

seen upon variation in E_{σ_1} . This result follows from the appearance of $\sigma_1^2\omega_2$ in the statistical weight of those configurations which have trans states for the first bonds in branches 2 and 3. The pertinent elements occur in the first column of ${}_2U_1$ or ${}_3U_1$.

Altered distributions denoted by solid lines in Figures 8-10 are obtained using the reference statistical weights. In each case the distribution separates into three groups, the lowest population being in the group with the largest μ^2 , γ^2 , or mK . This change in distributions is achieved with little effect on $\langle\mu^2\rangle$ and $\langle\gamma^2\rangle$, but there is a significant decrease in $\langle mK\rangle$.

Comparison of Solid-State and Solution Configurations

Crystalline forms known as β -tricaprin¹² and β -trilaurin²⁹ contain similar conformations for the triglyceride. All dihedral angles in branches 1 and 2 occupy trans states. Branch 3 leaves the glycerol moiety perpendicular to the planar zigzag formed by branches 1 and 2. It then folds, primarily through a g^+ placement at ${}_3\phi_4$. This fold permits the hydrocarbon tail of branch 3 to run parallel to, and in contact with, the hydrocarbon portion of branch 2. This conformation has aptly been described as a "tuning fork."^{12,29} For this conformation μ^2 is $1.7 D^2$, while measured values for tripalmitin and tristearin in solution are $8.1 \pm 0.8 D^2$.²⁰⁻²³ Clearly the solid-state configuration for the glycerol moiety, which merits a statistical weight of $\sigma_1\sigma_2$, cannot be dominant in solution. The reference set of statistical weights yields about 1% of the triacetin molecules in solution with values of ${}_1\phi_{n1}$, ${}_2\phi_1$, ${}_2\phi_2$, ${}_3\phi_1$, and ${}_3\phi_2$ which correspond to those found for β -tricaprin and β -trilaurin in the crystalline state. The rotational isomeric state treatment is required to account for the configuration-dependent properties exhibited by triglycerides in solution.

Acknowledgment. The authors wish to express their gratitude for fellowship support by the John Simon Guggenheim Memorial Foundation (W.L.M.) and the Program of Cultural Cooperation between the United States of America and Spain

(E.S.). Special thanks is due to Professor Flory for his interest and suggestions concerning the formulation of $\hat{\alpha}$ for triacetin. This work was supported by National Science Foundation Grants PCM76-23235 and DMR-73-07655 A02.

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Dynamics of Light-Induced Redox Processes in Microemulsion Systems

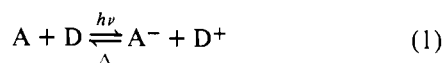
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Abstract: Photoredox processes of the kind shown in eq 1 were investigated in oil/water microemulsions (water content >80%) by means of laser photolysis and steady-state illumination techniques. The following two redox couples were employed: (1) A = duroquinone (DQ), D = diphenylamine (DPA), and (2) A = methylviologene (MV²⁺), D = N-methylphenothiazine (MPTH). In the first system, the two reactants are both solubilized in the lipid interior of the microemulsion droplet. The electron transfer from DPA to photoexcited DQ was found to occur in two steps: a rapid subnanosecond reaction involving DQ singlet states and a slower triplet reaction occurring in the microsecond time range. The diphenylamine cation produced associates with parent DPA molecules to yield multimer complexes. This process is controlled by the statistics of probe distribution among the droplets. A detailed account of the kinetics of formation and spectral characteristics of the multimers is given. In the second system, the electron transfer occurs from MPTH excited states inside the droplet to MV²⁺ which is absorbed on the droplets' surface. It exhibits also a fast (nanosecond) and a slower (microsecond) component resulting from the reaction of singlet and triplet states. The fate of the radical ions produced is examined and photobiological implications are discussed.

Introduction

Photoinduced electron transfer reactions of the type



where A and D stand for the acceptor and donor, respectively, have recently attracted attention as potentially useful systems to convert light into chemical energy. The reversible character of process 1 has been a major obstacle in the practical utilization of these systems. Reactions that are endoergic in the

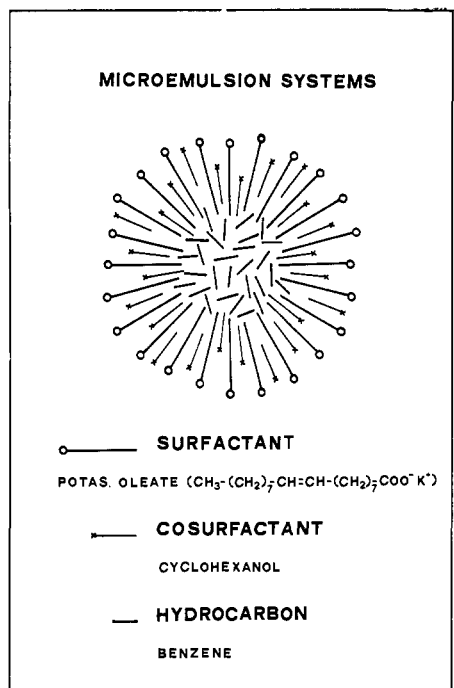


Figure 1. Schematic representation of a microemulsion droplet.

forward direction frequently back-react in homogeneous solution at a diffusion-controlled rate leading to rapid thermal dissipation of the chemical energy present in the radical ions A^- and D^+ .

Microscopically heterogeneous systems such as artificial membranes¹ or micelles² have successfully been employed to inhibit the back-reaction. The kinetic effects are achieved on the basis of hydrophobic and electrostatic interactions of the participants in the redox reaction I with the distinctive microenvironment provided by these molecular aggregates.

The scope of suitable molecular organizations has recently been enlarged in our laboratory to include oil in water microemulsions. These systems usually are comprised of four components: the solvent water, a surfactant as well as a cosurfactant, and the hydrocarbon constituent. In aqueous solution spontaneous aggregation is observed resulting in the formation of spherical particles with a diameter of 50–1500 Å.³ The interior of the aggregate is constituted of the hydrocarbon molecules and the tails of the surfactants while their head groups form the boundary to the aqueous bulk phase (Figure 1). The cosurfactant is present also largely in the interface where it creates disorder thereby increasing the entropy of the total system. This entropy increase has been suggested to account for the thermodynamic stability of microemulsions.⁴

The types of microemulsions employed in the present investigation were optically clear systems whose solubilizing power was found to be superior to micellar solutions. Two situations were examined by use of laser photolysis techniques. In the first case, both electron donor and acceptor are incorporated in the interior of the aggregates; in the second one, one reactant was kept inside and the other absorbed on the surface of the microemulsion assembly. Finally, the fate of the species produced by the light-induced charge transfer events was also examined.

Experimental Section

Materials. *N*-Methylphenothiazine was synthesized by the method of Normant and Carigny.⁵ The crude, pink-colored crystals were recrystallized several times from argon-saturated ethanol until the purity was better than 99.99%. One obtains colorless needles, mp 99.5

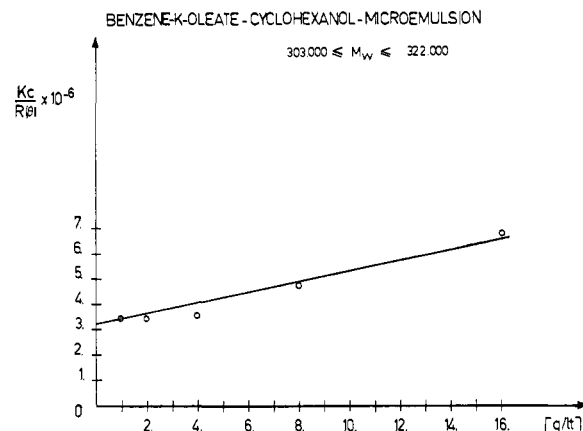


Figure 2. Molecular weight determination of the potassium/oleate microemulsion droplets via the light scattering method, Zimm plot.

°C (lit. 100 °C). Duroquinone (Aldrich) was purified by repeated sublimation. Methylviologene (Ferak) and diphenylamine (Fluka p.a.) were used as supplied. Deionized water was distilled from alkaline permanganate and subsequently twice from a quartz still. All other compounds used were analytical reagent grade.

Preparation of the Microemulsions. Two types of anionic microemulsions were used in this work.

The first one contained as a surfactant sodium hexadecylsulfate (7.6% wt), as a cosurfactant 1-pentanol (10.8% wt), and as the oil phase hexadecane (3.2% wt). A phase diagram of this system has been published by Mackay et al.⁶ The same authors give a droplet diameter of 100 Å as determined by low-angle X-ray technique. This value yields for our experimental conditions a droplet concentration of 5×10^{-4} M.

The second kind of microemulsion employed was a mixture of potassium oleate, cyclohexanol, benzene, and water. The weight percentages of these compounds are 1.1, 1.0, 2.4, and 95.5, respectively. Since the droplet size of the latter microemulsion is not available in the literature, a molecular weight determination was carried out using a laser low-angle scattering photometer (Chromatix Model KMX-6). This new small angle scattering technique has an advantage over the conventional wide-angle mode, in particular when multicomponent systems with structurally complex scattering units are considered.⁷ The molecular weight of the microemulsion droplets was obtained by measuring the Rayleigh factors of microemulsions with different droplet concentrations using water as reference (scattering intensity 1.08×10^{-6}). The excess Rayleigh factor is then plotted as a function of concentration (Figure 2). From the ordinate intercept, we obtain for the average molecular weight of the microemulsion the value

$$M_w = (3.13 \pm 0.10) \times 10^5$$

Apparatus. Laser photolysis experiments were carried out using a Q-switched J.K.-2000 ruby laser. The 347.1-nm pulse had a duration of 15 ns and an energy between 30 and 300 mJ. Transient spectra were recorded using a fast kinetic spectroscopy technique.⁸ Absorption spectra were recorded with a MIT-20 spectrophotometer. All samples were thoroughly freed from oxygen by flushing with nitrogen.

Results and Discussion

In the first part of this report, we shall examine photoredox systems where both the electron donor and acceptor are present in the interior of the microemulsion droplets. The kinetics and mechanism of the light-induced electron transfer reaction occurring inside the molecular assemblies will be analyzed as well as the fate of the radical ions produced. We shall confine our investigations to a model system that is a solution where the electron donor is represented by diphenylamine (DPA) and the acceptor by excited-state duroquinone (DQ). The hydrophobic nature of both species assures that they will be solubilized inside the microemulsion droplets.

The experimental investigations were started with an examination of the photoreactions of DQ in the absence of DPA.

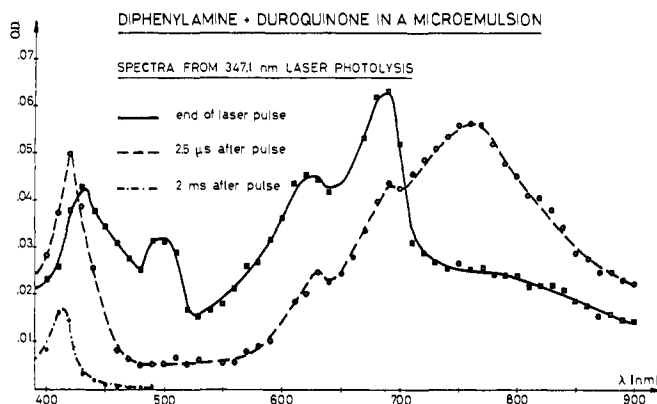
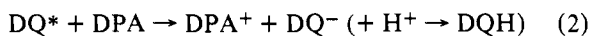


Figure 3. Transitory spectra obtained from the laser photolysis of 10^{-3} M DQ and 10^{-3} M DPA in hexadecyl sulfate microemulsion.

Excitation of DQ by the 347.1-nm laser light leads to the formation of $DQ(S_1)$ states. Subsequently, intersystem crossing occurs with a quantum yield of practically unity. The transitory spectrum obtained from 10^{-3} M DQ solutions in the hexadecyl sulfate microemulsion immediately after the laser pulse was found to be identical with the absorption spectrum of DQ triplet states.⁹ The triplets decay via first-order kinetics with a specific rate of $3 \times 10^5 \text{ s}^{-1}$ whereby semiquinone radicals are produced. This indicates reductive quenching of DQ^T by the microenvironment present inside the microemulsion droplets. It is suggested that the cosurfactant pentanol acts here as an electron donor and is oxidized by DQ^T to the α -alcohol radical. An analogous electron abstraction has been ascertained to occur from ethanol and acetone.¹⁰ It underlines the high oxidative power of the DQ triplet state. In the presence of diphenylamine, this reductive quenching by the microenvironment will play only a minor role in the process of excited-state deactivation. It is dominated by other redox processes which occur at a much faster rate as will be shown in the following section.

The laser photolysis experiments were continued with hexadecylsulfate microemulsion containing DQ and DPA both at a concentration of 10^{-3} M. Under these conditions, each droplet with DQ association contains also at least one DPA molecule. The temporal evolution of the system following light excitation is characterized by four different stages.

1. A very rapid process occurs which is terminated within the duration of the laser flash. The species produced during this period can be readily identified from the end of the pulse spectrum shown in Figure 3. Three absorption peaks can be distinguished which are located at 420, 490, and 680 nm. They are attributed to the transients durosemiquinone (DQH), DQ^T , and diphenylamine cation radicals (DPA^+), respectively. It is important to note the prompt formation of DPA^+ and DQH which must be interpreted as a reductive quenching of DQ excited states by DPA:



Apparently, this process occurs so rapidly that it can compete efficiently with intersystem crossing to the triplet state:



The time interval in which reaction 2 occurs could be at most a few nanoseconds. During this period, practically no diffusional displacement of the reactants can take place. Hence, it is concluded that DPA and DQ reside in very close vicinity inside the microemulsion droplet which allows the electron transfer to occur instantaneously after light excitation. The situation here is quite analogous to intramolecular electron

OSCILLOSCOPE TRACES FROM THE LASER PHOTOLYSIS OF DIPHENYLAMINE AND DUROQUINONE IN A MICROEMULSION

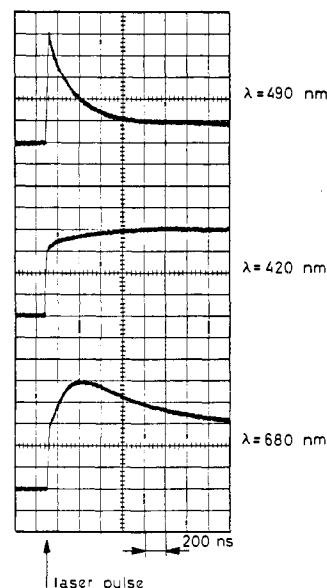
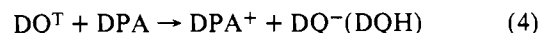


Figure 4. Oscilloscope traces showing DQ^T decay (λ 490 nm), DQ^- formation (λ 420 nm), and the formation and partial decay of DPA^+ at 680 nm after laser excitation of a solution of DQ and DPA in the hexadecyl sulfate microemulsion.

transfer processes¹¹ which can also occur on a subnanosecond time scale. The possibility should also be considered that donor/acceptor complexes of DPA and ground-state DQ are formed in the microemulsion. However, any interactions of this type must be quite weak since no significant EDA absorption could be detected.

2. The second process to be considered concerns the electron transfer quenching of DQ^T by diphenylamine:

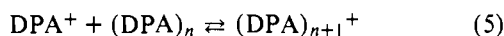


This reaction is slow enough to be kinetically resolved by nanosecond spectroscopy techniques. In Figure 4 are presented oscilloscope traces showing the temporal changes of the optical density at the pertinent wavelengths of DQ^T , DPA^+ , and DQH absorption. The 490-nm signal decreases with a time constant of $6 \times 10^6 \text{ s}^{-1}$. At 680 and 420 nm, the optical density increases in two steps: an immediate deflection of the signal occurs during the laser pulse and reflects the prompt formation of DPA^+ and DQH discussed already above; it is followed by a slower component matching kinetically the 490-nm decay. These observations show that eq 4 describes correctly the triplet deactivation process. In the microemulsion we evidently deal with two types of light-induced electron transfer reactions: a very rapid one which occurs immediately within the laser pulse and is likely to involve DQ singlet excited states, followed by a slower triplet state reaction comprising about 20% of the total number of excited states produced. Only the latter process can be observed in homogeneous solution where it occurs at a diffusion-controlled rate.¹⁰ Hence, the fast component of the photoredox reaction is a result of the specific molecular organization found in the microemulsion.

3. The third phase of photoinduced events is associated with spectral changes in the red wavelength region and thus concerns only the DPA^+ cation radicals. Examination of the 685-nm oscilloscope trace in Figure 4 reveals that the increase in optical density due to reaction 4 is followed by a partial

decay which attains a plateau within 2.5 μs . The transitory spectrum obtained from the plateau region is included in Figure 3. In the short-wavelength region, the spectral features remain essentially unchanged demonstrating the presence of durosemiquinone. On the other hand, considerable alterations are noted in the red wavelength region where a broad band appears with a maximum at 760 nm. Apparently, the DPA^+ produced in the excited-state reaction is converted at least partially into products absorbing in this region of the spectrum. Proton transfer from DPA^+ to water cannot account for this transformation as the neutral amine radical has a different spectrum.¹² Furthermore, in this case deprotonation should have occurred in the water/alcohol solvent mixture—which we failed to observe.

A more plausible explanation of these phenomena is found when the interaction of DPA^+ with its parent molecule DPA is considered. In analogy with other aromatic cation radicals,¹⁴ DPA^+ may associate with neutral DPA to form multimers of the type



Such a process is greatly favored by the close proximity of the diphenylamine species in the microemulsion droplets. It can, of course, only take place in droplets which at the time of light excitation contain already at least two diphenylamine molecules, since reaction 5 is much faster than the exchange of DPA between different droplets.

The fraction of droplets with multiple DPA association can be calculated from Poisson's statistics provided that the DPA distribution in the microemulsion is random in character.¹⁵ For the experimental conditions applied in Figures 3 and 4, the Poisson law predicts that 60% of all droplets should have two or more DPA molecules incorporated. Hence, a fraction of 60% at most of the DPA^+ produced via electron transfer to excited DQ should participate in multimer formation.

An experimental assessment of this conjecture is rendered difficult by the mutual overlap of the absorption spectra of DPA^+ monomers and multimers. In particular at 680 nm where the monomer cation shows a distinct maximum, the multimers contribute also substantially to the transient absorption. The latter contribution appears to become less significant at wavelengths below 650 nm, as is evident from the similarity of the spectra in this region taken immediately and 2.5 μs after the laser pulse. At λ 630 nm, where the DPA^+ spectrum has a shoulder, the ratio of absorbances, $r = \text{OD}(t = 0)/\text{OD}(t = 2.5 \mu\text{s})$, obtained from Figure 3, is 0.6. Neglecting any contributions of multimers to the absorbance at this wavelength, one derives from this ratio a value $f = 1 - r = 0.4$ for the fractional decay of DPA^+ cations. In calculating the amount of DPA^+ initially produced, we have considered so far only the prompt formation via reaction 2. Additional DPA^+ (ca. 20%) arises from the DQ triplet reaction 4. Taking this into account one arrives at the value $f = 0.52$. Thus, a surprisingly good agreement with the predictions from Poisson's law is obtained.

If the fast spectral changes observed in the red wavelength region are caused by an association process such as formulated in eq 5, then it is expected that they depend strongly on the DPA concentration. In order to test this prediction, laser photolysis experiments were carried out with two microemulsion solutions containing a DPA concentration of 5×10^{-4} and 2×10^{-3} M, respectively. In Figure 5 are shown oscilloscope traces which illustrate the temporal behavior of the absorbance at 760 and 680 nm after laser excitation. One notices that two significant effects are induced by increasing the DPA concentration: (a) the rates of the absorbance decay at 680 nm and of the absorbance buildup at 760 nm are both enhanced; (b) the fraction of the signal at 680 nm which decays rapidly

OSCILLOSCOPE TRACES FROM THE LASER PHOTOLYSIS OF DIPHENYLAMINE AND DUROQUINONE
IN A MICROEMULSION

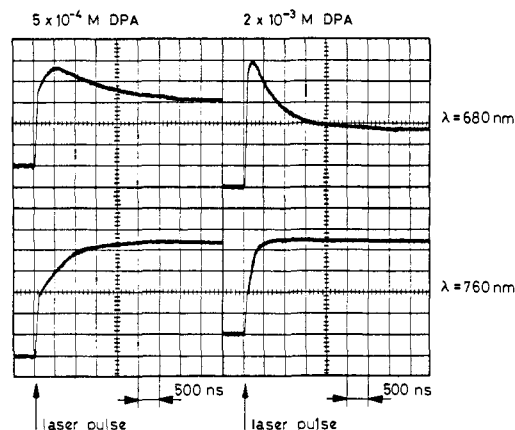


Figure 5. Oscilloscope traces showing the effect of DPA concentration on the decay of DPA^+ (680 nm) and the formation of DPA^+ multimers.

is increased. At the same time, one notices an increase in the absorbance produced at 760 nm.

From the first observation it may be inferred that DPA is a participant in the reaction that leads to partial depletion of DPA^+ and to the formation of products with an absorption maximum at 760 nm. It is thus justified to describe the DPA^+ decay process by an equation such as 5. The second observation lends further support to the concept of DPA^+ complex formation with DPA. As the fraction of droplets with multiple DPA association augments from 27 to 90% upon increasing the DPA concentration, so does the number of sites where reaction 5 can occur. Hence, at the higher DPA concentration, a larger fraction of DPA^+ will participate in multimer formation.

These experimental results confirm the assignment of the region above 600 nm of the spectra of Figure 3 obtained 2.5 μs after the laser pulse to DPA^+ -cation complexes with the general formula $(\text{DPA})_{n+1}^+$, where $n = 0, 1, 2, \dots$. The precise number of n will depend both on the stability of the associate and on the number of DPA available in the droplet for association. As the occupancy of droplets by DPA is governed by Poisson's statistics, the same statistical distribution should prevail for these complexes. Hence, within the spectral envelope, contributions from a variety of complexes with a different association number n should be contained therein. That this is indeed the case becomes evident from an examination of the shape of the 2.5- μs spectra at the three different DPA concentrations employed. With 5×10^{-4} M DPA one obtains the lowest value (720 nm) for the wavelength of maximum absorption. Upon increasing the DPA concentration, the spectrum broadens and shifts to the red. For example, λ_{max} is 760 nm at 10^{-3} M DPA and 790 nm at 2×10^{-3} M DPA. This finding is easy to rationalize in terms of the statistical model discussed above. The fraction of droplets with multiple DPA association increases with DPA concentration. Thus, within the ensemble of $(\text{DPA})_{n+1}^+$ associates contributing to the absorption spectra, those with larger numbers of n absorbing further in the red become more prominent. This leads to the observed red shift of the spectra.

An important point which remains to be examined concerns the kinetics of DPA^+ multimer formation. This process is different from a conventional reaction in homogeneous medium in the sense that it involves the interaction of only one species (DPA^+) with another or several other reactant mole-

cules (DPA) in their host droplet. It is evident that reaction 5 can proceed faster in droplets with a large number of DPA inside than in those where only one DPA reactant is available. Incidentally, the same is true for the transfer of electrons from DPA to DQ triplets, eq 4. The time course of DPA⁺ association is monitored by measuring the optical density of the solution, which is a macroscopic parameter. Hence, an average of all the states from the whole ensemble of droplets is measured as a function of time. An analogous situation is frequently found in the case of fast reactions in micellar systems. The kinetics of these processes can be satisfactorily described in terms of a phenomenological model that has been recently developed.^{15,16} The analysis is performed with a set of first-order rate laws where the rate constant is assumed to increase linearly with the number of reactants present in the host aggregates. The individual contributions of these kinetic terms to the overall rate law are weighted by a Poisson distribution function. A straightforward application of the rate equations obtained to the present case of DPA⁺ association is not possible since we deal here with the complicated case that two processes, namely, reactions 4 and 5, occur in parallel and at the same time consecutively. Nevertheless, efforts are presently under way to develop closed kinetic expressions also for this situation which would permit a more detailed analysis of the DPA⁺ association reaction in the microemulsion system.

A close inspection of the end of pulse spectrum shown in Figure 3 reveals another feature which appears interesting in the context of the kinetics of (DPA)_{n+1}⁺ multimer formation. This curve exhibits a conspicuous tail above 750 nm extending toward the red wavelength region. As the DPA⁺ monomer does not absorb above 750 nm,¹⁷ this absorption must be attributed to (DPA)_{n+1}⁺ multimers that are already produced during the laser pulse. Apparently, these species can only originate from DPA molecules that are already associated with small clusters—dimers or multimers—within the microemulsion droplets. In these aggregated states the DPA molecules are in close contact with each other. Hence, after electron transfer to excited duroquinone has occurred, no diffusion of DPA⁺ is required to form the complexes (DPA)_{n+1}⁺ allowing the reaction to occur immediately and within the laser pulse.

It should be noted that the effects observed here are quite pertinent for photobiological systems. For example, in photosynthesis the light-induced electron transfer involves also a dye aggregate, i.e., dimer chlorophyll, and leads to the formation of dimer cation radicals of chlorophyll.¹⁸

4. The last phase in the photoinduced reactions that take place in the DPA/DQ microemulsion system concerns the decay of the radical ions DQH and (DPA)_{n+1}⁺. The fate of the former species is readily unraveled by following the temporal behavior of the transient optical density at 420 nm. It decays in the micro- to millisecond time range via second-order kinetics with a rate parameter $k/\epsilon_{420} = 4.4 \times 10^4 \text{ cm}^{-1} \text{ s}^{-1}$. Taking for the extinction coefficient of DQH the value¹⁹ $\epsilon = 4700 \text{ M}^{-1} \text{ cm}^{-1}$, one obtains a rate constant $k = 2.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

The second-order nature of the decay kinetics indicates that durosemiquinone does not back-react with its counterpart DPA⁺ within the droplet where it was found initially via electron transfer from DPA. Such a process always obeys a first-order rate law. Apparently, DQ⁻ escapes from the droplet into the aqueous phase before the back-reaction with DPA⁺ can occur. An analogous effect was observed in the case of the light-induced electron transfer from chlorophyll a to duroquinone in anionic micelles.²⁰ The main factor contributing to the rapid ejection of the DQ⁻ anion from these negatively charged surfactant aggregates was found to be the electrostatic interaction with its microenvironment. The same type of forces may also produce the effective separation of the oppositely charged ionic radicals in the microemulsion system. Once DQ⁻

has escaped from the sphere of influence of its counterpart DPA⁺, it is unlikely to return into the droplet since its approach is impaired by the negative surface potential. The alternative pathway which is pursued here comprises first protonation of DQ⁻ to yield the neutral semiquinone, which subsequently undergoes the dismutation reaction $2\text{DQH} \rightarrow \text{DQ} + \text{DQH}_2$,¹⁹ leading to the formation of durohydroquinone. The second-order decay of the absorbance at 420 nm is attributed to the latter process.

As regards the cation radical DPA⁺, we have learned in the preceding section that this is prone to form multimers with the parent molecules DPA. In contrast to DQ⁻, the species (DPA)_{n+1}⁺ shows attractive electrostatic interactions with the surface region of the microemulsion droplets. Hence, it is likely to remain associated with the interfacial part of the aggregates. Once in contact with the aqueous phase the cation is subject to proton transfer to water. The neutral radical has a pK value of 3¹³ and therefore is the stable form at pH < 3. This proton transfer reaction accounts for the first-order decay of the absorption in the red which takes place at a specific rate of $5 \times 10^4 \text{ s}^{-1}$. As shown in Figure 3, the absorption spectrum obtained 2 ms after the laser pulse displays only the peak at 420 nm which is due to DQH. The (DPA)_{n+1}⁺ absorption in the red wavelength region has practically disappeared at this time. This finding underlines the independent nature of the decay of the two species.

The second part of this report deals with a redox system where the electron donor is located inside the microemulsion droplet while the acceptor is absorbed on its surface. In such a solution the light-induced redox reaction involves the flow of electrons across the charged interface separating the lipid from the aqueous regions. *N*-Methylphenothiazine (MPTH) and methylviologene (MV²⁺) were selected as donor and acceptor, respectively. As the latter constitutes a doubly charged organic cation, it will be tightly bound to the surface of the droplets while the former will reside in the interior region. In this system, MPTH is the photoactive species which interacts with the 347.1-nm laser light. The excited states produced are powerful reductants and should readily be able to reduce methylviologene.

The laser photolysis experiments were carried out with the potassium oleate/cyclohexanol/benzene microemulsion in which the droplet concentration was adjusted to $1.5 \times 10^{-4} \text{ M}$. To the microemulsion were added $3 \times 10^{-4} \text{ M}$ methylviologene and 10^{-4} M MPTH. Laser photolysis results obtained from such a solution are presented in Figure 6. The end of pulse spectrum consists of four bands with maxima located at 395, 460, 515, and 600 nm. These absorptions can be assigned to MPTH triplet states (MPTH^T, 460 nm), MPTH cation radicals (MPTH⁺, 515 nm), and reduced methylviologene (MV⁺, 395, 600 nm). The presence of the latter two species indicates the occurrence of a very rapid electron transfer from excited MPTH to MV²⁺ during the laser pulse:



This process is competing with intersystem crossing to the triplet state:



The MPTH triplets produced can also reduce methylviologene:



This process manifests itself as an increase in the absorptions at 390, 515, and 600 nm occurring over a time range of several hundred nanoseconds, and a concomitant decrease of the triplet peak at 400 nm. Two microseconds after the laser pulse, the latter has vanished indicating the completion of reaction 8. The

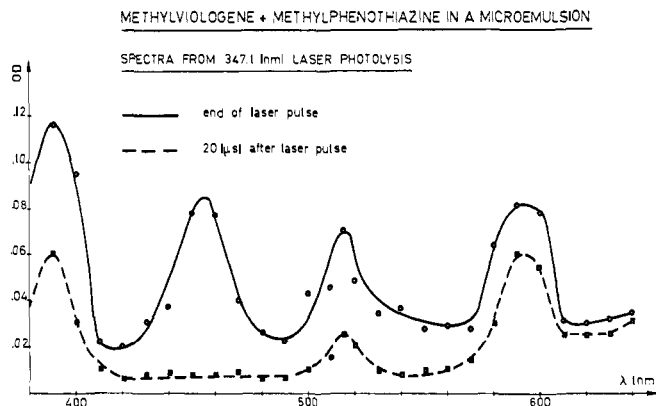
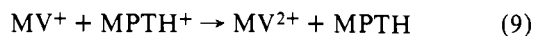


Figure 6. Transitory spectrum obtained from the laser photolysis of 10^{-4} M MPTH and 3×10^{-4} M MV^{2+} in the potassium/oleate microemulsion.

spectrum present at this time has been omitted from Figure 6 for clarity of representation. The fraction of MV^+ produced via reduction by triplet states accounts for approximately 30% of the total reduction yield.

The third and final phase of the photoinduced events comprises the decay of the radical ions MV^+ and $MPTH^+$. A kinetic analysis carried out in the microsecond to millisecond time domain showed that the absorptions at 390, 515, and 600 nm disappears simultaneously via the same second-order rate law. This fact is noticeable also in Figure 6 in which is included the spectrum obtained 100 μ s after the laser pulse. Within the spectrum contributions from the two radical ions MV^+ and $MPTH^+$ are still contained.

From these observations, it is inferred that the species MV^+ and $MPTH^+$ react jointly:



The kinetic analysis yields for reaction 9 a rate constant $k_9 = 9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

A summary of the light-initiated reactions taking place in the MPTH/ MV^{2+} microemulsion is given in Figure 7. In complete analogy to the DQ/DPA system, we can kinetically distinguish two electron transfer processes. The first and fast component is likely to involve MPTH singlet excited states. It is followed by a slower reaction in which MPTH triplets participate. In contrast to DPA^+ , MV^+ does not associate with its parent molecules. The second-order nature of its decay indicates that it dissociates rather readily from the droplet where it originated. This escape into the solution bulk must kinetically dominate over the intradroplet back-transfer of an electron to $MPTH^+$. While diffusing through the bulk solution, MV^+ will eventually be trapped by a droplet with $MPTH^+$ association where reaction 9 will occur. Such a mechanism leads to the observed second-order rate law.

Conclusions

In this report, a first attempt was made to explore some basic features of light-driven redox reactions in microemulsion solutions. During the course of the investigations with two photochemical model systems, several unique effects were detected which must be attributed to the distinct microenvironment provided by these molecular assemblies since they are absent in conventional solvent systems. These comprise a pronounced catalytic effect on the forward rate of the redox process, the association of the cation radicals produced with parent molecules to form multimer cations, and the local separation of radical ions which carry opposite charges. While the first two

LIGHT INDUCED ELECTRON TRANSFER IN MICROEMULSION SYSTEMS

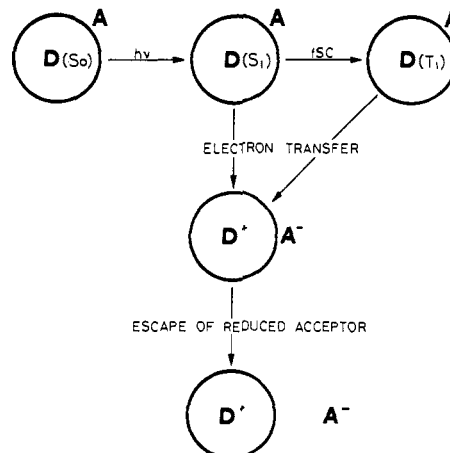


Figure 7. Schematic illustration of the photoinduced events occurring in the potassium/oleate microemulsion in the presence of MPTH and MV^{2+} .

phenomena originate from the proximity of the reactants within the droplet, the last is a consequence of the difference between the electrostatic potentials prevailing in the droplets and the solution bulk.

Although electrostatic and proximity effects can also be found in micellar solutions, the microemulsions have two advantages over the micellar systems if the aspect of light energy conversion is considered: (1) a higher solubilizing power which makes it possible to dissolve very hydrophobic sensitizers insoluble in micellar media; (2) a larger droplet diameter which allows incorporation of a greater number of dye molecules and hence augments the absorption cross section of the solution. Also, it assists in the charge separation process since the intradroplet back-transfer of an electron from A^- to D^+ is retarded.

Acknowledgment. The authors are indebted to Mr. T. Bally for the preparation of the drawings. Financial support of the Swiss National Fund is gratefully acknowledged. We would also like to thank Dr. A. M. Braun for supplying us with a sample of *N*-methylphenothiazine.

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Study of the Micelle Formation and the Effect of Additives on This Process in Reversed Micellar Systems by Positron Annihilation Techniques¹

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Abstract: The positron annihilation technique was applied to the study of the micelle formation process in reversed micellar systems, Aerosol OT and dodecylammonium propionate in apolar solvents, such as benzene, isooctane, and cyclohexane. The results indicate that the positronium formation probability responds very sensitively to microphase changes in reversed micellar solutions. The abrupt changes in positronium formation probability observed at certain surfactant concentrations appear to coincide with variations in the aggregation state of the surfactant molecules in solutions, as postulated by the modified pseudophase model which considers the possibility of conformational changes between premicellar aggregates, and the surfactant concentrations at which they occur may be interpreted as operational critical micelle concentrations. Additives or probe molecules can affect these changes and shift them to lower surfactant concentrations. The additions of H₂O and its solubilization in form of clusters inside the reverse micelle leads to microphase changes also detectable by the positron annihilation technique. From a comparison of the rate constants between positronium and probe molecules observed in the neat solvents and in the corresponding micellar solutions it was concluded that the probe molecules are attracted to various degrees by the reverse micelles, the nature of the surfactant and solvent determining the relative distribution of the probe molecule in the outer hydrocarbon layer and in the bulk apolar solvent of the reversed micelles.

Introduction

The importance of reversed micellar systems formed by the aggregation of surfactant molecules in nonpolar solvents in today's industrial applications, energy storage and conservation, tertiary oil recovery, and dry cleaning processes as well as catalysts in chemical and biological reactions, and biomembrane transport phenomena has recently been more and more recognized.^{2,3}

Reversed or inverted micelles can be characterized as aggregates of surfactant molecules with their polar groups concentrated in the interior of the aggregate while their hydrophobic moieties extend into, and are surrounded by, the bulk apolar solvent.

While there is a relatively large body of experimental details available about aqueous micellar systems,² information on the physical chemical properties of reversed micelles is still scarce.³ This is mainly due to the fact that experimental techniques, such as specific conductance, interfacial tension, light scattering, NMR, and other spectroscopic measurements traditionally used for the study of aqueous micelles, are much more difficult to perform in the reversed micellar systems because of the relatively small aggregation number of surfactant molecules in the latter systems as compared to aqueous micellar solutions.

In a previous paper we have reported on the application of the positron annihilation technique as a new, sensitive tool for the study of phenomena involved in the micelle formation and solubilization processes in aqueous media.^{4,5} This new method is based on the fact that the reactions as well as the formation of the positronium atom, which is the bound state of an electron and a positron, are greatly dependent on the environment in which these interactions occur.⁶ Thus by applying this tech-

nique we were able to study the location of solubilisates, such as nitrobenzene, benzyl alcohol, benzene, hexane, and hexanol, in a variety of aqueous micellar solutions.^{4,5} We have also demonstrated^{4,5} that the positron annihilation method can serve as a superior analytical probe for the accurate determinations of an important physical chemical property in aqueous micellar systems, namely, the critical micelle concentration (cmc), which is defined as the surfactant concentration at which micelles become first detectable. We were able to show that at the cmc the positronium formation undergoes an abrupt and drastic change, which allows a precise determination of the cmc.

In reversed micellar systems where the number of monomers involved in the formation of the aggregates is rather small, the question exists whether the aggregation can be characterized by a monomer \rightleftharpoons *n*-mer type association as postulated in aqueous micelles or whether a multiple equilibrium model applies, which assumes stepwise formation of aggregation in an indefinite association process monomer \rightleftharpoons dimer \rightleftharpoons trimer \rightleftharpoons . . . *n*-mer.^{3,8}

While the indefinite self-association model would predict that changes in physical properties of reversed micellar solutions with increasing surfactant concentrations are expected to be gradual, ¹H NMR plots, e.g., were found to show obvious breaks at certain surfactant concentrations, which were defined as operational cmc's.⁹⁻¹² Even more pronounced and abrupt changes at these cmc's were observed in our laboratory when the positronium formation probability was determined as a function of surfactant concentration.⁷

We therefore have systematically investigated the formation of reversed micelles in a series of apolar solvents by using the positron annihilation technique and included an assessment of the effects of the presence of a third component, an added