Electrochemical and Optical Study of Carotenoids in TX100 Micelles: Electron Transfer and a Large Blue Shift

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The first oxidation waves of 8′-apo-β-caroten-8′-al (**I**) and 8′-apo-β-caroten-8′-nitrile (**II**) in TX100 micelles are clearly observed in their cyclic voltammograms (CVs). The CV of β-carotene (**III**) in TX100 micelles shows that **III** is not oxidized. It is proposed that the hydrophobic barrier of the micelle is an important reason for the failure to oxidize **III**, which is totally located in the hydrophobic center of the micelle. The oxidation of **I** and **II** demonstrates that electrons can be transferred through the terminal groups over a distance of ca. 22 Å. An unusually large blue band shift (100 nm, relative to that in CH_2Cl_2) is observed in the optical absorption spectrum of 7′-apo-7′,7′-dicyano-β-carotene (**IV**) in TX100 micelles. This phenomenon is not observed in the absorption spectra of other studied carotenoids. A change in the ground-state electronic structure of **IV**, due to the influence of water near the terminal dicyanomethylidene group, is proposed to be the major reason for this large band shift.

Introduction

Carotenoids, found in plants, animals, and algae,[1] play important photoprotection and light-harvesting roles in photosynthetic organisms.[2−4] It has also been suggested that carotenoids may act as anticancer agents[5] probably because of their antioxidant and free radical quenching properties.[6,7] The behavior of a variety of carotenoids in organic solvents has been studied by electrochemical, optical absorption spectroscopic, HPLC, EPR, and ENDOR (electron nuclear double resonance) methods.[8−13] These compounds can easily lose two electrons by electrochemical or chemical oxidation (by $FeCl_3$, I_2, etc.). The resulting radical cations and dications of some carotenoids are fairly stable in organic solvents (for example, β-carotene and canthaxanthin in CH_2Cl_2), while the oxidation products of other carotenoids are very unstable (for example, isozeaxanthin and 7,7′-diapo-7,7′-diphenyl-15,15′-didehydro-carotene in CH_2Cl_2). The electrode and homogeneous reactions that take place in electrochemical processes of carotenoids in organic solvents are shown in Scheme 1.[8,9,14−17] In natural systems, in which the environment is very different from that in organic solvents, radical cations of carotenoids are usually short-lived. In organic solvents, carotenoids can move freely, whereas in natural systems they are fixed in their positions and have an ordered environment, which can change their behavior. For example, in photosynthetic organisms, the ordered protein environment has been shown to affect the properties of carotenoids through intermolecular interaction.[18−20] The carotenoid to (bacterio)-chlorophyll energy-transfer efficiency in reconstituted light-harvesting complexes also depends on the protein structure.[21] This matrix dependence is one reason for our study of carotenoids in micelles in which carotenoids can be arranged in an ordered way. In addition to this ordered environment, micelles also provide an interface of a hydrophilic and a hydrophobic region. This interface can be a simple model for studying the processes occurring at biological membranes.

SCHEME 1[a]

electrode reactions

$$\mathrm{Car} \rightleftharpoons \mathrm{Car}^{\bullet+} + \mathrm{e}^- \quad (1)$$

$$\mathrm{Car}^{\bullet+} \rightleftharpoons \mathrm{Car}^{2+} + \mathrm{e}^- \quad (2)$$

$$^{\#}\mathrm{Car}^{\bullet} \rightleftharpoons {}^{\#}\mathrm{Car}^{+} + \mathrm{e}^- \quad (3)$$

homogeneous reactions

$$\mathrm{Car}^{2+} + \mathrm{Car} \rightleftharpoons 2\mathrm{Car}^{\bullet+} \quad (4)$$

$$\mathrm{Car}^{2+} \rightleftharpoons {}^{\#}\mathrm{Car}^{+} + \mathrm{H}^+ \quad (5)$$

$$\mathrm{Car}^{\bullet+} \rightleftharpoons {}^{\#}\mathrm{Car}^{\bullet} + \mathrm{H}^+ \quad (6)$$

[a] $^{\#}$Car represents the carotenoid with one less proton.

In natural systems, carotenoids are usually located in a hydrophobic environment. However, their terminal polar groups may extend out of the hydrophobic environment to be in contact with water, which may affect the properties of carotenoids. Because carotenoids are extremely insoluble in pure water, it is difficult to study its effects. In solvent mixtures of water and an organic solvent that is miscible with water and can dissolve carotenoids (ethyl alcohol, acetone, etc.), carotenoids can be dissolved. However, aggregation of carotenoids occurs as the concentration of water is increased, whereas at low concentrations of water, the effects of water cannot be observed correctly. In micelles, carotenoids can be dissolved and do not aggregate when their concentrations are appropriate. The long conjugated hydrocarbon chains of carotenoids are located in the hydrophobic regions of micelles, but their terminal polar groups may be in contact with water.

In this paper, we describe the behavior of carotenoids in nonionic Triton X100 micelles observed by electrochemical and optical absorption spectroscopic studies. The electron transfer of incorporated carotenoids to an electrode and the influence of water on carotenoids are investigated. The structures of the studied carotenoids are shown below.

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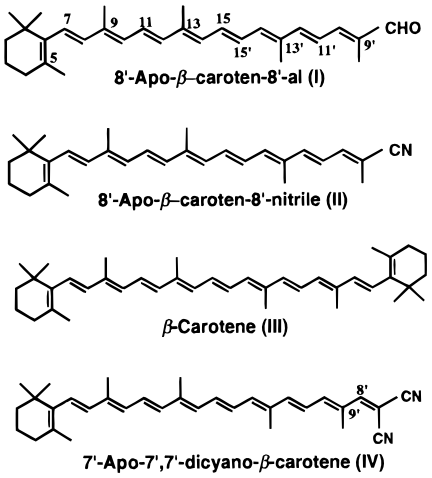


Experimental Section

8′-Apo-β-caroten-8′-al (**I**) was obtained from Roche Vitamins and Fine Chemicals (Nutley, NJ). 8′-Apo-β-caroten-8′-nitrile (**II**) was synthesized from the 8′-aldoxime by reaction with trifluoroacetic anhydride.[22] β-Carotene (**III**) was obtained from Fluka. 7′-Apo-7′,7′-dicyano-β-carotene (**IV**) was synthesized as previously described.[23] All carotenoids were all-trans and stored over Drierite at −16 °C in containers that were wrapped with Parafilm and foil to avoid exposure to moisture and light. Anhydrous dichloromethane (Aldrich) was opened and kept in a drybox under a nitrogen atmosphere. All CH_2Cl_2 solutions of carotenoids were prepared in the drybox. Ethyl alcohol (absolute, 99.5+%) and methyl alcohol (HPLC grade, 99.93%) were from Aldrich. The supporting electrolyte (0.1 M) used in cyclic voltammetry (CV) of carotenoids in CH_2Cl_2 was tetrabutylammonium hexafluorophosphate (TBAHFP, Fluka, polarographic grade), whereas the supporting electrolyte used in the CV of carotenoids in Triton X100 (TX100, Fluka) micelles was potassium chloride (Br < 0.005%, Fluka, 0. 1 M).

Incorporation of carotenoids into TX100 micelles was carried out by dissolving TX100 and the desired carotenoid in CH_2Cl_2, removing the solvent by rotary evaporation under reduced pressure (initially at 20 °C, then at 30 °C after the solvent was almost completely evaporated and kept at this temperature for 30 min) and then dissolving the dried mixture in water (≥ 18 MΩ). The molar ratios of carotenoid to TX100 were ca. 1:100. After rotary evaporation, the sample was dried for 4.5 h at ≤0.1 mmHg and room temperature and showed no difference in our results. Also, when 1% CH_2Cl_2 (volume, relative to the mixture of carotenoids and TX100) was added to the mixture of carotenoids and TX100, no difference was observed in our results.

CVs were carried out with the Bio Analytical System BAS-100W electrochemical analyzer. The working electrode was a glassy carbon disk (diameter 3.0 mm), the counter electrode was a platinum wire, and SCE worked as reference electrode. Optical absorption spectra were recorded using a double-beam Shimadzu 1601 UVPC spectrophotometer. The optical path length was 1 mm.

AM1 (Austin model 1) semiempirical molecular orbital calculations were carried out using UniChem 4.0 software[24] on a Silicon Graphics computer.

Results and Discussions

Cyclic Voltammetry. Figure 1a (solid line) shows the cyclic voltammogram (CV) of **I** in TX100 micelles. A well-shaped

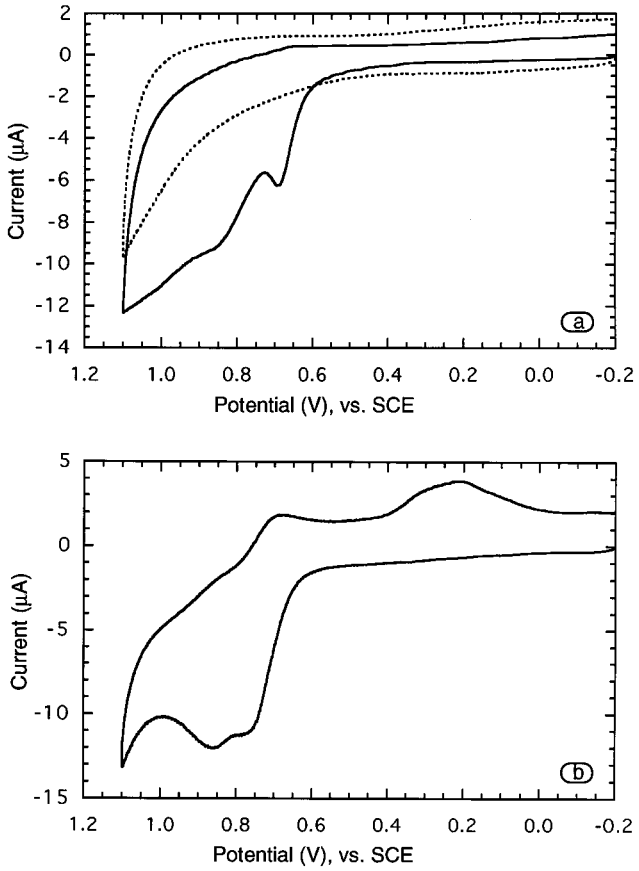


Figure 1. (a) (−) CV of 0.53 mM **I** in 56 mM TX100 micelle and (···) CV of 56 mM TX100 micelle; (b) CV of 0.62 mM **I** in CH_2Cl_2. Scan rate is 0.1 V s^{-1}.

oxidation wave at 0.69 V and a broad shoulder around 0.85 V are observed. Since no reduction waves appear in the subsequent cathodic scan, the oxidation products are short-lived in micelles. The two oxidation waves are attributed to **I** because TX100 micelle itself has no such waves in its CV, as shown by the dotted line in Figure 1a. In the CV of **I** in CH_2Cl_2 (Figure 1b), two oxidation waves appear. One has a peak potential of ca. 0.77 V (oxidation of neutral **I**), the other ca. 0.86 V (oxidation of the radical cation of **I**). The reduction wave of the radical cation of **I** appears at ca. 0.70 V, but no obvious reduction wave of the dication is observed. An additional reduction wave at ca. 0.25 V is attributed to the reduction of $^{\#}Car^{+}$ derived from Car^{2+} by loss of one proton (eq 5 in Scheme 1). By analogy to the oxidation potentials of **I** in CH_2Cl_2, the oxidation wave at 0.69 V in TX100 micelles is assigned to the oxidation of neutral **I**.[25] The peak current (I_p) of the first oxidation wave of **I** in micelles is smaller than that in CH_2Cl_2 (I_p/C^* decreases by a factor of 1.5, where C^* is the bulk concentration of **I**). One major reason for the decrease of I_p in micelles is that the diffusion coefficient (D_0) of **I** incorporated in micelles is smaller than that in homogeneous solutions because of the larger size of micellar particles than of **I** itself. The reason for the broad oxidation shoulder around 0.85 V is not clear, but it cannot be assigned to the oxidation of $Car^{\bullet+}$ because of the instability of $Car^{\bullet+}$ (no corresponding reduction wave in the cathodic scan).[26] It may be due to the oxidation of a decay product of $Car^{\bullet+}$. The $^{\#}Car^{+}$ reduction wave is absent in the micelles. Two possible reasons for this are that less Car^{2+} decays to $^{\#}Car^{+}$ due to other rapid decay paths or that $^{\#}Car^{+}$ itself decays faster in micelles than in CH_2Cl_2.

Figure 2 shows the CVs of **II** in (a) TX100 micelles and (b) CH_2Cl_2. Results similar to **I** are obtained. In the micelles, an

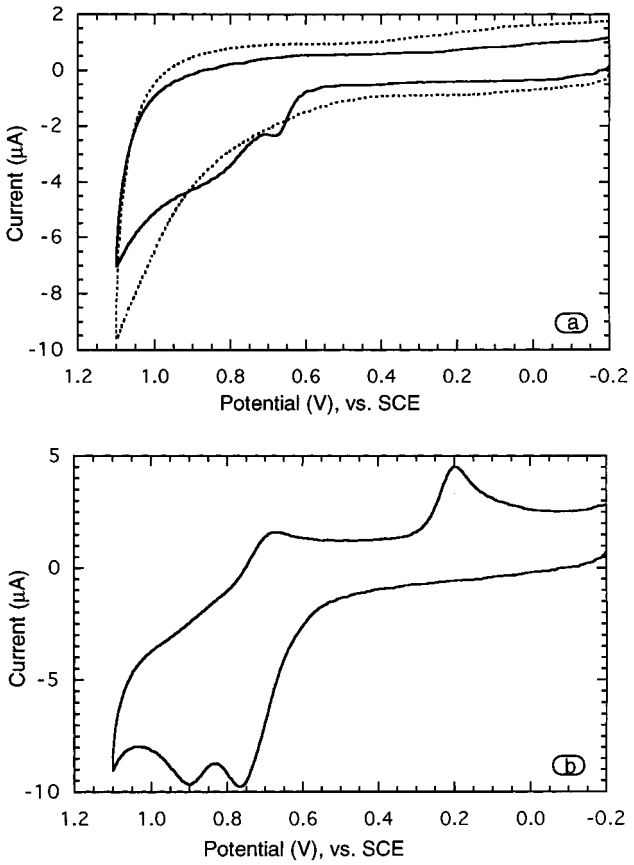


Figure 2. (a) (−) CV of 0.26 mM **II** in 28 mM TX100 micelle and (···) CV of 56 mM TX100 micelle; (b) CV of 0.30 mM **II** in CH_2Cl_2. Scan rate is 0.1 V s^{-1}.

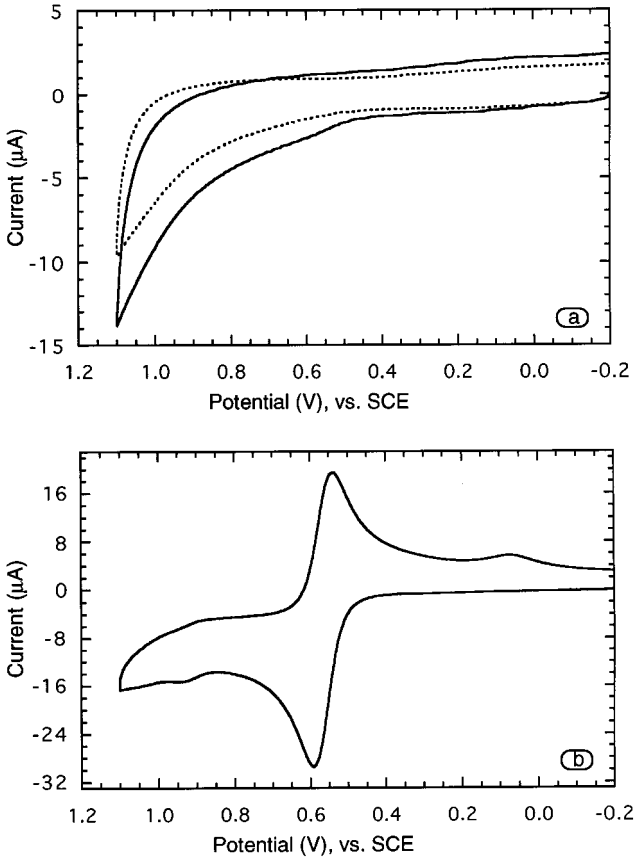


Figure 3. (a) (−) CV of 0.54 mM **III** in 57 mM TX100 micelle and (···) CV of 56 mM TX100 micelle; (b) CV of 1.53 mM **III** in CH_2Cl_2. Scan rate is 0.1 V s^{-1}.

obvious oxidation wave of **II** appears at ca. 0.68 V and a shoulder around 0.80 V. No reduction waves appear in the subsequent cathodic scan. In CH_2Cl_2, two oxidation waves appear at ca. 0.77 and 0.90 V. As in the case of **I**, the oxidation wave at ca. 0.68 V in the micelles is assigned to the oxidation of neutral **II**. Its peak current is also smaller than that in CH_2Cl_2 (I_p/C^* decreases by a factor of 4.2).

However, in the CV of **III** in TX100 micelles, neither oxidation nor reduction waves are obvious (Figure 3a). In CH_2Cl_2, **III** has strong oxidation−reduction waves (Figure 3b), and their potentials are lower than those of **I** and **II**, which shows that neutral **III** loses electrons more easily than **I** and **II** in CH_2Cl_2. The absence of the oxidation wave of **III** in TX100 micelles can only be explained in terms of its position in micelles. According to the structure of TX100 micelles,[27,28] these micellar particles include a hydrated crown with a thickness of 17 Å on its surface and a hydrophobic center with a diameter of 52 Å. Since compound **III** is a symmetrical hydrocarbon, it is totally nonpolar and located in the hydrophobic center. However, compounds **I** and **II** have polar terminal groups (CHO and CN, respectively). These polar groups tend to enter the hydrated crown, while the rest of the molecules stay in the hydrophobic center. Therefore, **I** and **II** are closer than **III** to the surface of micellar particles (also to an electrode) by approximately the length of the CHO and CN groups, respectively. Although a greater distance from an electrode is an unfavorable factor for **III** to transfer electrons to the electrode, this cannot be the only reason for the failure of **III** to lose electrons because this difference in distance from an electrode is not large. Furthermore, the distance from the CHO (or CN) group of **I** (or **II**) to the electrode cannot be the limiting distance for electron transfer between an electrode and carotenoids because **I** and **II** exhibit well-defined oxidation waves in TX100 micelles. An important reason for the failure to oxidize **III** in micelles is the existence of a hydrophobic barrier in the hydrophobic center of the micelles.[29,30] Electrons must overcome this barrier to transfer from **III** to an electrode. This is not so for electron transfer from the terminal polar group (CHO or CN) of **I** or **II** to an electrode because these polar groups are located outside the hydrophobic center.

Our observation of oxidation waves of **I** and **II** in TX100 micelles demonstrates that (1) electrons can be transferred between an electrode and molecules over a long distance. If the outer Helmholtz plane of the double layer on an electrode is ca. 5 Å from the surface of the electrode[31] and the CHO (or CN) group of **I** (or **II**) is approximately 17 Å from the micellar surface, the maximum distance for the electron transfer could be more than 22 Å. The electron transfer between Cu_a and heme a_3 was observed at a distance of 19 Å,[32] and a distance of 35 Å between heme a (or heme a_3-Cu_b) and an electrode was estimated to be sufficient for electron transfer.[33] (2) Electrons can be transferred through terminal groups of molecules. In our case, the only difference among **I**, **II**, and **III** is that **I** and **II** have their terminal polar groups extending beyond the hydrophobic center of micelles. Their long conjugated hydrocarbon chains are in a similar environment as **III** (inside the hydrophobic center). Therefore, the electron transfer from **I** and **II** to an electrode occurs via the terminal CHO and CN groups, respectively. In homogeneous solutions, electron transfer may not be limited to the terminal groups because a molecule can approach an electrode by any part of its structure. In other words, the hydrophobic barrier in micelles may facilitate electron transfer from only one part of a molecule.

TABLE 1: Optical Absorption Maxima (nm) of Carotenoids in Various Matrices

	CH_2Cl_2	C_2H_5OH	CH_3OH	TX100
I	468	460	460	468
II	456	448	445	454
III	461	451	450	459
IV	555	535	533	455 (532)

Optical Absorption Spectrometry. Table 1 lists the absorption maxima of carotenoids **I**−**IV** in TX100 micelles. For comparison, their absorption maxima in CH_2Cl_2, C_2H_5OH, and CH_3OH are also listed. These maxima show that **I**−**III** in TX100 micelles are in an environment with a polarity similar to that of CH_2Cl_2 because their absorption maxima are very close to those in CH_2Cl_2. Because carotenoids are extremely insoluble in water, they are located in micelles. As mentioned above, all of compound **III** is inside the hydrophobic center, whereas the terminal polar groups of **I** and **II** tend to be in the hydrated crown, and their long conjugated hydrocarbon chains are inside the hydrophobic center. Although the CHO and CN groups of **I** and **II** are in the hydrated crown, the change in their absorption maxima is similar to that of **III** as the matrix is changed from organic solvents to the TX100 micelle. This indicates that water in the hydrated crown has little effect on their optical absorption (absorption band shapes in micelles are also very similar to those in CH_2Cl_2). The interesting phenomenon is the very large spectral change of **IV** in micelles with time after dissolving the mixture of TX100 and **IV** in water (Figure 4a). First, the absorption maximum of **IV** appears at 532 nm together with a small shoulder near 455 nm. Later, the 532 nm band decreases while the 455 nm band increases. Finally, after ca. 3 h, the 455 nm band becomes a strong peak while the 532 nm band becomes a small shoulder. No similar phenomenon occurs with **I**, **II**, or **III**. After water is evaporated from the micellar solution and after the mixture of TX100 and **IV** is dissolved in CH_2Cl_2, the resulting solution quantitatively (within experimental error) gives the same absorption spectrum as fresh **IV** in CH_2Cl_2 (Figure 4b). This result shows that **IV** does not decompose in micelles. The change in the absorption spectrum of **IV** with time shows the change of its location in micelles. At first, molecules of **IV** are primarily surrounded by TX100 molecules, resulting in a low polar environment of **IV** and an absorption maximum at 532 nm. Because micellar solutions are dynamic systems, molecules in the micelles rearrange with time until an equilibrium state is reached. In this state, the dicyanomethylidene groups of compound **IV** are primarily located in the hydrated crown, while their long conjugated hydrocarbon chains are imbedded in the hydrophobic center (like **I** and **II**), resulting in an absorption maximum at 455 nm.

The situation of carotenoids in TX100 micelles is different from that in homogeneous organic solvents. In TX100 micelles, one end of a carotenoid molecule with a terminal polar group is located in the hydrated crown while the rest of the same molecule is located in the hydrophobic center. Therefore, one molecule has two different environments. Current theories concerning the absorption band shift in terms of n (solvent refractive index),[34,35] $\Delta\mu$ (the difference in carotenoid dipole moment between ground and excited states),[36,37] and ϵ (solvent dielectric constant)[37] cannot explain the large blue band shift of **IV** in TX100 micelles. We propose that this specific large band shift, from 555 nm in CH_2Cl_2, 535 nm in C_2H_5OH, and 533 nm in CH_3OH to 455 nm in TX100 micelles, is due to a change in the ground-state electronic structure of **IV**. In organic solvents, the electronic structure of **IV** resembles structure **a** (Chart 1), which can be considered to be a combination of several resonance structures. In TX100 micelles, one of the resonance structures, structure **b** (Chart 1), becomes the major contributor. As early as 1939, Förster calculated the effect of changes in ground-state electronic structures of polyenes on their absorption maxima.[38] According to his calculations, polyenes with an electronic structure of type **a** absorb at much longer wavelengths than those with an electronic structure of type **b**.

The ground-state electronic structural change of **IV** in TX100 micelles can occur under the influence of water near the dicyanomethylidene group of **IV** in the hydrated crown of micelles. This influence can be due to the polar−polar interaction between water and the dicyanomethylidene group, which is strongly electron-withdrawing. In the organic solvents studied,

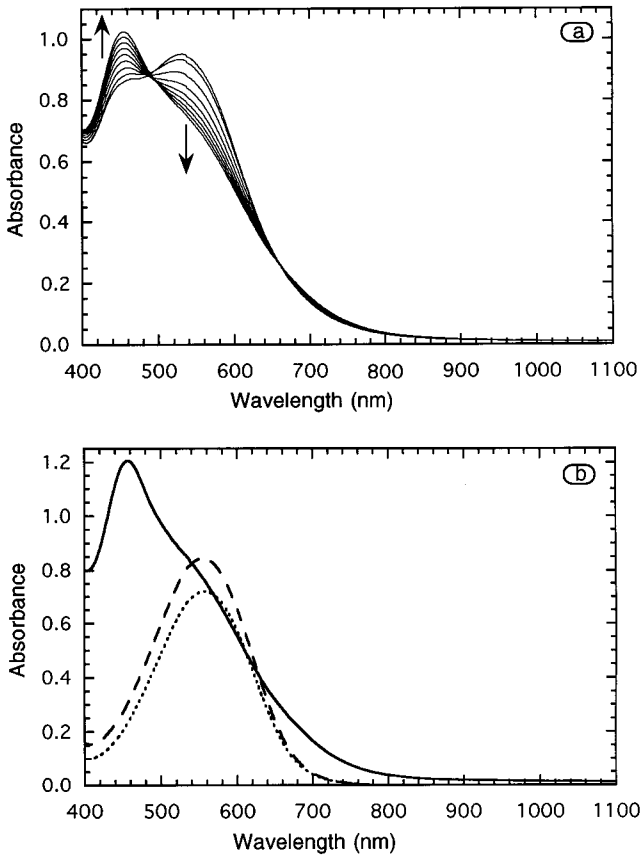
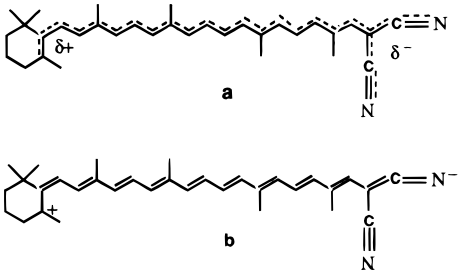


Figure 4. (a) Change of optical absorption spectrum of 0.27 mM **IV** in 30 mM TX100 micelle. First measurement was made 1 h after dissolving a mixture of **IV** and TX100 in H_2O, then recording spectra at 15 min intervals. Measurements starting 6 min after adding H_2O to the mixture of **IV** and TX100 to 1 h showed the same trend (data not shown). The optical path length is 1 mm. (b) Optical absorption spectrum of (−) 0.31 mM **IV** in 35 mM TX100 micelle 15 h after dissolving a mixture of **IV** and TX100 in H_2O; (- - -) the above sample after removal of H_2O and dissolving the residue in 3 times its volume of CH_2Cl_2; (···) 0.09 mM fresh **IV** in CH_2Cl_2. The optical path length is 1 mm.

CHART 1



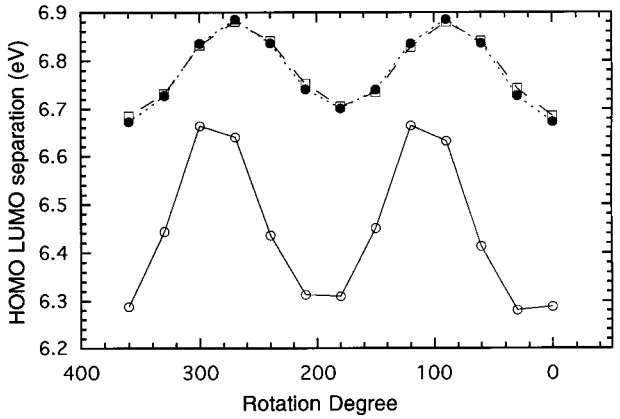


Figure 5. Change of HOMO−LUMO separation with rotation around the C10′−C11′ (**I** and **II**) or the C8′−C9′ (**IV**) bond: (•••) **I**; (- - -) **II**; (−) **IV**.

there is only a partial negative charge on this group. In the TX100 micelles, the polar−polar interaction causes further charge separation on **IV**. The resonance structure **b** becomes the predominant structure. H-bonding may occur between H_2O and N^- in **IV**. For **I** and **II**, CHO and CN groups are not as strongly electron-withdrawing as the dicyanomethylidene group, and their polar−polar interaction with water is weaker. Evidently, the electronic structures of **I** and **II** are not changed in micelles.

The possibility of aggregation of **IV** in TX100 micelles was investigated. At the TX100 concentration in Figure 4a, the aggregation number of TX100 is 143.[28] Therefore, on average, there are 1.3 molecules of **IV** in one micellar particle with 143 TX100 molecules. The possibility of **IV** aggregation is small, although we cannot exclude that a small portion of **IV** molecules may aggregate. When 0.88 molecules of **IV** exist in one micellar particle (on average), we observed similar spectral changes. Furthermore, the decrease of the 532 nm band with time in micelles is almost equal to the increase of the 455 nm band (Figure 4a). In other words, the total absorbance does not decrease with the spectral shift. However, during the aggregation of **IV** in EtOH and H_2O mixtures, since the H_2O content is $\geq$40% (volume), the band at shorter wavelength increases only slightly but the band at longer wavelength decreases considerably. Aggregation of **IV** results in a decrease of total absorbance.

When **I** is in H_2O and EtOH mixtures (98% H_2O by volume), the absorption shift from 460 nm in EtOH to 438 nm occurs, suggesting that aggregates are formed. When **IV** is in the same H_2O and EtOH mixtures, a much larger shift occurs (from 535 nm in EtOH to 457 nm). The optical absorption maximum of **IV** in this H_2O and EtOH mixture is similar to that in TX100 micelles. We suggest that this similarity stems primarily from the following: H_2O is the major solvent in both systems. The interaction between H_2O and **IV** also exists, since **IV** is in H_2O and EtOH mixtures, which causes the much larger blue shift of **IV** than of **I** and also results in the similarity between the cases in micelles and H_2O and EtOH mixtures.

The effect of possible conformation change of carotenoids in micelles on their optical absorption spectra was also investigated by AM1 calculations. The changes of HOMO−LUMO separations with rotation around the C10′−C11′ (**I** and **II**) or the C8′−C9′ (**IV**) bond are shown in Figure 5. With conformation changes, the HOMO−LUMO separations of all studied carotenoids are changed. However, the changes are not large. For **IV**, the maximum change is only 6%. Furthermore, the large blue band shift in absorption occurs only for **IV**, not for **I** and **II**, but the HOMO−LUMO separations of **I** and **II** are also changed with changes of their conformations. Only a small contribution, if any, to the large blue band shift of **IV** can be attributed to a conformation change in micelles.

Conclusions

Electrons can be transferred over a distance of ca. 22 Å from the terminal polar groups of carotenoids that are incorporated in TX100 micelles to an electrode. However, the location of carotenoids in micelles is important to their electron transfer. The hydrophobic barrier in the micelles can prohibit electron transfer from carotenoids that are located inside the hydrophobic barrier. Water is not necessary to have effects on carotenoids if it is in contact with only their terminal groups. However, it can change the ground-state electronic structures of some type of carotenoids if they have strong terminal electron-withdrawing groups. This specificity may allow these carotenoids to have special applications.

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(25) In Osteryoung square wave voltammetry (scan rate: 0.06 V s^{-1}), the first oxidation wave of **I** appears at 0.67 V in micelles and 0.68 V in CH_2Cl_2. I_p/C^* decreases by a factor of 3.2 in micelles, relative to that in CH_2Cl_2.
(26) The lifetime of $Car^{\bullet+}$ cannot be deduced from our CV experiments. Even at 5 V s^{-1} scan rate, no reduction wave was observed. According to

published results of T. G. Truscott (ref 28), the lifetime of $Car^{\bullet+}$ depends on the additives in the aqueous phases. In the presence of 0.3 M Br^-, $Car^{\bullet+}$ of β-carotene generated by pulse radiolysis has a lifetime of 50 ms, whereas it has a lifetime of 4.5 ms in the presence of 0.3 M SCN^-. In our CV experiments of micellar solutions, 0.1 M KCl was used as the supporting electrolyte.

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