarity, fluidity, and electric field of the O-protonated stilbazolium betaine's solvating environment. In another study,¹³ the solvatochromism of the merocyanine form of the C_{16} homologue has been employed to obtain estimates of the mean interfacial solvent properties of micelles. On the basis of these estimates, the solvating media studied in the present work can be ranked in order of their effective polarity: $\text{H}_2\text{O} > \text{SDS} > \text{OG} > \text{CTAC} \approx \text{Brij-35}$. As can be seen from the values in Table I, with the exception of the SDS system, α is lower in the solvating media with the lower polarity. This trend is the same as that observed for the cis-trans photoisomerization of some substituted

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Table I. Principal Data for Cis-Trans Photoisomerization of C₅ Homologue in Water and C₁₆ Homologue in Aqueous Micellar Systems^a

system	λ_{\max} (± 1 nm)	$\epsilon^{\text{trans}} \times 10^{-4}$, M ⁻¹ cm ⁻¹	$\epsilon^{\text{cis}} \times 10^{-4}$, M ⁻¹ cm ⁻¹	α^b		$\Phi_{\lambda}^{\text{cis}}/\Phi_{\lambda}^{\text{trans}}$	Φ_{deg}
				254 nm	λ_{\max}		
H ₂ O ^c	374	3.73	1.14	0.34	0.73	1.21	2.24
Brij-35 ^{d,e}	394	1.98	0.60	0.28	0.61	2.11	7.65
OG ^{d,f}	394	3.15	1.02	0.31	0.67	1.52	1.08
CTAC ^{d,f}	394	2.92	1.11	0.30	0.66	1.36	4.49
SDS ^{d,f,g}	394	3.14	1.13	0.39	0.73	1.03	0.67

^a The position of the long-wavelength absorption band maximum of the trans form of the O-protonated stilbazolium betaine (λ_{\max}), the extinction coefficient of the pure trans form at λ_{\max} (ϵ^{trans}), the calculated extinction coefficient of the pure cis form at λ_{\max} (ϵ^{cis}), the extent of trans \rightarrow cis conversion (α) after the photostationary state has been reached by irradiation with light at select wavelengths, the ratio of the quantum yields for cis \rightarrow trans and trans \rightarrow cis conversion ($\Phi_{\lambda}^{\text{cis}}/\Phi_{\lambda}^{\text{trans}}$), and the quantum yield for photodegradation under continuous irradiation with 254-nm light (Φ_{deg}). ^b Unless stated otherwise ± 0.01 . ^c C₅ homologue. ^d C₁₆ homologue. ^e [surfactant] = 0.01 mol dm⁻³. ^f [surfactant] = 0.05 mol dm⁻³. ^g 0.1 mol dm⁻³ NaCl.

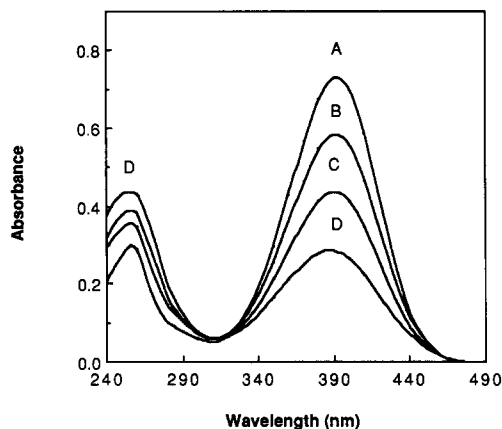


Figure 1. UV-vis absorption spectra of the C₁₆ homologue (2.5×10^{-5} mol dm⁻³) in 0.05 mol dm⁻³ CTAC solution: (A) spectrum of pure trans form; (B) photostationary-state spectrum for irradiation at 254 nm; (C) photostationary-state spectrum for irradiation at 394 nm; (D) calculated spectrum of pure cis form.

styrenes²⁹ and some other stilbene-based dyes in organic solvents.^{30,31} The effect has been explained as a stabilization of the twisted "perpendicular intermediate" (PI) state relative to the first excited singlet state (S_1) with increasing solvent polarity²⁹ (see Figure 3). As a consequence of the PI state possessing intramolecular charge transfer character,³² the energy of the PI state is progressively lowered as the solvating environment becomes more polar.²⁹ This basically leads to a reduction in the energy barrier involved in crossing from the S_1 state to the PI level and a concomitant increase in the degree of trans \rightarrow cis conversion, with increasing solvent polarity. Although the PI state is stabilized relative to the S_1 state of both the cis and trans forms, our steady-state results imply that the stabilization enhances the crossover rate from the singlet trans form to the PI state more than it does the equivalent passage from the cis form. This is consistent with the S_1 state of the cis form lying appreciably higher than the S_1 state of the trans form and in general^{33,34} showing a much faster intersystem crossing to the PI state.

The degree of trans \rightarrow cis conversion will also be a function of the effective microviscosity experienced by the O-protonated stilbazolium betaine chromophore. In

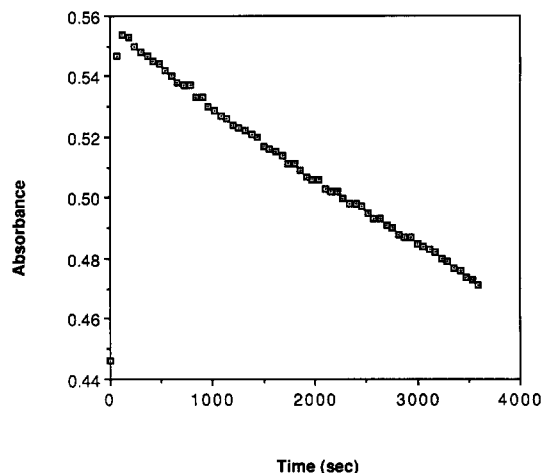


Figure 2. Absorbance value at the λ_{\max} of the C₁₆ homologue (2.5×10^{-5} mol dm⁻³) in 0.05 mol dm⁻³ CTAC solution as a function of the time of continuous irradiation with 254-nm light.

the case of the SDS micellar system, to enable the requisite pH adjustment procedure to be followed (vide supra) it was necessary to add electrolyte. Therefore, the effective microviscosity of the SDS interfacial microenvironment examined in this study may be significantly different from that of the other micellar systems. This could explain why the reproducible α values for the SDS system are incongruous with the polarity sequence. Alternatively, the high anionic surface charge density may influence the stabilization of the PI state.

It is also apparent from Table I that for each system the α value varies with the wavelength of illumination. This is readily ascribed to a change in the extinction coefficients, ϵ_{λ} , of the cis and trans forms with wavelength according to the relationship²⁶

$$\frac{[\text{trans}]_{\lambda}}{[\text{cis}]_{\lambda}} = \frac{\Phi_{\lambda}^{\text{cis}} \epsilon_{\lambda}^{\text{trans}}}{\Phi_{\lambda}^{\text{trans}} \epsilon_{\lambda}^{\text{cis}}} \quad (1)$$

where $\Phi_{\lambda}^{\text{cis}}$ and $\Phi_{\lambda}^{\text{trans}}$ are the quantum yields for cis \rightarrow trans and trans \rightarrow cis conversion, respectively. The ratio of the quantum yields is generally assumed to be a constant over the entire absorption spectrum.²⁶ Hence, the photostationary-state levels of the cis and trans forms are dependent on the variation in the ratio of the extinction coefficients. The quantum yield ratios ($\Phi_{\lambda}^{\text{cis}}/\Phi_{\lambda}^{\text{trans}}$) are included in Table I.

In all the media examined, it was found that under continuous irradiation with 254-nm light there was a gradual irreversible decrease in the absorbance value of the λ_{\max} of the O-protonated stilbazolium betaine, after the quasi-photostationary state value had been attained. A typical example is shown in Figure 2. The quantum yields

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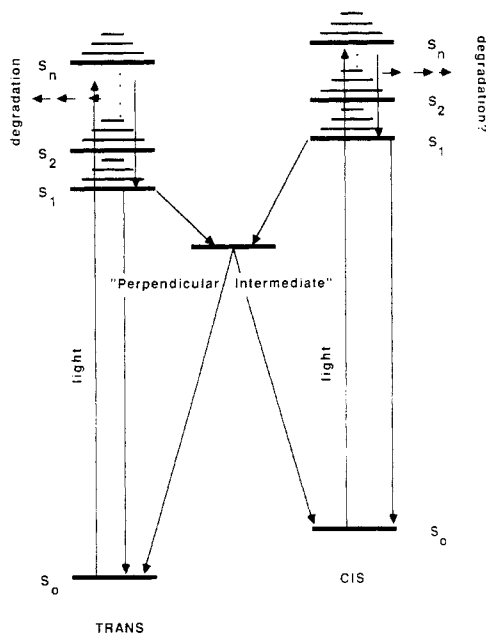


Figure 3. Schematic diagram showing the photophysical chemical processes occurring between different energy states of the O-protonated stilbazolium betaine molecule. The "perpendicular intermediate" can be reached from the singlet states of both the trans and cis forms of the stilbazolium betaine. However, the energy barrier involved in reaching the PI state from the trans form is greater than that of the cis form (see text). Deactivation of the PI-state to the ground-state trans form may also involve deprotonation of the stilbazolium betaine.²³ Degradation of the stilbazolium betaine is believed to occur from the higher excited state(s) of the trans form (see text).

of photodegradation at 254 nm are given in Table I. This photodegradation was also found to occur in a CTAC system that had been deoxygenated with nitrogen. Photodegradation of the O-protonated stilbazolium betaine was not apparent ($\Phi_{\text{deg}} < 10^{-4}$) under continuous irradiation with light of the other selected wavelengths. The fact that the loss of the stilbazolium betaine is not observed when higher wavelength light (of comparable photon intensity) is used to excite the systems suggests that the stilbazolium betaine loss must occur from some higher S_n level, as depicted in Figure 3. Although we do not have any direct evidence to assist in the assignment of the excited-state form of the stilbazolium betaine which leads to the loss, we speculate that it is the trans form. This is based on the observation that the quantum yields for photodegradation are generally higher for the cases where the lowest conversion percentages to the cis form exist (see Table I). Photodegradation of the chosen O-protonated stilbazolium betaine by UV light has not previously been reported. Photodegradation of similar molecules has, however, been noted.^{33,35}

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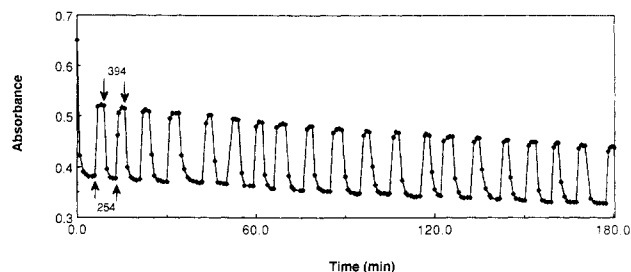


Figure 4. Variation in the absorbance value at the λ_{max} of the C_{16} homologue ($2.5 \times 10^{-5} \text{ mol dm}^{-3}$) in 0.05 mol dm^{-3} CTAC solution on alternate irradiation with 254- and 394-nm light.

With potential device applications in mind, it was decided to assess what effect this photodegradation has on switching (cycling) between two disparate photostationary states (e.g., the 254- and 394-nm photostationary states in micellar solution). Figure 4 shows the changes in the absorbance value at the λ_{max} of the C_{16} homologue ($2.5 \times 10^{-5} \text{ mol dm}^{-3}$) in 0.05 mol dm^{-3} CTAC solution on alternate irradiation with 254- and 394-nm light. From Figure 4, it is evident that both the absorbance value at λ_{max} and the amplitude of the oscillation from one photostationary state to the other decrease with the number of cycles. This observation precludes the utilization of the cis-trans photoisomerization of the chosen O-protonated stilbazolium betaine in any molecular electronic device that requires a long life.

Air/aqueous solution surface tension measurements were made with the C_5 , C_8 , C_{10} , and C_{16} homologues in order to determine whether or not long-chain homologues of the O-protonated stilbazolium betaine can form micelles. The C_8 , C_{10} , and C_{16} homologues had very limited solubility in water, and it was found that these homologues did not depress the air/aqueous solution surface tension when present in concentrations less than or equal to their respective solubility limits. The C_5 homologue was found to depress the surface tension at concentrations in excess of $1 \times 10^{-3} \text{ mol dm}^{-3}$. However, there was no (cmc) break in the surface tension versus $\log [\text{surfactant}]$ curve for concentrations below $4.0 \times 10^{-2} \text{ mol dm}^{-3}$, the approximate solubility limit of the C_5 homologue. Thus, it is inferred that long-chain homologues of the O-protonated stilbazolium betaine do not aggregate to form micelles in water at 25 °C.

Summary

It has been found that long-chain homologues of the chosen O-protonated stilbazolium betaine (i) undergo reversible cis-trans photoisomerization in an assembled surfactant phase, (ii) are photodegraded when irradiated with UV light of 254 nm, and (iii) do not form micelles in water at 25 °C.

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