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MICELLAR EFFECTS ON PHOTOPROCESSES IN RETINYL POLYENES†

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Abstract - The effects of micellar solubilization on excited-state properties of several retinyl polyenes have been examined primarily by nanosecond laser flash photolysis. The relative intensity of band system III (254-256 nm) in the ground state absorption spectrum of 11-cis retinal decreases significantly on going from methanol to micellar solutions, suggesting that the 12-s-trans form of 11-cis retinal is relatively favored in the organized media. In addition to microsecond transient phenomena due to triplets, the laser flash photolysis of all-trans and 11-cis retinal and all-trans retinyl Schiff base incorporated into micelles leads to 'permanent' absorption changes attributable to photoisomerization (in the case of retinals) and protonation and/or complexation with water (in the case of Schiff base). All-trans retinol and retinyl acetate in micellar solutions undergo ionic photodissociation leading to long-lived retinyl carbocation (λ_{max} = 585-600 nm), the process being monophotonic in the case of retinyl acetate and predominantly biphotonic in the case of retinol. The trends in the location of ground-state absorption maxima ($^1B_u^{+*}$ <---- ^1A_g) and triplet yield of retinals, and photodissociation yield of retinyl acetate suggest that the polarity of the environment probed by the polyene systems increases in the order: Triton X-100 < CTAB < NaLS.

INTRODUCTION

The photophysical and photochemical properties of retinyl polyenes have been extensively studied[1] because of the roles they play as chromophores in visual and photosynthetic pigments. Surprisingly, however, very little is known as to whether or how the excited-state properties of these polyenes are significantly affected by nonhomogeneous media mimicking those experienced in biological systems. Several of the photophysical properties of retinals and their analogues are recognized to be environmentally sensitive, and hence show promise as probes for multiphase systems. In particular, in an aqueous organized system, the role of water in increasing the polarity of the environment in the vicinity of a solubilized substrate, and as a hydrogen-bonding or protonating agent, should reflect itself in the modified excited-state behaviors of the predominantly hydrophobic, heteroatom-containing π-systems.

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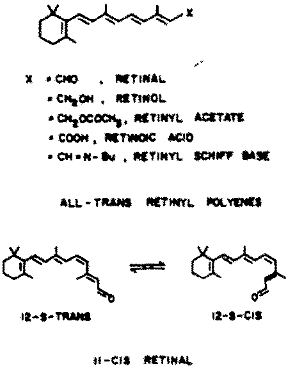
In this paper we are presenting the results of a laser flash photolysis study of several retinyl polyenes solubilized in three representative normal micelles, namely, neutral Triton X-100, anionic sodium lauryl sulfate (NaLS) and cationic cetyltrimethyl ammonium bromide (CTAB). The results suggest a great deal of micellar control on the photophysicochemical processes in these biologically important polyene systems. The retinyl substrates under study are shown in Chart I.



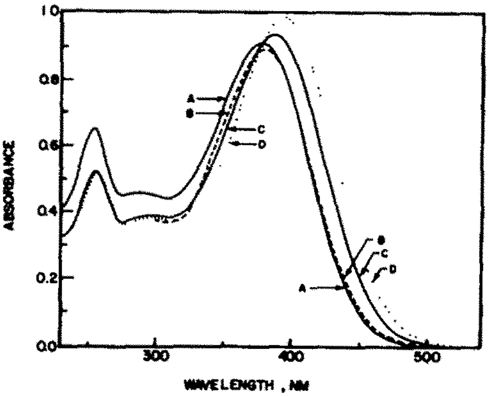


Chart I: Retinyl Substrates under Study.
(left)

Figure 1: The ground-state absorption spectra of 1.96 x 10^{-4} M 11-cis retinal
(right) **in (A) methanol, (B) 40 mM Triton X-100, (C) 20 mM CTAB and (D) 25 mM NaLS. Cell path length: 2 mm.**

EXPERIMENTAL

Except for 11-cis retinal and the Schiff base of all-trans retinal, the retinyl substrates were purchased from Sigma. Among these, all-trans retinyl acetate and retinoic acid were used as received, all-trans retinal was recrystallized from n-hexane, and all-trans retinol was purified, before use, by thin layer chromatography (silica gel, n-hexane + 15% ethyl acetate). 11-cis retinal, a gift from Hoffmann-LaRoche, was also subjected to thin layer chromatography (silica gel, n-hexane + 10% methyl-tert-butyl ether) and then stored under argon at 0°C. All-trans retinal Schiff base was freshly prepared from purified retinal by the reaction of the latter with excess of n-butyl amine (Aldrich, distilled) in dry methanol over 3A molecular sieves at 0°C under an atmosphere of argon. The details of the procedure are given elsewhere.[2] Triton X-100 (Eastman) was used without further purification. CTAB and NaLS, both from Aldrich, were recrystallized twice from ethanol. The solvents were of spectrophotometric grades.

The steady-state absorption and emission spectral measurements were preformed in a Cary 219 spectrophotometer (1 nm bandpass) and in an SLM photon-counting spectrofluorimeter[3,4] (2-4 nm bandpass), respectively. For fluorescence quantum yield (ϕ_F) measurements, solutions of quinine bisulfate in 1N H_2SO_4 (ϕ_F = 0.55)[5], optically matched with the solutions under examination, were used as the reference. The laser flash photolysis experiments were mostly carried out using, for excitation, nitrogen laser pulses (337.1 nm, 2-3 mJ, ~ 8 ns) from a Molectron UV-400 system. For some experiments, use was also made of 355 nm laser pulses (~ 6 ns, attenuated to < 10 mJ, third harmonic) from a Quanta Ray DCR-1 Nd-YAG system. Details of the kinetic spectrophotometer used for absorption-spectral observation of laser-flash-photolytic transients and the computer-controlled data collection system are available elsewhere.[3,4,6] A front face geometry was employed for laser excitation with respect to the direction of the monitoring light. Rectangular quartz cells (2-3 mm path lengths) containing 1-2 ml of solutions were used in 'static' experiments for measurement of kinetics or quantum yields. To determine transient absorption spectra wavelength by wavelength, the solutions were made to drain from a reservoir through a quartz cell of ~ 3 mm pathlength. The deoxygenation of solutions was effected by saturation with oxygen-free argon.

The micellar solutions of retinyl substrates were prepared by injecting microliter quantities of concentrated methanolic solutions of the substrates into 2-10 ml of aqueous solutions of the detergents. In all of the experiments, the detergent concentrations in terms of monomers were 40, 20, 25 mM for Triton X-100, CTAB and NaLS, respectively. The concentrations of retinyl substrates were $< 1 \times 10^{-4}$ M. In order to avoid the hydrolysis of some of the retinyl derivatives, namely retinals and retinyl Schiff base, the experiments with micellar solutions were conducted within 1/2 hr. after their preparation. Also, care was taken to minimize or avoid exposure of the solutions to room light; most of the operations were carried out in the dark or under red light. The absorbances of the solutions used for laser flash photolysis were kept in the range 0.2-0.7 in 2 mm cells at laser excitation wavelengths.

RESULTS

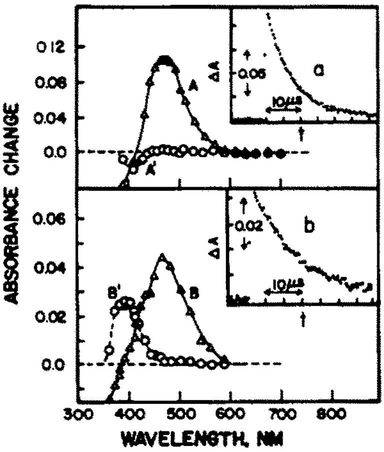
(a) All-trans and 11-cis Retinals. In shape and location, the ground-site absorption spectra of all trans and 11-cis retinal solubilized in micelles are comparable to those in alcoholic solutions. For both isomers, the maxima (λ_{max}^{abs}) of the observable, lowest-energy absorption band-systems (designated as I), assignable[7] to the strongly allowed $^1B_u^{*+}$ <--- ^1A_g transition, are red-shifted in the order: MeOH < Triton X-100 < CTAB < NaLS. The absorption spectral data are summarized in Table I. As shown in Figure 1, two other band-systems, designated as II and III, are distinctly observed in the case of 11-cis retinal at 275-320 and 230-270 nm, respectively. At the corresponding spectral regions in the case of all-trans retinal, only band system III is discernible as constituting a weakly allowed transition (λ_{max}^{abs} = 250-252 nm). Interestingly, the relative intensity of band system III in 11-cis retinal is found to decrease significantly on going from methanol to micelles.

Table I. Absorption Spectral Data of All-trans and 11-cis Retinal in Micelles.

retinal isomer	medium	λ_{max}^{abs}, nm (ε_{max}, 10^3 $M^{-1}cm^{-1}$)			$\varepsilon_{max}^{III}/\varepsilon_{max}^{I}$
		I	II	III	
all-trans	methanol	380(47)	[a]	250(6.2)	0.13
	Triton X-100	383(41)	[a,b]	[b]	
	CTAB	388(41)	[a]	250(6.3)	0.15
	NaLS	393(42)	[a]	252(6.1)	0.15
11-cis	methanol	378(23)	288(12)	254(16.5)	0.72
	Triton X-100	380(23)	[b]	[b]	
	CTAB	387(24)	294(10)	255(12.8)	0.53
	NaLS	393(25)	296(9.8)	256(13.2)	0.53

[a] Band system II is not discernible in the case of all-trans retinal.
[b] The strong absorption of Triton X-100 < 300 nm makes it impossible to observe band systems II and III.

The fluorescence of retinals in micelles is difficult to observe under steady-state lamp excitation ($\phi_F < 10^{-4}$). Their weakly fluorescing character, however, becomes apparent under laser pulse excitation. Micellar effects on the emissive behavior of retinals were not pursued in any detail in the present study. Upon laser flash photolysis (337.1 nm), micellar solutions of retinals produce short-lived absorbance changes at 400-500 nm, attributable to their triplets (see Figure 2). In well-degassed solutions the triplets decay over microseconds by clean first-order kinetics. As expected, their lifetimes become shortened by an order of magnitude upon saturation with air. Using benzophenone triplet formation in acetonitrile ($\phi_T = 1$, $\epsilon^T_{max} = 6.5 \times 10^3$ M^{-1} cm^{-1} at 520 nm)[8] for actinometry, we determined the quantum yields (ϕ_T) of the intersystem crossing process. We employed the comparative technique[9] in which the end-of-pulse absorbances due to the triplets at their maxima were measured under 337.1 nm laser pulse excitation of optically matched solutions. For retinals in micelles, the maximum triplet extinction coefficients (ϵ^T_{max}) were taken to be the same as those in methanol (namely, 3.4×10^4 and 2.7×10^4 M^{-1} cm^{-1} for all-trans and 11-cis retinal, respectively).[10] The triplet-related photophysical data are summarized in Table II.



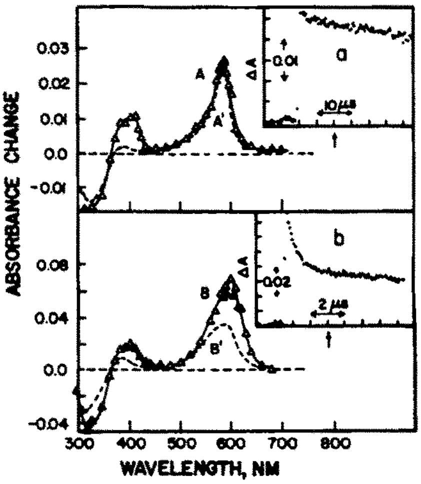


Figure 2: (left) Transient absorption spectra at (A) 0.5 (A') 35, (B) 0.8 and (B') 35 μs following 337.1 nm laser pulse excitation of (A, A') all-trans retinal and (B, B') 11-cis retinal solubilized in 40 mM Triton X-100 (argon-saturated). Insets: representative kinetic traces at (a) 470 and (b) 460 nm for all-trans and 11-cis retinal solutions, respectively.

Figure 3: (right) Transient absorption spectra (A) 1.0, (A') 35, (B) 0.1 and (B') 10 μs following 337.1 nm laser pulse excitation of (A,A') all-trans retinol in 25 mM Triton X-100 and (B,B') all-trans retinyl acetate in 20 mM CTAB (both argon-saturated). Insets: representative kinetic traces at (a) 585 and (b) 600 nm for retinol and retinyl acetate solutions, respectively.

As evident from Figure 2, following the decay of the triplets, permanent absorption spectral changes are observed in the regions of ground state absorption (350-450 nm). For all-trans retinal (Figure 2A'), the changes are negative understandably because of trans ---> cis photoisomerization, the cis isomers having lower ground-state extinction coefficients. The opposite is the case with 11-cis retinal (Figure 2B') for which permanent positive absorbance changes are noted as a result of cis ---> trans isomerization. Based on the assumption that in the case of 11-cis isomer the photoisomerization leads only to the all-trans form, the quantum yields of photoisomerization (ϕ_{PI}) were determined from the laser-flash-photolytic absorbance changes at the end of triplet decay. ϕ_{PI} data for 11-cis retinal are given in Table II. The ϕ_{PI} values were found to remain practically unchanged under air-saturation; this suggests that the thermally relaxed triplets constituting the observed oxygen-quenchable transient absorption, are not the principal mediators of photoisomerization. The involvement of short-lived singlets and/or unrelaxed triplets have been suggested in earlier studies[11,12] of photoisomerization of retinals.

Table II. Photophysical and Photochemical Properties of All-trans and 11-cis Retinal in Micelles, as Observed by 337.1 nm Laser Flash Photolysis.

retinal isomer	medium	λ_{max}^{T}, nm	ϕ_T[a]	ϕ_{PI}[b]	τ_T, μs[c]
all-trans	methanol	460	0.13[d]		12
	Triton X-100	470	0.20		7.6(1.0)
	CTAB	470	0.09		7.1(0.64)
	NaLS	470	0.04		6.6(0.60)
11-cis	methanol	455	0.10[d]	0.10	9.0
	Triton X-100	460	0.16	0.13	9.3(1.1)
	CTAB	460	0.10	0.16	13(0.68)
	NaLS	460	0.03	0.11	14(0.63)

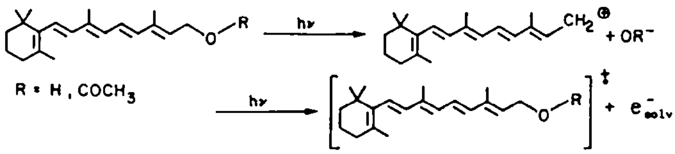
[a] Based on ϵ_{max}^{T} = 3.4 x 10^4 and 2.7 x 10^4 M^{-1} cm^{-1} for all-trans and 11-cis retinal, respectively (as measured in methanol).[10]

[b] Calculated for 11-cis retinal, based on the assumption that it is photoisomerized to the all-trans form only.

[c] The lifetimes in the parentheses are in air-saturated solutions.

[d] The ϕ_T values in the literature[10] are 0.12 and 0.11 for all-trans and 11-cis retinal, respectively (λ_{ex} = 353 nm).

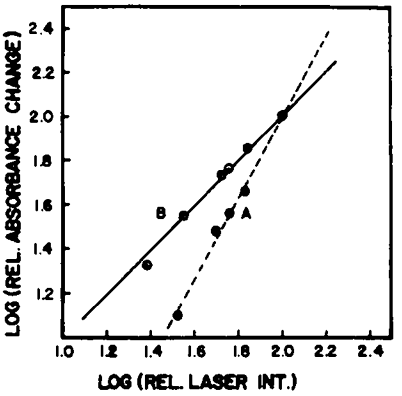
(b) All-trans Retinol and Retinyl Acetate. The major transient (Figure 3) observed upon 337.1 nm laser flash photolysis of retinol and retinyl acetate in micelles is the retinyl carbocation (λ_{max} = 585-600 nm) produced as a result of ionic photodissociation (equation 1). This photoprocess has been recognized[13-15] in previous studies of retinol derivatives in polar solvents. Since the radical cations[15,16] of retinol derivatives are spectrally similar to the retinyl carbocation,[17,18] it is important to determine if photoionization (equation 2) leading to radical cation and e_{solv}^- occurs under laser excitation. Note that the photoejection of electron can be particularly facile in the anionic micelle, NaLS, because the coulombic repulsion from negatively charged micellar boundary helps the separation of e_{solv}^- from the geminate radical cation.[19] Furthermore, Lo et al.[15] have noted evidence for onset of photoionization in retinyl acetate in methanol upon addition of water to the alcohol. However, in spite of our best efforts using moderately defocussed laser pulses (337.1 nm), with neither retinol nor retinyl acetate in any of the three micelles could we observe transient absorptions at long wavelengths (650-750 nm) that could be ascribed to e_{aq}^-. Thus photoionization under the conditions of our experiments can be considered negligible.



(1)

(2)

The dependence of quantum yield (ϕ_{diss}) of ionic photodissociation on laser intensity was examined in detail. In these experiments, the intensity of the laser pulse (337.1 nm, < 3 mJ/pulse) was varied by placing neutral density filters (Balzers) in its path and was measured in terms of end-of-pulse absorbance due to benzophenone triplet in an optically matched solution of the ketone in acetonitrile. Figure 4 shows two representative log-log plots of relative photodissociation yield in NaLS vs. relative laser intensity. Evidently, the slope (1.8) in the case of retinol (Figure 4A) is much higher than in the case of retinyl acetate (slope = 1.0, Figure 4B). Clearly, the photoprocess is monophotonic for retinyl acetate and predominantly biphotonic for retinol. This laser intensity dependence of ϕ_{diss}, also observed in the other two micelles, is in agreement with analogous behaviors in methanol as noted in previous studies.[14,15]



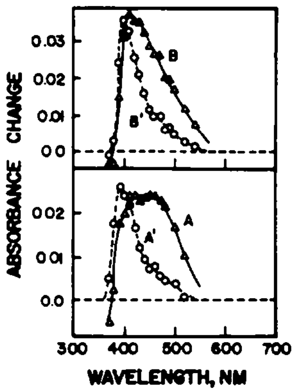


Figure 4: (left) Log-log plots of relative yield of retinyl carbocation vs. relative laser intensity, for (A) all-trans retinol and (B) all-trans retinyl acetate solubilized in 25 mM NaLS.

Figure 5: (right) Transient absorption spectra at (A) 0.2, (A') 10, (B) 0.1 and (B') 10 μs following 355 nm laser flash photolysis of all-trans retinyl Schiff base solubilized in (A,A') CTAB and (B,B') Triton X-100 micelles (both air-saturated).

Using a value of 4.4 x 10^4 M^{-1} cm^{-1} for ϵ_{max} of retinyl carbocation (as measured in methanol + 51.1 mole % H_2SO_4 at -45°C),[17] we have determined ϕ_{diss} values for retinyl acetate. These values as well as some fluorescence data are presented in Table III. Under a given set of conditions of ground-state absorbance, laser intensity, etc., the end-of-pulse absorbance due to the retinyl carbocation of biphotonic origin from retinol is found to decrease in the order: NaLS < CTAB < Triton X-100. This order is the same as that found for the monophotonic photodissociation of retinyl acetate (Table III).

Table III. Photophysical and Photochemical Properties of All-trans Retinol and Retinyl Acetate in Micelles.

Substrate	medium	λ^F_{max}, nm [a]	ϕ_F [b]	ϕ_{diss} [c]
retinol	methanol	500		
	Triton X-100	490	0.02	
	CTAB	490	0.007	
	NaLS	500	0.006	
retinyl acetate	methanol			0.11
	Triton X-100	505	0.053	0.06
	CTAB	500	0.025	0.10
	NaLS	520	0.015	0.17

[a] ± 5 nm. [b] λ_{exc} = 340 nm. [c] Based on ϵ_{max} = 4.4 x 10^4 M^{-1} cm^{-1} for retinyl carbocation.[17]

The decay of retinyl carbocation photogenerated from retinyl acetate in micelles occurs slowly and is insensitive to the presence of oxygen. Estimated from decay profiles over ~ 100 μs, the typical lifetimes are 130 and 180 μs in Triton X-100 and NaLS, respectively. Interestingly, in CTAB, the decay of retinyl carbocation exhibits two components associated with lifetimes of 0.7 and 20 μs. The transient absorption spectrum at the beginning of the fast component (i.e., the end-of-pulse spectrum) is similar in shape and location to that following its completion, except that the maximum of the latter is slightly blue-shifted (by ~ 5 nm). The laser flash photolysis of retinyl acetate in another cationic micelle, namely, cetyltrimethylammonium chloride (CTAC) also leads to retinyl carbocations that display the biphasic decay behavior (τ_1 = 0.7 μs and τ_2 = 90 μs).

In addition to the carbocation absorbing at long wavelengths, transient phenomena related with shorter-lived triplets are observed at 360-430 nm, particularly with retinol in Triton X-100 and CTAB. Oxygen-sensitive, the decay of the triplets occur with lifetimes of 8-14 μs (in Ar-saturated solutions). The maximum triplet yield was observed for retinol in CTAB (ϕ_T ~ 0.01), understandably because of an external heavy-atom effect from bromide counterions.[20]

(c) <u>All-trans Retinoic Acid and N-Butylamine Schiff Base of Retinal</u>. Virtually no transient phenomena are observed upon 337.1 nm laser pulse excitation of all-trans retinoic acid in micelles. In the light of a previous report[15] on biphotonic photoionization of this retinyl system in methanol, we expected this photoprocess to occur in the aqueous systems, particularly in the anionic micelle NaLS. Our failure to observe retinoic acid radical cation (λ_{max} = 590 nm in methanol)[15] or photoejected e^-_{aq} is attributable to the relatively low intensity of laser pulses used.

The ground-state absorption spectrum of all-trans retinal Schiff base in Triton X-100 is almost identical to that in methanol (λ_{max} = 363 nm), while that in CTAB is only nominally red-shifted (λ_{max} = 364 nm). Upon acidification of the solutions in methanol and Triton X-100 by addition of perchloric acid (1.7 mM), the low-energy absorption band system ($^1B_u^{+*}$ <--- ^1A_g) becomes considerably red-shifted (λ_{max}'s = 443 and 435 nm, respectively); this is due to the protonation of the Schiff base. Because of the relatively low pH available in NaLS, the dissolution of retinal Schiff base in this micelle results in extensive protonation as evidenced by the low-energy location of its absorption (λ_{max} = 445 nm); upon addition of perchloric acid (1.7 mM), the absorption maximum becomes further red-shifted (i.e., to 452 nm), but only slightly. Since the pK_a of the protonated form of retinal Schiff base is 6.95 (in aqueous methanol),[21] this result suggests that the effective pH of the environment probed by this substrate in NaLS is close to this value.

The laser flash photolysis of retinal Schiff base solubilized in Triton X-100 and CTAB results in weak transient phenomena due to its triplet (λ_{max} ≥ 460 nm, τ = 10-11 μs), see Figure 5. Interestingly, in both micellar solutions, residual "permanent" absorptions are noted at the end of the decay of the triplets. These absorptions occupy the spectral region 370-480 nm and maximize at 400-410 nm. Ground state depletion is observed at 300-370 nm at the expense of the formation of the triplets as well as the long-lived photoproducts. The deliberate quenching of the triplets by oxygen (in air-saturated solutions) does not make any difference in the yields of the long-lived photoproducts, suggesting that the latter are formed via short-lived singlets or prethermalized triplets.

DISCUSSION

Relevant to solubilization in micelles, a desirable structural feature possessed by the retinyl polyenes is that they are also, to a certain extent, amphiphilic. While the trimethyl-substituted cyclohexene end (β-ionylidene moiety) constitutes the most hydrophobic portion of these molecules, the heteroatom-bearing functional groups at the other end of the polyene chain are predominantly hydrophilic. Based on this structural feature, one would expect the retinyl polyenes to orient themselves parallel to the monomer components of a micelle, with the β-ionylidene end residing at or near the micellar core. Because of these micelle-controlled pre-orientations, the functional groups become subject to specific interactions with charged micellar boundary and water molecules at the interface as well as with counter ions at or near the interface.

The preorientational effect[19,20] in micelles is seen to manifest itself significantly in the absorption spectra of 11-cis retinal. From detailed studies[22-24] of solvent and temperature dependence of absorption spectra and NMR structural investigations[25,26], it has been shown that 11-cis retinal exists in isotropic solutions as an equilibrium mixture of two conformers, namely, distorted 12-s-trans and distorted 12-s-cis (see Chart I). The relative population of these two conformers is dependent on solvent nature and temperature. The 12-s-trans has a dipole moment 2.2 D larger than the 12-s-cis and becomes preferred in polar solvents or at low temperatures (because of the increasing importance of the contribution of an electrostatic term to solvation energy at the expense of that of a cavity formation term).[24] Although the assignment of the transition responsible for band system III (λ_{max} = 250-256 nm in 11-cis retinal) is still ill-understood and controversial,[7] there is no doubt about the experimental fact that it is linked, in general, with the cissoid nature of the polyene geometry. Specifically in 11-cis retinal, band system III is recognized to be more intense for the 12-cis-conformer. [7,22-24,27,29] As evident from the absorption spectral data of 11-cis retinal in micelles (Table I), the relative intensity of the maximum of band system III with respect to band system I (that is, $\varepsilon_{max}^{III}/\varepsilon_{max}^{I}$) becomes considerably lower on going from methanol to CTAB and NaLS. This is not due to a polarity effect because, in comparison, the change in $\varepsilon_{max}^{III}/\varepsilon_{max}^{I}$ on going from n-heptane to methanol is rather negligible. It appears that the 12-s-trans form of 11-cis retinal can pack itself better among the linear monomer units of a micelle (relative to the 12-s-cis form). The latter is more bent, and hence, less compatible with the linear structural units of the micelles under consideration. Needless to say, more definitive evidence for preferred conformations under micelle packaging should be obtained from NMR investigations similar to those of Rowan et al.[26]

The triplet yields of retinals are known to be sensitive to the polarity of the medium. For example, on going from hexane (or benzene) to methanol (or dimethylsulfoxide), ϕ_T values drop by factors of four to ten.[10,29] This is explained in terms of reversal of low-lying $^{1,3}(n,\pi^*)$ and $^{1,3}(\pi,\pi^*)$ states directly involved in the intersystem crossing process.[10,29] The ϕ_T values of retinals in micellar media (Table II) are small (0.03-0.20) and are of the general order of those in methanol. This suggests that the polarity of their environment in micelles is close to that of methanol. For both all-trans and 11-cis retinal, ϕ_T's decrease in the order: Triton X-100 > CTAB > NaLS. This trend, indicating that the polarity of the medium increases in the same order, is in agreement with the findings obtained through the use of other probes, namely, fluorescence maximum of pyrene-3-carboxaldehyde[30] and ANS derivatives[31] and UV absorption maximum of benzophenone.[32]

Another interesting finding that reflects a difference in the behavior of the three micelles concerns retinal triplet lifetimes in air-saturated micellar solutions. Assuming that the solubility of oxygen in the bulk aqueous phase of the micellar solutions is the same as that in neat water (0.265 mM under air-saturation at 25°C)[33] and that the bimolecular rate constant for oxygen quenching in water is not different from that in a nearly equally viscous solvent, cyclohexane ($\underline{k}_{q,O_2}^{T}$ = 4 x 10^9 M^{-1} s^{-1} for all-trans retinal triplet),[34] one would calculate the retinal triplet lifetimes in air-saturated aqueous solutions to be close to 0.8 μs. The observed lifetimes (τ_T) in air-saturated micellar solutions (0.6-1.1 μs, Table II) hover about this value. What is interesting, however, is the fact that for both isomeric retinals, τ_T's in Triton X-100 are considerably longer than those in CTAB and NaLS. After subtracting the intrinsic component, the component of the rate of triplet decay arising from oxygen quenching is about twice slower in Triton X-100 than in the other two micelles. It seems unlikely that this difference arises from that in the concentration of oxygen in the bulk water and/or in the micelle. One probable reason is that the diffusion of oxygen into the micelle is slower in the case of Triton X-100 because of its higher microviscosity.[20] The quenching of polyene triplets by oxygen is dominated by energy transfer.[34] For dynamic energy transfer, the diffusional approach of the interacting partners toward each other is crucial for the sake of good overlap necessary for exchange interaction.

The photoisomerization efficiencies (ϕ_{PI}) of 11-cis retinal in micelles are slightly higher than, but comparable to, ϕ_{PI} in methanol. However, ϕ_{PI} values do not show a definitive trend with polarity or microviscosity of the micelles. It is tempting to relate the higher ϕ_{PI}'s in micelles to the fact the micellar solubilization favors the 12-s-trans form (vide supra), which is recognized to have a dipole-forbidden A_g^{-*} state as the lowest singlet excited state.[35] The barrier to photoisomerization from this state is lower.[35] Such an interpretation, however, must await more precise and detailed studies of photoisomerization (including isomer distribution of products) in various organized assemblies under both steady-state and pulsed irradiation.

The efficiencies of ionic photodissociation (ϕ_{diss}, Table III) of retinyl acetate solubilized in the three micelles are close to ϕ_{diss} in methanol. In an order opposite to that observed for ϕ_T's of retinals, ϕ_{diss} increases systematically on going from Triton X-100 to CTAB to NaLS. Again, this reflects the parallel increase in the polarity of the environment experienced by the polyene. Note that the fluorescence yield (ϕ_F) changes in an order opposite to that of ϕ_{diss}; this is probably due to the increase in the rate of photodissociation from singlet with increase in polarity. In analogy to photoionization,[19] one would expect the charge separation in the course of the ionic dissociation to be facilitated by the anionic micelle, NaLS, and retarded by the cationic micelle, CTAB. But the observed trend in ϕ_{diss} suggests that the effect of the boundary charge, if any, is small and is over-ridden by the polarity effect.

It is difficult to give a straightforward explanation for the biphasic decay of retinyl carbocation (R^+) photogenerated from retinyl acetate in the cationic micelles, CTAB and CTAC. The major quenchers for a carbocation in these micelles are the halide counteranions. The rate constant measured[18] for the quenching of R^+ by Br^- in 2-propanol is 1.9 x 10^9 M^{-1} s^{-1}. It appears that in the microsecond time domain the carbocations occupy two distinct sites. One is close to the aqueous interface where halide ions become easily available as quenchers. The other is possibly the interior of the micelle wherein the carbocation is less susceptible to the quenching by the counteranions.

The long-lived residual absorbance changes (λ_{max} = 400-410 nm) observed as a result of the laser flash photolysis of all-trans retinyl Schiff base solubilized in CTAB and Triton X-100 micelles (Figure 5) cannot be due to photoisomerization. This inference is based on the consideration that the cis isomers have lower ground-state extinction coefficients than the all-trans isomer[36] and hence trans --> cis conversion should lead only to depletion. Also, the cis isomers absorb essentially in the same region as the all-trans isomer[36] and hence their formation should not lead to the red-shifted absorbance changes at 380-480 nm. Since the pK_a of protonated retinal Schiff base increases enormously (i.e., from 6.95 to ~ 16.95) on going from the ground state to the fluorescing state,[21] the high basicity of the Schiff base in the singlet excited state should render protonation facile upon photoexcitation in an aqueous environment. Thus, one can interpret the observed absorbance changes in terms of photoinduced, singlet-mediated protonation. However, if the residual absorbance change in the course of laser flash photolysis in micellar media is only due to the conversion of all-trans unprotonated Schiff base to its all-trans protonated form, the maximum of this change should be displayed at longer wavelengths (435-445 nm). In practice, the maximum is observed at 400-410 nm (Figure 5). Thus, the straightforward protonation alone cannot explain all of the observed absorption changes. It is possible that the Schiff base in the singlet excited state forms complex(es) with water which are not necessarily totally protonated. Also, we cannot rule out ionic photointermediates in which water is bonded via oxygen atom to the carbon atom of the C=N bond. Such intermediates would lead to the hydrolysis of the Schiff base to aldehyde under photoexcitation of the former.

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