

Electron Transfer Studies in C₇₈ (C_{2v}'), C₇₆ (D₂), C₇₀ (D_{5h}), and C₆₀ (I_h) Surfactant Aqueous Solutions

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C₆₀ (I_h) and several higher fullerenes, namely, C₇₀ (D_{5h}), C₇₆ (D₂), and C₇₈ (C_{2v}'), have been solubilized via capping with suitable surfactants. Excited states and reduced states of these surfactant systems were probed by photolytic and radiolytic techniques. Flash photolytic irradiation at 355 nm of surfactant solutions of C₆₀, C₇₀, C₇₆, and C₇₈ revealed the rapid grow-in of transient (*S₁ → *S_n) absorptions with λ_{max} at 920, 660, 650, and 890 nm, respectively. The associated intersystem crossing rates to the energetically lower lying excited triplet states are typically on the order of 9.0 × 10⁸ s⁻¹. Reductive quenching of the excited triplet states by diazabicyclooctane (DABCO) occurs with (0.8–7.4) × 10⁷ M⁻¹ s⁻¹ and yields the fullerene π-radical anions. Direct reduction of surfactant capped fullerene monomers have been studied by means of time-resolved pulse radiolysis with measurements being conducted in the near-IR region. Radiolytic reduction of (C₇₆)_{surfactant} and (C₇₈)_{surfactant} resulted in the formation of characteristic π-radical anion bands positioned at 920 and 980 nm, respectively. Rate constants have been measured for the reduction of these fullerene–surfactant systems with hydrated electrons (k_{et} = (2.6–3.9) × 10¹⁰ M⁻¹ s⁻¹) and (CH₃)₂C(OH) radicals (k_{et} = (3.0–7.2) × 10⁸ M⁻¹ s⁻¹).

Introduction

The combination of excellent electron acceptor properties^{1–3} accompanied by a small reorganization energy,⁴ distinct chromophoric and photosensitizer features,^{5,6} high quantum yield for the excited triplet state, and efficient ¹O₂ production^{7–10} evoked an interdisciplinary interest to study the participation of fullerenes in biologically relevant key processes.¹¹ For example, fullerenes are the subject of a broad spectrum of measurements ranging from free-radical scavenging,¹² antiviral activity,^{13–15} and DNA cleavage^{16,17} to photodynamic therapy.^{18,19} Investigations in aqueous solutions are, however, rather difficult and complex. This can be rationalized, at least in part, in terms of the predominant hydrophobic surfaces of these carbon allotropes inhibiting their solubility in polar solvents or leading to the instantaneous formation of colloidal fullerene clusters of undefined sizes.

The development of methodologies implementing the functionalization of the most abundant fullerene (C₆₀) with hydrophilic addends is regarded as one successful strategy for overcoming these difficulties.^{20–24} Indeed, solubilizing side chains with cationic or anionic head groups promote the water solubility of C₆₀.^{25–27} As a consequence of the relatively large fullerene surface, truly monomeric dissolution necessitates, however, at least two addends linked to the C₆₀ core.²⁷ On the other hand, covalent attachment of functionalizing addends at the C=C junction of two hexagons leads to a modification of the fullerene's 60 π-electron system. Accordingly, this perturbation impacts the electronic and photophysical properties of the fullerene core, for example, the reduction potentials of C₆₀, ¹*C₆₀ and ³*C₆₀ reveal a cathodic shift of ~100 mV upon functionalization.^{28,29}

In contrast to the macroscopically produced C₆₀ (I_h), more than a single isomer satisfying the isolated-pentagon rule have been isolated for higher fullerenes, e.g., C₇₆ (chiral D₂ symmetry) and C₇₈ (C_{2v}, C_{2v}', D₃ symmetry).^{30–34} Although only a single

stable 6–6 closed isomer originates from pristine C₆₀,^{20–24} functionalization of pristine C₇₀ affords, hypothetically, the formation of four regioisomeric monoadducts.^{35–37} Six isomers were even characterized recently for the C₇₆ analogue.³⁵

An alternative approach envisages the incorporation of the fullerene core into the hydrophobic cavity of several macro-molecular host structures, such as γ-cyclodextrine or calix[8]arene.^{38–40} The limited cavity size of cyclodextrines restricts, however, the successful fullerene complexation to the smallest member, namely, C₆₀. Although calix[8]arene inclusion complexes with C₆₀ and C₇₀ can be isolated, the host's π-system is, however, redox active and itself reacts, for example, rapidly with hydrated electrons without reduction of the fullerene.

A very promising further possibility in support of solubilization is micellarization by surfactants.^{41–44} The amphiphilic structure of the surfactant, a hydrophobic tail and a hydrophilic head group, is advantageous to cap and, thus, solubilize pristine C₆₀ and various monofunctionalized C₆₀ derivatives. In contrast to supramolecular hosts, Triton X-100 (reduced form) and cetyltrimethylammonium chloride are (i) redox-inactive substrates and (ii) should not exert any size limitation. Solubilization of higher fullerenes by surfactants also ensures their monomeric dissolution. This method has been applied for the current investigation in which several higher fullerenes C₇₀ (D_{5h}), C₇₆ (D₂), and C₇₈ (C_{2v}') have been solubilized via capping with suitable surfactants and subjected, for the first time, to time-resolved electron-transfer studies by photolytic and radiolytic techniques.

Experimental Section

C₆₀ (I_h) and C₇₀ (D_{5h}) were purchased from SES Research, Inc. (Texas). Fullerene isomers, C₇₆ (D₂) and C₇₈ (C_{2v}'), were purchased from Techno Carbo (France). The purity of the fullerene samples were checked by HPLC, indicating at least 99.85% purity for D₂-C₇₆ and 98.93% for C_{2v}'-C₇₈ (containing ~0.44% of a minor isomer).

Absorption spectra were recorded with a Milton Roy Spectronic 3000 array spectrophotometer.

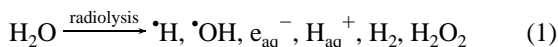
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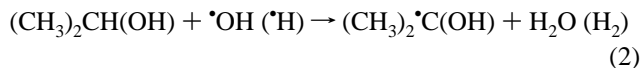
Laser Flash Photolysis. Picosecond laser flash photolysis experiments were carried out with 532 nm laser pulses from a mode-locked, Q-switched Quantel YG-501 DP Nd:YAG laser system (pulse width = 18 ps, 2–3 mJ/pulse). Nanosecond experiments were performed with laser pulses from a Qunta-Ray CDR Nd:YAG system (355 nm, 6 ns pulse width, 5–10 mJ/pulse) or from a Molecron UV-400 nitrogen laser system (337 nm, 8 ns pulse width, 1 mJ/pulse) in a front face excitation geometry. The details of the experimental setup and its operation are described elsewhere.⁴⁶

Pulse Radiolysis. Pulse radiolysis experiments were performed by utilizing 50 ns pulses of 8 MeV electrons from a Model TB-8/16-1S electron linear accelerator. Basic details of the equipment and the data analysis have been described elsewhere.⁴⁷ Dosimetry was based on the oxidation of SCN[−] to (SCN)₂^{•−}, which in N₂O-saturated aqueous solutions takes place with $G = 6$ (G denotes the number of species per 100 eV, or the approximate micromolar concentration per 10 J of absorbed energy). The radical concentration generated per pulse amounts to $(1–3) \times 10^{-6}$ M for all the systems investigated in this study.

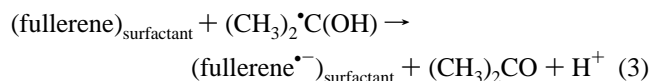
Radiolytic Reduction Reactions. Radiolytic reduction of fullerene surfactant solutions were studied in either N₂- or N₂O-saturated, dilute aqueous solution containing 10 vol % 2-propanol. Under these experimental conditions •H, •OH, and e_{aq}[−] species are produced in addition to molecular products (H₂, H₂O₂) and H_{aq}⁺.



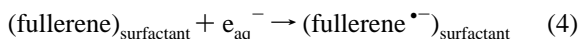
Reaction of the •OH and •H radicals with 2-propanol leads to their conversion into (CH₃)₂•C(OH) radicals.



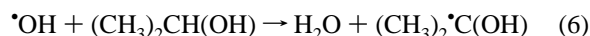
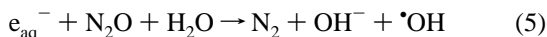
The fairly strong reducing (CH₃)₂•C(OH) radicals, with $E_o = -1.39$ V versus NHE,⁴⁸ are then expected to transfer an electron to the fullerene core.



Under N₂-saturated conditions the hydrated electrons may directly reduce the fullerene via



while in N₂O-purged solutions they are first converted to hydroxyl radicals and, subsequently, to (CH₃)₂•C(OH).



The presence of 2-propanol also serves an additional purpose. Fullerenes, known as efficient radical sponges, would probably add all nonreducing radicals possibly formed in a reaction of •OH with the surfactant molecules. The defined transformation of •OH into the reducing (CH₃)₂•C(OH) radical thus avoids any complication that may arise from the unwanted processes.

Results and Discussion

Absorption Spectra. Surfactant capped fullerene solutions were prepared by stirring a mixture of Triton X-100 (reduced

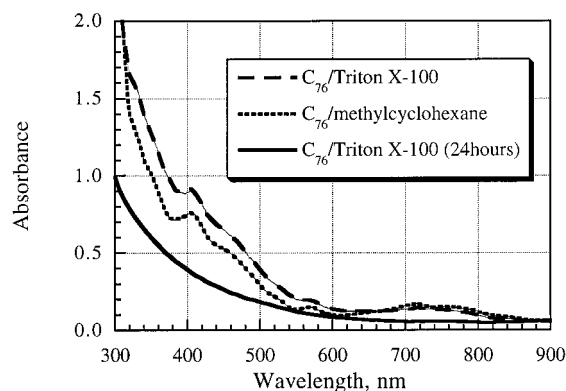


Figure 1. Absorption spectra of 8.8×10^{-5} M (C₇₆)_{surfactant} (dashed line), 7.4×10^{-5} M C₇₆ methylcyclohexane (dotted line), and 8.8×10^{-5} M (C₇₆)_{surfactant} (solid line) (after 24 h).

TABLE 1: Absorption Maxima of Fullerene–Surfactant Solutions at Room Temperature

| compound | absorption maxima in the vis range ^a [nm] |
|--|--|
| (C ₆₀) _{surfactant} (I _h) | 330, 403, 422, 533, 569, 602 (sh), 620 |
| (C ₇₀) _{surfactant} (D _{5h}) | 331, 358, 379, 467, 546, 589 (sh), 610, 637 |
| (C ₇₆) _{surfactant} (D ₂) | 327 (sh), 408, 450 (sh), 565, 714, 761, 830 |
| (C ₇₈) _{surfactant} (C _{2v} ') | 320, 359 (sh), 373 (sh), 420, 468, 522 |

^a (sh) denotes a shoulder.

form) and C₆₀, C₇₀, C₇₆, and C₇₈ at 50 °C for approximately 30 min. The resulting yellow-colored solution of (C₇₆)_{surfactant} was then diluted by water and either filtered off or centrifuged to separate undissolved fullerene solids.

Absorption spectra of 8.8×10^{-5} M C₇₆ solubilized by Triton X-100 (dashed line) and a methylcyclohexane solution of 7.4×10^{-5} M C₇₆ (dotted line) are compared in Figure 1. A typical (C₇₆)_{surfactant} solution displays maxima at 327 (sh), 408, 450 (sh), 565, 714, 761, and 830 nm. The close resemblance with an organic solution (methylcyclohexane) of C₇₆ and the lack of any cluster-induced broadening suggest monomeric dissolution of C₇₆ within the hydrophobic part of the micellar assembly. Surfactant solutions of C₆₀, C₇₀, and C₇₈ displayed (Table 1) similar resemblances to the corresponding organic solutions.

The well-resolved spectral features of (C₇₆)_{surfactant} transformed over a time range of 24 h into broad absorptions (see Figure 1, solid line) dominated by a strong UV onset. Fullerene clusters of either pristine fullerenes or functionalized derivatives and closely packed fullerene films are known to display similarly broad absorption characteristics.²⁷ Thus, this time-dependent transformation can be rationalized in terms of fullerene clustering that is govern by strong π – π interaction among these carbon allotropes. Further corroboration for this assumption emerges from heat-induced changes. For example, keeping the fullerene–surfactant solutions for more than 30 min at 50 °C resulted in a noticeable color change (for example, C₆₀ displays a color change from magenta to brownish yellow) and, subsequently, in an overall broadening of the respective absorption spectra. Consequently, these featureless and broad absorptions can be used as an indicative marker for the identification of colloidal fullerene clusters.

Excited States. Flash photolytic, e.g., nanosecond- and picosecond-resolved, techniques were employed to generate excited and reduced states of surfactant capped fullerene complexes. The excitation wavelength was 355 nm. Differential absorption changes, as recorded upon picosecond photolysis of, for example, 5.0×10^{-5} M C₇₆ (1.0×10^{-3} M Triton X-100 reduced form), indicate the immediate formation of new absorption with λ_{max} around 650 nm (Figure 2). These

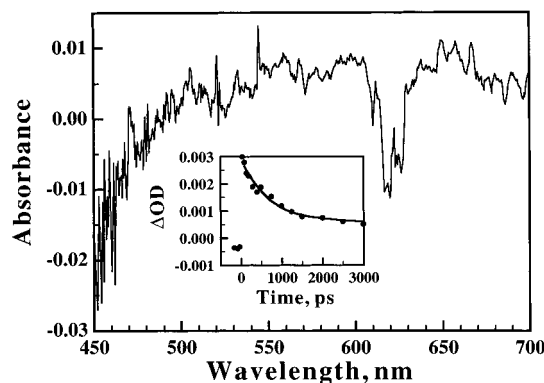


Figure 2. Differential absorption spectra obtained upon picosecond photolysis at 355 nm of 3.0×10^{-5} M $(C_{76})_{\text{surfactant}}$ /Triton X-100 reduced form; (inset) absorption time profile for the decay of $(^*S_1 \rightarrow ^*S_n)$ transition (at 650 nm) of $(^1C_{76})_{\text{surfactant}}$.

spectral characteristics are tentatively assigned to the fullerene's excited singlet state $(^1C_{76})_{\text{surfactant}}$, despite its remarkable blue shift relative to a surfactant solution of pristine C_{60} ($\lambda_{\text{max}} \approx 920$ nm). Parallel to the decay of $(^1C_{76})$ the grow-in of some absorptions around 550 nm was monitored. The half-life of $(^1C_{76})$ derived from the decay at 650 nm and the grow-in at 550 nm was 750 ps (see inset to Figure 2), slightly faster than a previous corresponding finding for C_{60} .⁴⁹ The resemblance of the decay and grow-in kinetics suggests this process to be a direct transformation of the excited singlet state into the energetically lower lying excited triplet state.



Similarly, surfactant solutions of C_{70} and C_{78} showed the rapid grow-in of transient $(^*S_1 \rightarrow ^*S_n)$ absorptions with λ_{max} at 660 and 890 nm, respectively. The associated intersystem crossing rates were typically on the order of 9.0×10^8 s⁻¹.

Corresponding photolytic studies in the nanosecond time regime were performed with the aim of characterizing the spectral features described in the above experiment and of further substantiating the formation of the fullerene's excited triplet state. Differential absorption changes recorded immediately upon nanosecond photolysis of 1.0×10^{-5} M C_{76} exhibit absorption bands with λ_{max} at 550 and 650 nm. These spectral characteristics are reminiscent of those reported for the excited triplet states of C_{76} in aprotic media⁵⁰ and, furthermore, resemble those observed during the course of the picosecond experiments (see above). Accordingly, the spectral changes, as shown in Figure 3a, can be ascribed to the excited triplet state of $(^3C_{76})$ evolving from intersystem crossing from the excited singlet state $(^1C_{76})$. The above assumption is further substantiated by the observation of fine-structured minima around 400, 460, and 560 nm, a region that corresponds to where the ground-state $(C_{76})_{\text{surfactant}}$ absorbs with $\lambda_{\text{max}} = 406, 450,$ and 565 nm.

Kinetic analysis of time-absorption profiles, as observed throughout the UV-vis-near-IR range, revealed a recovery of the transient absorption to the original baseline in an exponential manner. This indicates no noticeable chemical reaction of the photoexcited fullerenes with the surfactant. The excited triplet states of C_{76} and C_{78} decayed with half-lives typically in the range of 20 μ s (see Figure 3b). These values are in significant contrast to the much longer-lived excited triplet states of the C_{60} and C_{70} surfactant system with $\tau_{1/2}$ of 130 and 250 μ s, respectively. A possible rationale for this acceleration may be deactivation of $(^3C_{76})_{\text{surfactant}}$ and $(^3C_{78})_{\text{surfactant}}$ by self-quenching with ground-state fullerenes in combination with the significant

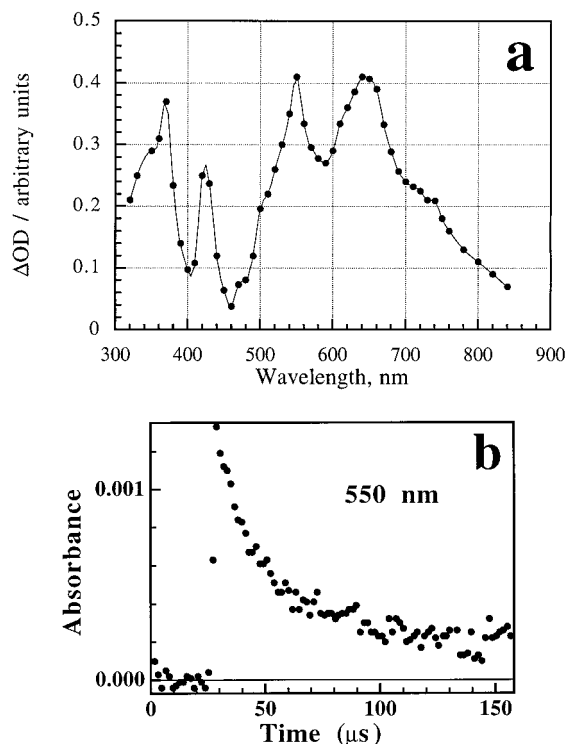


Figure 3. (a) Differential absorption spectra obtained upon flash photolysis at 337 nm of 3.0×10^{-5} M $(C_{76})_{\text{surfactant}}$ /Triton X-100 reduced form; (b) absorption time profile for the decay of $(^*T_1 \rightarrow ^*T_n)$ transition (at 550 nm) of $(^3C_{76})_{\text{surfactant}}$.

lower quantum yields for the excited triplet states of C_{76} ($\Phi_{\text{triplet}} = 0.05$) and C_{78} ($\Phi_{\text{triplet}} = 0.12$).⁵⁰

It should also be noted that aggregation among the fullerene moieties resulted in a dramatic impact on the lifetimes of the excited triplet states. For example, no detectable $(^*T_1 \rightarrow ^*T_n)$ absorption was observed upon exciting $\{C_{76}\}_n$ clusters (a monomeric solution that was kept in the dark for approximately 24 h; see absorption spectra), suggesting rapid intermolecular triplet-triplet annihilation. Similar observations have been made for fullerene clusters of various monofunctionalized derivatives (e.g., $\{C_{60}C(COO^-)_2\}_n$, $\{C_{60}(C_9H_{11}O_2)(COO^-)\}_n$, and $\{C_{60}(C_4H_{10}N^+)\}_n$).²⁷

Reductive Quenching. Intermolecular electron transfer of the fullerenes' excited triplet state with sacrificial electron donors is a well-established process as demonstrated,^{5,39,51} for example, with diazabicyclooctane (DABCO) (IP = 7.5 eV) or ferrocene (IP = 6.9 eV). In the present study, photoexcited surfactant solutions of C_{60} (I_h), C_{70} (D_{5h}), C_{76} (D_2), and C_{78} (C_{2v}) were subjected to electron-transfer processes with DABCO (eq 9). Accordingly, addition of variable amounts of DABCO ($(0.5-2.8) \times 10^{-2}$ M) to a surfactant solution of the fullerene (2.0×10^{-5} M) resulted in the expected accelerated decay of the excited triplet states of $(^3C_{76})_{\text{surfactant}}$. The quenching rates were determined from the decay kinetics of the respective transient triplet-triplet absorptions following excitation at 355 nm. In all cases, the quenching of the excited states by DABCO followed eq 8, where k_{obs} is the observed first-order decay rate constant of fullerene's excited triplet state, k_d is the rate constant without addition of any quencher, k_q is the bimolecular quenching rate constant, and $[Q]$ is the concentration of the quencher.

$$k_{\text{obs}} = k_d + k_q[Q] \quad (8)$$

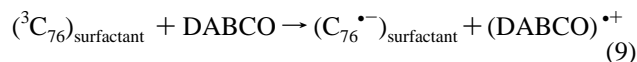


TABLE 2: *S₁ → *S_n and *T₁ → *T_n Absorptions of Fullerene–Surfactant Solutions

| compound | *S ₁ → *S _n absorption [nm] | *T ₁ → *T _n absorption [nm] |
|--|--|--|
| (C ₆₀) _{surfactant} (I _h) | 920 | 750 |
| (C ₇₀) _{surfactant} (D _{5h}) | 660 | 700, 400 |
| (C ₇₆) _{surfactant} (D ₂) | 650 | 650, 550 |
| (C ₇₈) _{surfactant} (C _{2v} ') | 890 | 500 |

TABLE 3: Rate Constants for the Radical-Induced Reduction of (Fullerene)_{surfactant}, Reductive Quenching of the Excited Triplet States of (Fullerene)_{surfactant}, and First Reduction Potential (Measured in Deoxygenated CH₂Cl₂)

| compound | k _{electron} [M ⁻¹ s ⁻¹] | k _{(CH₃)₂C(OH)} [M ⁻¹ s ⁻¹] | k _{quenching} (DABCO) [M ⁻¹ s ⁻¹] | E _{1/2} ^a [V] vs Fc/Fc ^{•+} |
|--|---|--|---|---|
| (C ₆₀) _{surfactant} (I _h) | 2.6 × 10 ¹⁰ | 6.1 × 10 ⁸ | 7.4 × 10 ⁷ | -1.06 |
| (C ₇₀) _{surfactant} (D _{5h}) | 3.9 × 10 ¹⁰ | 3.0 × 10 ⁸ | 8.0 × 10 ⁶ | -1.02 |
| (C ₇₆) _{surfactant} (D ₂) | 3.3 × 10 ¹⁰ | 7.1 × 10 ⁸ | 2.0 × 10 ⁷ | -0.83 |
| (C ₇₈) _{surfactant} (C _{2v} ') | 3.6 × 10 ¹⁰ | 7.2 × 10 ⁸ | <i>b</i> | -0.77 |

^a Taken from ref 53. ^b Could not be analyzed.

The observed first-order rates (*k*_{obs}) were linearly dependent on the DABCO concentration. The intercepts agreed well with the *k*_d value obtained in the absence of quencher. The rate constant of 8.0 × 10⁶ M⁻¹ s⁻¹ for C₇₀ and 2.0 × 10⁷ M⁻¹ s⁻¹ for C₇₆ derived from these measurements are slower than the DABCO-induced quenching of (C₆₀)_{surfactant}, which occurs at 7.4 × 10⁷ M⁻¹ s⁻¹. A rate constant for the C₇₈ system could, unfortunately, not be evaluated owing to the small signals.

The participation of the nitrogen's free electron pair in the proposed electron-transfer reactions was corroborated by the effect that acidification exposes on the quenching reaction. Although addition of 0.01 M HClO₄ to the (C₇₆)_{surfactant} solution did not alter the yield and lifetime of the triplet states, the DABCO-related quenching was completely abolished. This shut-off mechanism was reversible, and the quenching was reactivated by addition of 0.01 M KOH. This can be rationalized in terms of protonation and deprotonation of the tertiary nitrogen, which, in the earlier case, prevents the electron transfer from taking place.

Recent studies on C₆₀ surfactant systems demonstrated that their core(fullerene)–shell(surfactant) type structure promotes the stabilization of (C₆₀•⁻)/(DABCO)^{•+} radical pairs relative to a homogeneous aprotic system (e.g., in which fullerenes are dissolved in toluene or benzonitrile) and host–guest inclusion complexes with γ-cyclodextrine.²⁷ In the surfactant solutions with the higher fullerenes (C₇₀ (D_{5h}), C₇₆ (D₂), and C₇₈ (C_{2v}')), the rates for charge-recombination were found to be on the order of ~6 × 10² s⁻¹ compared to ~1 × 10⁴ s⁻¹ for the C₆₀/γ-cyclodextrine system.²⁷ These rates are well in line with various monofunctionalized fullerene derivatives and can be considered to reflect an efficient shielding of (DABCO)^{•+} molecules from the reduced fullerene moiety through the surfactant shell.

Pulse Radiolytic Reduction. Pulse radiolysis is another important source for fast kinetic spectroscopic studies and for the generation of π-radical anions of pristine fullerenes and functionalized fullerene derivatives.^{39,52} As a consequence of the moderate redox potential of pristine fullerenes (see Table 3), radical-induced reduction by hydrated electrons or (CH₃)₂C(OH) radicals takes place rapidly. Surprisingly, pulse radiolysis experiments failed to substantiate any reduction of some water soluble monoadducts in aqueous solution. The decay of the hydrated electron at 720 nm was virtually unaffected over the applied fullerene concentration, parallel to the lack of any indication for the π-radical anion's fingerprint (e.g., near-IR absorption band).²⁶ These can be rationalized in

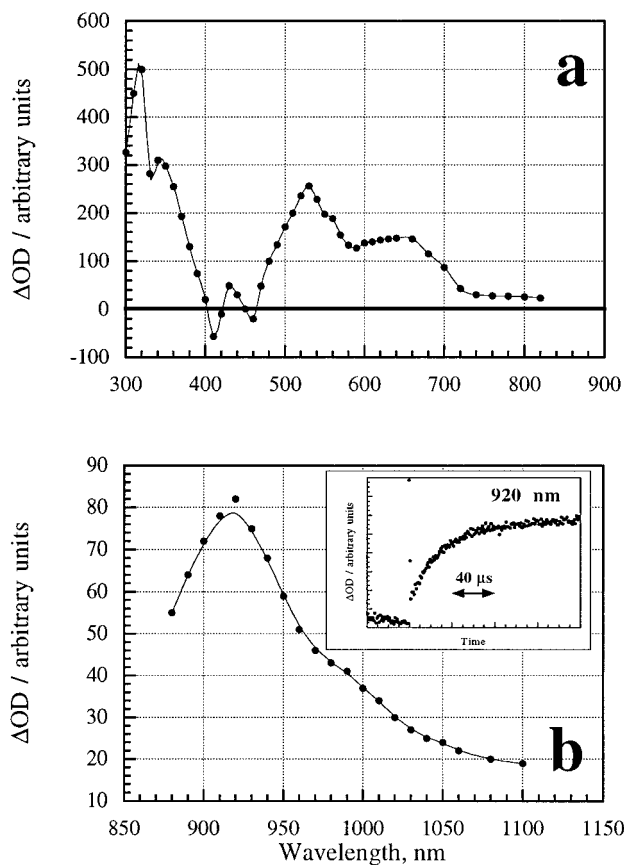
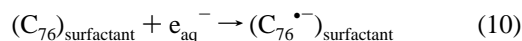


Figure 4. Transient absorption spectrum of (C₇₆•⁻)_{surfactant}: (a) UV–vis part and (b) near-IR part obtained upon pulse radiolysis of 2.0 × 10⁻⁵ M (C₇₆)_{surfactant} (10⁻³ M Triton X-100 reduced form) in nitrogen-saturated aqueous solution (10 vol % 2-propanol).

view of the instantaneous formation of colloidal fullerene clusters with indefinite sizes and, more important, indefinite concentrations. Thus, it is essential to ensure monomeric distribution of C₆₀, C₇₀, C₇₆, and C₇₈ in the apparent surfactant systems. Differential absorption changes at 720 nm (absorption maximum of the hydrated electron), recorded upon pulse radiolysis of 3.0 × 10⁻⁵ M C₇₆ (1.0 × 10⁻³ M Triton X-100 reduced form) in deoxygenated aqueous/2-propanol solution (9:1 v/v), confirm that the apparent fullerene monomer is susceptible to a reaction with hydrated electrons. The spectral changes throughout the UV–vis–near-IR range, as depicted in Figure 4, resemble those reported for the formation of (C₇₆•⁻) in homogeneous organic solutions, e.g., a toluene/2-propanol/acetone (8:1:1 v/v/v) mixture.⁵⁰ Variation of the fullerene concentration ((1.0–4.5) × 10⁻⁵ M) changed the decay rate of the hydrated electron absorption at 720 nm in a linear manner (see Figure 5). Furthermore, its excellent agreement with the grow-in rate of the fullerene's π-radical anion absorption (920 nm) suggests that the observed reaction can be unambiguously ascribed to the reduction of the fullerene by hydrated electrons.



From the slope of the linear plot (*k*_{obs} versus [C₇₆]) the electron-transfer rate constant (eq 10) was estimated to be 3.3 × 10¹⁰ M⁻¹ s⁻¹. The rate constants are summarized in Table 3.

Time–absorption profiles, recorded at 920 nm in the presence of 10 vol % 2-propanol, as shown in the inset to Figure 4b, indicate that the rapid electron-induced reduction of C₇₆ is followed by yet a second, distinctly slower process. The latter is attributed to a reaction of the fullerene moiety with the reducing α-hydroxy radicals, namely, (CH₃)₂C(OH). Indeed,

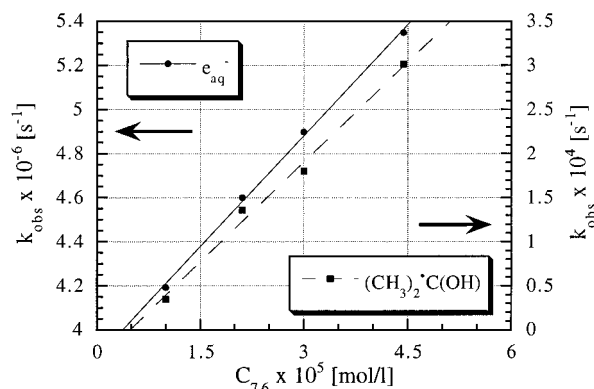


Figure 5. Plot of k_{obs} vs $[C_{76}]_{\text{surfactant}}$ at 720 nm (hydrated electron) and 920 nm ($(\text{CH}_3)_2\text{C}(\text{OH})$ radical) for the reduction of $(C_{76})_{\text{surfactant}}$ in deoxygenated aqueous solution (10 vol % 2-propanol).

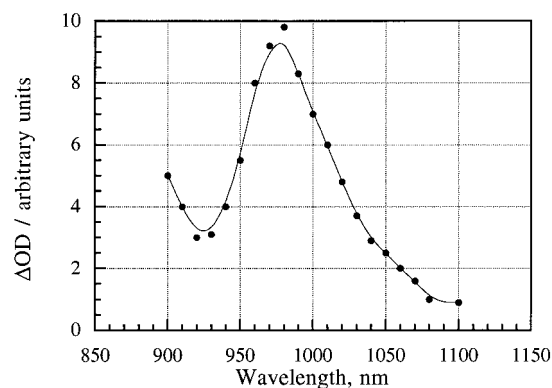
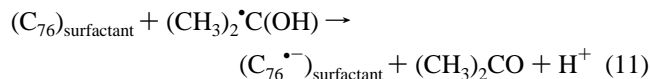


Figure 6. Transient absorption spectrum (near-IR) of $(C_{78})_{\text{surfactant}}^{•-}$ obtained upon pulse radiolysis of 2.0×10^{-5} M $(C_{78})_{\text{surfactant}}$ (10^{-3} M Triton X-100 reduced form) in nitrogen-saturated aqueous solution (10 vol % 2-propanol).

differential absorption changes recorded after the completion of the $(\text{CH}_3)_2\text{C}(\text{OH})$ -induced reaction (e.g., 200 μs after the pulse) closely resemble those shown in Figure 4. This substantiates formation of $(C_{76})_{\text{surfactant}}^{•-}$ via electron transfer from $(\text{CH}_3)_2\text{C}(\text{OH})$. The associated kinetics were linearly dependent on the fullerene concentration (Figure 5) with a bimolecular rate constant of $7.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (see Table 3).



The determined rate constants reflect a slow-down of the reduction process relative to the radical-induced reduction of C_{76} in organic media, where rate constants typically were in the range $(8\text{--}16) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.⁵⁰ This suggests that the rate-determining step for the formation of $(C_{76})_{\text{surfactant}}^{•-}$ is the initial encounter of the $(\text{CH}_3)_2\text{C}(\text{OH})$ radical with the incorporated fullerene core rather than the electron transfer itself.

Similarly, irradiation of deoxygenated surfactant solutions of C_{78} (2.0×10^{-5} M C_{78} ; 1.0×10^{-3} M Triton X-100 reduced form) resulted in the rapid grow-in of a near-IR absorption band with λ_{max} at 980 nm. The spectral features are displayed in Figure 6. They are reasonably in line with those found upon reduction of monomeric solutions of pristine C_{78} in nonpolar solvents.⁵⁰ In line with an earlier observation, λ_{max} of the π -radical anion is very sensitive to the polarity of the accommodating assembly. In surfactant media, the maxima were generally blue-shifted relative to the nonaqueous media, e.g., toluene/2-propanol/acetone (8:1:1 v/v/v).⁵⁰ For comparison, radiolytic reduction of C_{76} and C_{78} in the latter solvent resulted

in the formation of characteristic π -radical anion bands positioned at 905 and 975 nm, respectively.

Aggregation induces an uncertainty with respect to the effective concentration and the derived rate constants. Consequently, rate constants may be regarded as a crucial and sensitive measure of a monomeric versus colloidal distribution of any solute. In the present study, a direct comparison of the surfactant with the γ -cyclodextrine system is, unfortunately, limited to C_{60} with the rate constants for the reduction of C_{60} by hydrated electrons in the two environments ($k_{\text{red}(\text{surfactant})} = 2.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$; $k_{\text{red}(\gamma\text{-CD})} = 1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$)²⁷ being in good agreement with each other. The progressively larger radii of the higher fullerenes (C_{70} , C_{76} , and C_{78}) exceed the cavity size of the host structure and, thus, inhibit formation of the respective γ -cyclodextrine inclusion complexes. The resemblance of all the investigated fullerene surfactant systems supports, also in these systems, the above assumption of true fullerene monomers and demonstrates the stabilization of fullerene monomers in surfactant solutions.

Conclusion

In summary, the water solubility of higher fullerenes (C_{70} , C_{76} , and C_{78}) is efficiently promoted by employing suitable surfactants. Capping the surface of the hydrophobic fullerene core with surfactants resulted in the formation of stable fullerene monomers and discrimination of fullerene clusters. Surfactant solutions of C_{60} , C_{70} , C_{76} , and C_{78} , both in the ground and electronically excited state, are susceptible to reduction to generate the corresponding π -radical anions with characteristic absorption bands in the near-IR. Electron-transfer rate constants were on the order of 3.0×10^{10} and $6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for hydrated electrons and $(\text{CH}_3)_2\text{C}(\text{OH})$ radicals, respectively.

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References and Notes

- (1) Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 7773–7774.
- (2) Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978–3980.
- (3) Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050–1051.
- (4) Imahori, H.; Hagiwara, K.; Akiyama, T.; Aoki, M.; Taniguchi, S.; Okada, T.; Shirakawa, M.; Sakata, Y. *Chem. Phys. Lett.* **1996**, *263*, 545–550.
- (5) Ghosh, H. N.; Pal, H.; Sapre, A. V.; Mittal, J. P. *J. Am. Chem. Soc.* **1993**, *115*, 11722–11727.
- (6) Nonell, S.; Arbogast, J. W.; Foote, C. S. *J. Phys. Chem.* **1992**, *96*, 4169–4170.
- (7) Foote, C. S. *Top. Curr. Chem.* **1994**, *169*, 348–363.
- (8) Anderson, J. L.; An, Y.-Z.; Rubin, Y.; Foote, C. S. *J. Am. Chem. Soc.* **1994**, *116*, 9763–9764.
- (9) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 1–12.
- (10) Arbogast, J. W.; Foote, C. S. *J. Am. Chem. Soc.* **1991**, *113*, 8886–8889.
- (11) Jensen, A. W.; Wilson, S. R.; Schuster, D. I. *Bioorg. Med. Chem.* **1996**, *4*, 767–779.
- (12) Krusic, P. J.; Wasserman, E.; Parkinson, B. A.; Malone, B.; Holler, E. R.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *J. Am. Chem. Soc.* **1991**, *113*, 6274–6275.
- (13) Friedman, S. H.; DeCamp, D. L.; Sijbesma, R.; Srdanov, G.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 6506–6509.
- (14) Sijbesma, R.; Srdanov, G.; Wudl, F.; Castoro, J. A.; Wilkins, C.; Friedman, S. H.; DeCamp, D. L.; Kenyon, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 6510–6512.

- (15) Toniolo, C.; Bianco, A.; Maggini, M.; Scorrano, G.; Prato, M.; Marastoni, M.; Tomatis, R.; Spisani, S.; Palu, G.; Blair, E. D. *J. Med. Chem.* **1994**, *37*, 4558–4562.
- (16) Boutevine, A. S.; Tokuyama, H.; Takasugi, M.; Isobe, H.; Nakamura, E.; Helene, C. *Angew. Chem.* **1994**, *106*, 2526–2529.
- (17) Yamakoshi, Y. N.; Yagami, T.; Sueyoshi, S.; Miyata, N. *J. Org. Chem.* **1996**, *61*, 7236–7237.
- (18) Tokuyama, H.; Yamago, S.; Nakamura, E.; Shiraki, T.; Sugiura, Y. *J. Am. Chem. Soc.* **1993**, *115*, 7918–7919.
- (19) Deleted in proof.
- (20) Taylor, R.; Walton, D. R. M. *Nature* **1993**, *363*, 685–693.
- (21) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798–9799.
- (22) Hirsch, A. *Synthesis* **1995**, 895–913.
- (23) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317–323.
- (24) Diederich, F. *Pure Appl. Chem.* **1997**, *69*, 395–400.
- (25) Lamparth, I.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1727–1728.
- (26) Guldi, D. M.; Hungerbühler, H.; Asmus, K.-D. *J. Phys. Chem.* **1995**, *99*, 13487–13493.
- (27) Guldi, D. M. *J. Phys. Chem. A* **1997**, *101*, 3895–3900.
- (28) Guldi, D. M.; Hungerbühler, H.; Asmus, K.-D. *J. Phys. Chem.* **1995**, *99*, 9380–9385.
- (29) Arias, F.; Echegoyen, L.; Wilson, S. R.; Lu, Q.; Lu, Q. *J. Am. Chem. Soc.* **1995**, *117*, 1422–1427.
- (30) Kikuchi, K.; Nakahara, N.; Honda, M.; Suzuki, S.; Saito, K.; Shiromaru, H.; Yamauchi, K.; Ikemoto, I.; Kuramochi, T.; Hino, S.; Achiba, Y. *Chem. Lett.* **1991**, 1607–1610.
- (31) Kikuchi, K.; Nakahara, N.; Wakabayashi, T.; Honda, M.; Matsumiya, H.; Moriwaki, T.; Suzuki, S.; Shiromaru, H.; Saito, K.; Yamauchi, K.; Ikemoto, I.; Achiba, Y. *Chem. Phys. Lett.* **1992**, *188*, 177–180.
- (32) Knapf, M.; Knauff, O.; Golden, M. S.; Fink, J.; Bürk, M.; Fuchs, D.; Schuppler, S.; Michel, R. H.; Kappes, M. M. *Chem. Phys. Lett.* **1996**, *258*, 513–517.
- (33) Raghavachari, K.; Rohlfing, C. M. *Chem. Phys. Lett.* **1993**, *208*, 436–440.
- (34) Diederich, F.; Ettl, R.; Rubin, Y.; Whetten, R. L.; Beck, R.; Alvarez, M.; Anz, S.; Sensharma, D.; Wudl, F.; Khemani, K. C.; Koch, A. *Science* **1991**, *252*, 548–551.
- (35) Herrmann, A.; Diederich, F.; Thilgen, C.; ter Meer, H.-U.; Müller, W. H. *Helv. Chim. Acta* **1994**, *77*, 1689–1706.
- (36) Herrmann, A.; Rüttiman, M.; Thilgen, C.; Diederich, F. *Helv. Chim. Acta* **1995**, *78*, 1673–1704.
- (37) Bingel, C.; Schiffer, H. *Liebigs Ann.* **1995**, 1551–1553.
- (38) Andersson, T.; Nilsson, K.; Sundahl, M.; Westman, G.; Wennerström, O. *J. Chem. Soc., Chem. Commun.* **1992**, 604–605.
- (39) Dimitrijevic, N. M.; Kamat, P. V. *J. Phys. Chem.* **1993**, *97*, 7623–7626.
- (40) Suzuki, T.; Nakashima, K.; Shinkai, S. *Chem. Lett.* **1994**, 699–701.
- (41) Beeby, A.; Eastoe, J.; Heenan, R. K. *J. Chem. Soc., Chem. Commun.* **1994**, 173–175.
- (42) Beeby, A.; Eastoe, J.; Crooks, E. R. *J. Chem. Soc., Chem. Commun.* **1996**, 901–902.
- (43) Eastoe, J.; Crooks, E. R.; Beeby, A.; Heenan, R. K. *Chem. Phys. Lett.* **1995**, *245*, 571–577.
- (44) Hungerbühler, H.; Guldi, D. M.; Asmus, K.-D. *J. Am. Chem. Soc.* **1993**, *115*, 3386–3387.
- (45) Yamakoshi, Y. N.; Yagami, T.; Fukuhara, K.; Sueyoshi, S.; Miyata, N. *J. Chem. Soc., Chem. Commun.* **1994**, 517–518.
- (46) Ebbesen, T. W. *Rev. Sci. Instrum.* **1988**, *59*, 1307–1309.
- (47) Asmus, K.-D. *Methods Enzymol.* **1984**, *105*, 167–171.
- (48) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637–1755.
- (49) Ebbesen, T. W.; Tanigaki, K.; Kuroshima, S. *Chem. Phys. Lett.* **1991**, *181*, 501–504.
- (50) Guldi, D. M.; Liu, D.; Kamat, P. V. *J. Phys. Chem. A* **1997**, *101*, 6195–6201.
- (51) Arbogast, J. W.; Foote, C. S.; Kao, M. *J. Am. Chem. Soc.* **1992**, *114*, 2277–2279.
- (52) Guldi, D. M.; Hungerbühler, H.; Janata, E.; Asmus, K.-D. *J. Phys. Chem.* **1993**, *97*, 11258–11264.
- (53) Yang, Y.; Arias, F.; Echegoyen, L.; Chibante, L. P. F.; Flanagan, S.; Robertson, A.; Wilson, L. J. *J. Am. Chem. Soc.* **1995**, *117*, 7801–7804.