

the aqueous domain is of the *o/w* microemulsion type, down to the bottom of the cell. Although the description of the sample composition and structure (within the thermal range where the diffuseness is observed) is rather satisfactory, the main questions about the nature and the origin of the diffuseness are not fully answered. In fact the new behavior cannot be attributed without doubt to thermodynamically stable samples but it could be as well a stage of a very slow evolution toward a final state of Winsor I type. Whether thermodynamically stable or not, the samples studied present some interesting characteristics. It is demonstrated that a microemulsion is obtained down to a very low surfactant content. The fact that the studied state could be unstable does not change this conclusion because the trend of the evolution is clearly toward a homogeneous *o/w* microemulsion in equilibrium with an excess oily phase, if an evolution exists. The microemulsion interfacial film appears to be very rich in alcohol, presenting an alcohol/surfactant ratio 1 order of magnitude larger than for usual Winsor phases. Such a film rich in alcohol is expected to present peculiar mechanical characteristics corresponding to a quite low rigidity coefficient of the interface: the proximity in temperature of the zone in which the new behavior is observed to the solubilization limit of the surfactant and the high sensitivity of the sample to temperature changes. The diffuseness of the samples

seems not linked to a critical state but more likely to the coexistence of globules differing in size. At the present state of the measurements we have no information on the shape of the globules. The 1.5 ratio between the diameters of the globules of the intermediate and lower regions could support the hypothesis of an intermediate region mainly composed of oily dimeric aggregates. Moreover, the particular composition of the interfacial film could favor strong curvature fluctuations leading to polydispersity or aggregation.

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Registry No. SDS, 151-21-3; NaCl, 7647-14-5; toluene, 108-88-3; 1-butanol, 71-36-3.

Additive Effects on the CIDNP, Cage Effect, and Exit Rate of Micellized Radical Pairs

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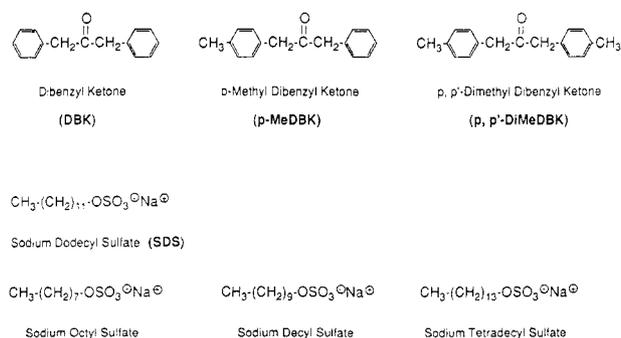
The effects of additives on the recombination efficiency and exit rates of micellized benzyl radicals have been studied by steady-state CIDNP, steady-state product analysis, and time-resolved optical absorption techniques. The results indicate that the efficiency of triplet geminate pair recombination increases monotonically as the micellar volume increases. Aggregation numbers of SDS micelles were deduced as a function of additive concentration from CIDNP measurements and were found to be consistent with literature values.

Introduction

Over the past decade, investigations of photochemical and photophysical processes in micelles have provided very useful information concerning the structure and dynamics of micellar aggregates. In addition, such studies have provided many examples of novel photochemical events and reactions.¹ An outstanding property of aqueous solutions of micelles is their ability to solubilize organic substrates and to respond in their solubilizing properties to the addition of electrolytes and other additives.² As part of a broad investigation of the structure and dynamics of micellar systems containing solubilized organic substrates, we are developing methods that employ organic photochemical reactions as probes.³ The expectation is that the multimethod approach will reveal information concerning both the mechanisms of the photochemical processes as well as the micellar structure and dynamics.

The substrate molecules employed in this investigation are dibenzyl ketone (DBK) and its simple derivatives, *p*-methyl-dibenzyl ketone (*p*-MeDBK) and *p,p'*-dimethyldibenzyl ketone (*p,p'*-DiMeDBK) (Scheme I). The photochemistry of this family of molecules is well established³ and is summarized in Figure 1,

SCHEME I



with *p*-MeDBK as an example. Absorption of light results in efficient homolytic cleavage of the bond adjacent to the carbonyl carbon to form a phenacyl:benzyl radical pair (the primary geminate radical pair, ³RP, Figure 1).⁴ The cleavage occurs from the triplet state of the ketone; thus a triplet radical pair is formed. The primary radical pair can then undergo intersystem crossing to form a singlet radical pair, or diffusional separation within the micelle and decarbonylation can occur to form a secondary geminate benzyl:benzyl radical pair (³RP', Figure 1).⁴ The secondary geminate radical pair can also undergo intersystem

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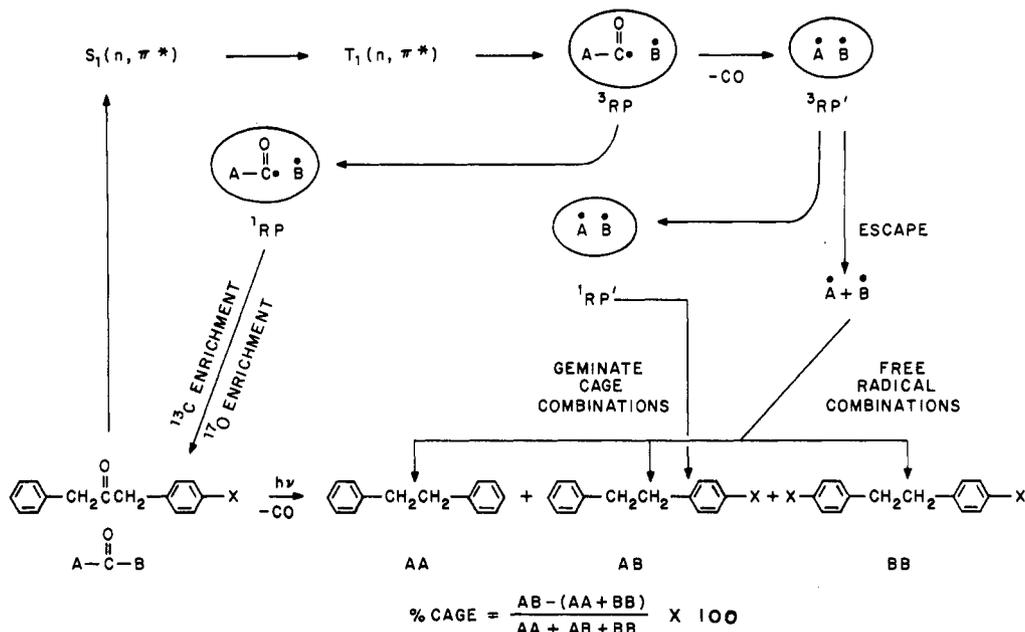


Figure 1. Paradigm for the photolysis of *p*-MeDBK in micellar solutions. The circles represent the micellar reaction space. After decarbonylation geminate benzyl radical pairs couple to produce AA, AB, and BB coupling products. The percent cage (fraction of geminate pairs that couple) can be calculated from the formula shown at the bottom of the figure.

crossing to form a singlet radical pair or diffusive separation can occur with eventual exit of one of the radicals from the micelle. For each geminate radical pair it is assumed that the rate-determining step for product formation is the intersystem crossing process, and that reaction from the geminate singlet radical pair is very fast. The only reaction products of consequence are the diphenylethanes which result from benzyl-benzyl radical coupling reactions. These are formed in nearly quantitative yield. The products from intramicellar recombination reactions of radicals from geminate pairs (i.e. radicals from the same ketone precursor) are termed "cage" recombination products. Radicals which exit the micelle before undergoing reaction recombine with other radicals from other precursor molecules in a random manner and form "escape" or "out-of-cage" products. In the case of *p*-MeDBK, three diphenylethanes are possible products as shown in Figure 1. In this case the fraction of the secondary geminate pairs which undergo intramicellar recombination reactions, termed the "cage effect", can be evaluated by using the equation shown in Figure 1.

The micellar systems investigated are aqueous solutions of sodium dodecyl sulfate (SDS, Scheme I) and its homologues (Scheme I). The properties of SDS have been extensively investigated and thus considerable literature data are available for comparison and design of experiments.⁵⁻⁷

In this work we describe a new method for the investigation of radical pair reactions in micelles: namely, the ratio of the polarizations produced in steady-state chemically induced dynamic nuclear polarization (CIDNP) experiments. This technique has been shown to be a powerful tool in investigating both the qualitative and quantitative aspects of numerous photochemical systems.⁸ In a previous paper^{9a} we reported the direct measurement of the rates of exit of benzylic radicals from SDS micelles using time-resolved optical absorption and time-resolved CIDNP techniques. It was found that the exit rate of the benzyl radical

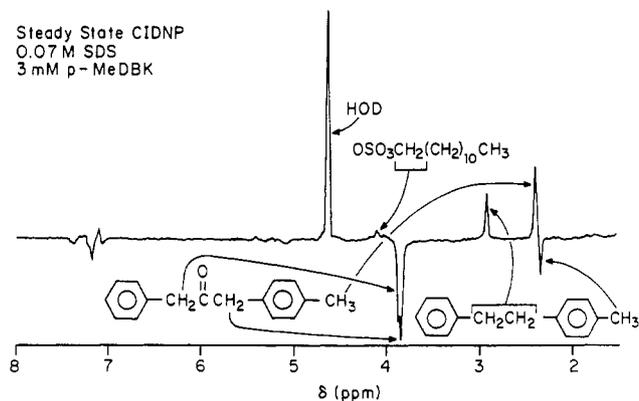


Figure 2. Steady-state ^1H CIDNP spectrum produced by the photolysis of *p*-MeDBK in SDS solution in an NMR spectrometer. The assignments of the polarizations (except for the aromatic protons) are shown in the figure.

from SDS micelles is $1.4 \times 10^6 \text{ s}^{-1}$, which is nearly identical with the exit rate of toluene from SDS micelles ($1.3 \times 10^6 \text{ s}^{-1}$).^{9b} In this paper we describe the influence of additives such as gegenions and organic solutes on the steady-state CIDNP, steady-state product ratios, and the exit rates of micellized radical pairs produced by photolysis of DBK's.

Results and Discussion

Figure 2 shows the NMR spectrum which is observed upon photolysis of *p*-MeDBK in aqueous SDS solution in an NMR spectrometer. As previously reported,¹⁰ photolysis of *p*-MeDBK in SDS generates emissive polarization in the ketone methylenes at 3.85 ppm, and enhanced absorption in the methylenes of the *p*-methylidiphenylethane formed from reaction of the geminate radical pairs (AB in Figure 1) at 2.94 ppm. The cage effect is ca. 20% under these conditions so that significant yields of the symmetrical coupling products diphenylethane (AA) and *p,p'*-dimethyldiphenylethane (BB) are also formed. However, no polarizations are observed in the AA and BB products, which are formed via intermicellar recombination reactions of nongeminate

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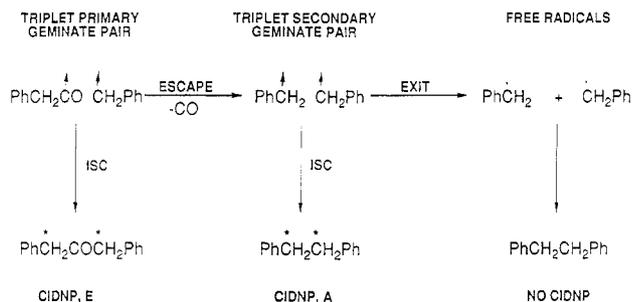


Figure 3. Abbreviated mechanism for generation of nuclear polarization in the photolysis of DBK in micelles.

radical pairs.¹⁰ The absence of polarization in these products has been attributed to nuclear relaxation which occurs in the benzyl radicals which exit the micelles before recombination reactions can occur. The rate of recombination for escaped radicals is considerably slower than that of the geminate radicals due to the second-order nature of the former process. A schematic representation of the competing processes which lead to the observed polarizations is shown in Figure 3.

Steady-state CIDNP within radical pairs produced upon photolysis of DBK in micelles results from the $T_0 \rightarrow S$ mechanism in which radicals of differing nuclear spin states are partitioned by nuclear spin accelerated intersystem crossing, which occurs in competition with a spin-independent "escape" process. An escape process for the primary radical pair may be diffusive separation and decarbonylation. Radical pairs with nuclear spin states that enhance intersystem crossing (ISC) are more likely to form singlet radical pairs and thus cage products, which are enhanced in those nuclear spin states. Radical pairs with nuclear spin states that enhance intersystem crossing less efficiently are more likely to form escape or out-of-cage products, with nuclear spin states opposite to those found in cage products. In principle, the spin polarization which is observed in the escape products should be equal and opposite to that observed in the cage products, i.e. the sum of the absorption and emission polarizations should be zero. In the triplet primary geminate phenacyl:benzyl radical pair formed upon photolysis of DBK, β nuclear spins in the methylene hydrogens of the benzyl radical accelerate ISC. Thus, the DBK which is re-formed from the triplet pair with excess β spins is observed as NMR emission in the CIDNP spectrum (Figure 3). Radical pairs which escape from the primary triplet geminate pair carry an excess α spin. The diphenylethanes which are formed from reactions of the secondary geminate radical pair (after decarbonylation) are observed as NMR-enhanced absorption in the CIDNP spectrum (Figure 3).

From the above discussion, it is expected that the steady-state CIDNP emission intensity observed in the ketone methylenes provides a measure of the total enhanced absorption polarization which is partitioned into the methylenes of the benzyl:benzyl radical pairs. The amount of the absorption polarization which is actually observed in the diphenylethane coupling products depends upon the fraction of the benzyl:benzyl radical pairs that undergo intramicellar recombination, since no polarization is observed in the diphenylethane products formed from reactions of radicals which have escaped the micelles in which they were formed.¹⁰ As previously mentioned, the lack of polarization in the products formed from intermicellar reactions is attributed to the slow second-order rate of reaction for micelles which have escaped the micelles in which they were formed. This rate is slow because of the relatively low steady-state concentration of radicals which are formed upon steady-state irradiation with a lamp source. As a result, nuclear spin relaxation within the benzyl radicals before recombination can occur. As a test of this hypothesis an experiment was performed in which the time-resolved CIDNP spectrum was recorded 15 μ s after pulsed laser photolysis of DBK in SDS in the presence of Fremy's salt (FS).¹¹ Fremy's salt is

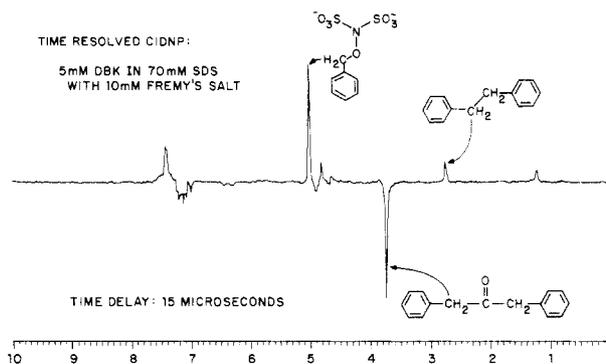


Figure 4. Time-resolved CIDNP spectrum obtained after laser flash photolysis of DBK in SDS solutions in the presence of Fremy's salt.

a water-soluble, anionic stable nitroxide which does not bind to the anionic SDS micelles, and efficiently scavenges benzyl radicals which exit the micelles into the water phase.⁸ Benzyl radicals which exit the micelles react with FS to form a hydroxylamine ether (Figure 4). From Figure 4 it can be seen that significant absorptive polarization is observed in this product (at 5.2 ppm), since fast *pseudo*-first-order reaction occurs between the benzyl radicals and FS before the nuclear spin polarization in the radicals is lost.

The amount of polarization which is observed in the diphenylethanes depends upon the fraction of the benzyl:benzyl radical pairs which undergo recombination in the micelles in which they were formed, i.e. the fraction of geminate intramicellar recombinations. This is equivalent to a definition of the cage effect for the reactions of the secondary benzyl:benzyl radical pair. If we assume that the DBK polarization is constant, the ratio of the diphenylethane (DPE*) to dibenzyl ketone (DBK*) polarizations is analogous to the product cage effect, and as such provides a spectroscopic method of determining its value. However, quantitative agreement between the polarization ratios and the micellar cage effects determined from steady-state product analysis may not be observed for at least two reasons. First, the CIDNP method only monitors the diamagnetic products which are formed as a result of the $T_0 \rightarrow S$ mechanism for producing polarization. The product cage effect is measured from steady-state product distributions which may also include products arising from reactions from T_+ or T_- radical pairs. Second, the measured steady-state polarization ratio is also dependent upon the spin-lattice relaxation times of the products. In these experiments polarization ratios are reported which are uncorrected for spin-lattice relaxation of the products, and it is assumed that these effects are unimportant since only relative trends are being considered.

Figure 5 shows the steady-state CIDNP polarization ratio (DPE*/DBK*) and the percent cage effect for the photolysis of *p*-MeDBK in 50 mM SDS, as a function of additive concentration. The cage effect studies were performed in the presence of a 2-kG magnetic field in order to minimize contributions from T_+ and T_- radical pairs. Clearly both sets of data show similar trends, although as discussed previously the results are expected to differ in their quantitative aspects. The figure clearly shows that the addition of the electrolytes NaCl, CsCl, and MgCl₂ (which result in an exchange of gegenion at the micelle surface) causes an increase in both the polarization ratio and the cage effect, whereas addition of the organic solutes benzyl alcohol and 1,10-decanediol causes a decrease in both of these quantities. The recombination efficiency of the geminate radical pairs is increased in the presence of electrolytes and decreased in the presence of organic solutes.

The rates of exit of the benzyl radical from the SDS micelles in the presence of the additives were determined by using the transient absorption technique previously described.⁹ Fremy's salt was used as a water-soluble trap for the benzyl radicals which exit the micelle. The exit rates were evaluated by monitoring the *pseudo*-first-order decay of the benzyl radicals at 317 nm and fitting the data to a kinetic model which assumes a steady-state relationship for the radicals in the aqueous phase.⁹ The exit rates obtained in the presence of 50 mM of each additive, the cage

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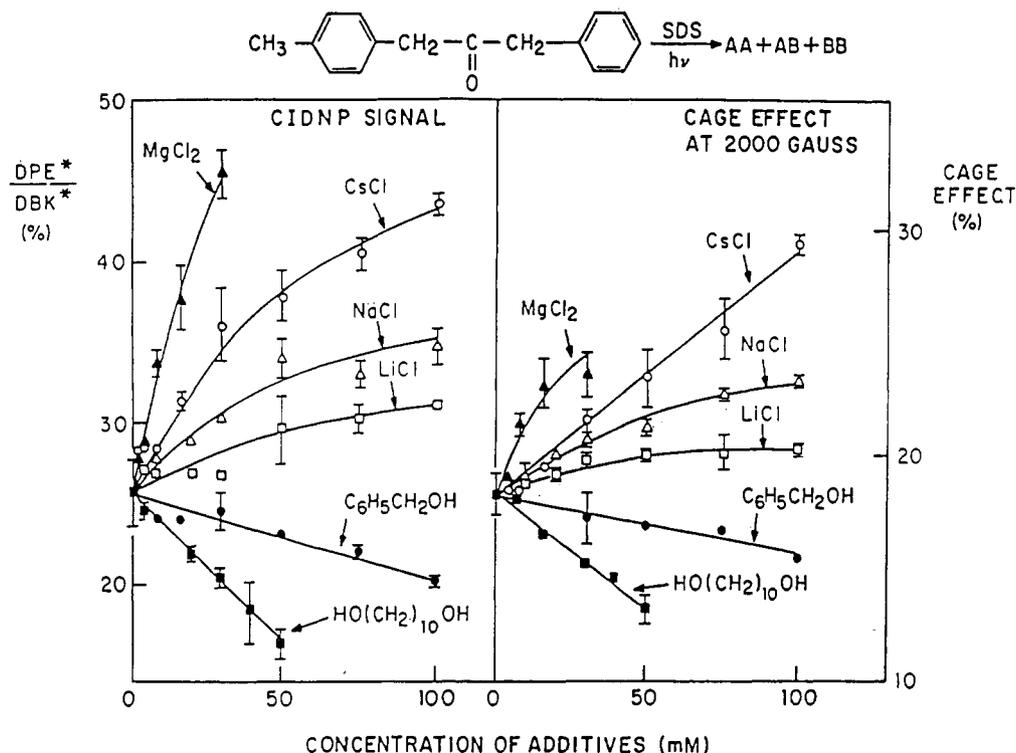


Figure 5. Comparison of the effects of additives on the steady-state CIDNP polarization ratio (DPE^*/DBK^*) and the percent cage.

TABLE I

additive	exit rate $\times 10^{-6}, s^{-1}$	cage effect, %	DPE^*/DBK^*
CsCl	1.40 ± 0.30	18.3 ± 1.0	24.5 ± 1.0
NaCl	1.13 ± 0.07	23.4 ± 1.5	37.8 ± 2.3
benzyl alcohol	1.30 ± 0.35	21.4 ± 0.1	32.2 ± 1.0
1,10-decanediol	2.1 ± 0.5	17.6 ± 0.3	23.4 ± 0.5
	3.0 ± 0.9	16.4 ± 0.2	21.0 ± 1.4

effects, and the polarization ratios are summarized in Table I.

In Figure 6 is shown the effect of changing the length of the alkyl chain of the surfactant upon the CIDNP polarization ratios and cage effects for DBK, *p*-MeDBK, and *p,p'*-DiMeDBK. Experiments were performed in sodium alkyl sulfate micelles with carbon chain lengths of 8, 10, 12, and 14. This figure shows that a linear relationship exists between the CIDNP ratio or cage effect and the product of the surfactant chain length and the micellar aggregation number.

The properties of micellar systems may be significantly altered by additives which serve to modify either the micellar structure and/or the dynamics of the solubilized substrates.² It is well-known that the addition of electrolytes to solutions of ionic surfactants results in an increase in the micellar aggregation number and consequently the micellar volume.⁷ Changes in the structure of the micelle are likely to be reflected in the dynamics of solubilized species such as radical pairs. For example, the observed increase in cage effect in the presence of salts indicates a structural change in the micelle which enhances the efficiency of geminate pair recombination by increasing the rate of ISC and/or decreasing the rate of radical exit from the micelle.

The possible physical basis for the correlation between the CIDNP polarization ratios and the cage effects (Figure 4) merits further comment. The CIDNP ratios, according to Figure 3, represent the competition in the primary geminate radical pair, between the nuclear-spin-dependent intersystem crossing process and the spin-independent escape process. Recent investigations of triplet radical pairs in micelles have suggested that diffusional motion within the micelle can serve as a form of escape, and that this escape process can occur on a time scale which is shorter than that required for complete exit of a radical into the water phase.⁶ Diffusional motion within a micelle is related to the microscopic viscosity experienced by a solute within the micellar aggregate.

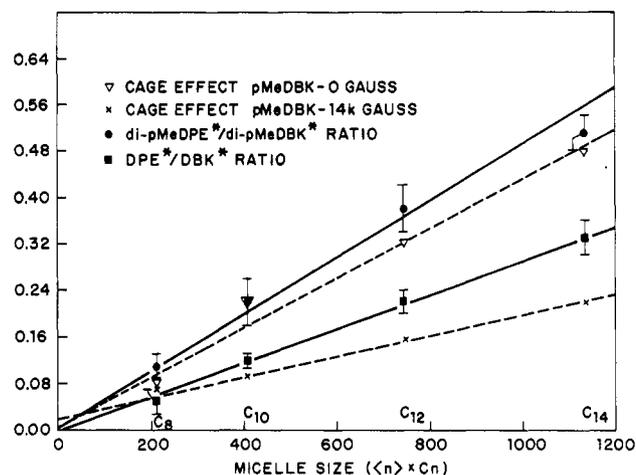


Figure 6. Correlation between the CIDNP ratios and the cage effect with micellar volume.

Although micellar microviscosity is not uniquely defined and tends to provoke controversy,¹² it is expected that the microviscosity of a micelle should be related to the rate of escape within the primary radical pair. Another property of micellar aggregates which could influence the radical pair dynamics is the hydrophobicity of the micellar interior. However, at this time there are no convincing methods for dissociating hydrophobic effects from microviscosity effects, or of defining these properties quantitatively. Because of this we have chosen the micellar volume as a more well-defined quantity related to micellar structure that can be correlated with the CIDNP ratios and cage effects. Support for this choice is provided by the data in Figure 6, in which a linear correlation is observed between these observables and the product of the surfactant chain length and the aggregation number which is an effective measure of the hydrocarbon volume or micellar size. The slope of the line increases with the hydrophobicity of the radical pair as can be seen in the CIDNP data in which a greater fraction of DPE^* is observed for *p,p'*-DiMeDBK compared to DBK. The slope of the 0-G line for the cage effect data is nearly twice as

TABLE II: Exit Rate of Benzyl Radicals from Micelles of Different Chain Lengths

surfactant	k_{ex}, s^{-1}
SDeS (C_{10})	$(2.7 \pm 0.3) \times 10^6$
SDS (C_{12})	$(1.8 \pm 0.2) \times 10^6$
STS (C_{14})	$(1.2 \pm 0.3) \times 10^6$

TABLE III: SDS Aggregation Number vs. Additive Concentration

additive, M	N	
	CIDNP	lit.
NaCl		
0.0	62 ^a	62 ^b
0.05	77	
0.1	88	90
CsCl		
0.0	62 ^a	
0.008	69	
0.02	82	
0.04	91	
0.1	118	
MgCl ₂		
0.0	62 ^a	68 ^c
0.004	72	79
0.008	80	87
0.020	91	96

^aAniansson, E. A. G., et al. *J. Phys. Chem.* **1976**, *80*, 905. ^bLianos, P.; Zana, R. *Ibid.* **1980**, *84*, 3339. ^cAlmgren, M.; Swarup, S. *Ibid.* **1983**, *87*, 876.

large as that for the 14-kG line, which is consistent with diminished participation of T_+ and T_- radical pairs at the higher field. The benzyl radical exit rates were also found to follow a similar trend. The data in Table II show that changing the surfactant chain length from 10 to 12 or from 12 to 14 decreases the exit rate by a factor of 1.5.

The micellar number (and thus the micellar volume) in the presence of added electrolyte can be estimated by measuring the DPE*/DBK* polarization ratio in the presence of the additive and then comparing the observed ratio with the data in Figure 6. The results of this procedure using CIDNP polarization data from the photolysis of DBK are summarized in Table III, in which aggregation numbers are given as a function of added NaCl and MgCl₂, together with literature data obtained by using fluorescence techniques. For NaCl the agreement is excellent; for MgCl₂ the results are in good qualitative agreement, but quantitative agreement is precluded, since the aggregation numbers in the absence of salt are different.

The influence of the electrolytes upon the micellar aggregation numbers, and hence the micellar volume, parallels the effects of these additives on the measured radical exit rates. For example the addition of Cs⁺ decreases the exit rate to a larger extent than does the same amount of added Na⁺. Cs⁺ is also more effective in changing the aggregation number than Na⁺ (Table II). A concentration of 0.1 M NaCl increases the SDS aggregation number by ca. 40% compared to the no salt value, whereas only ca. 0.02–0.03 M CsCl must be added to SDS to achieve the same effect. The larger effect of Cs⁺ is the result of a stronger binding of Cs⁺ compared to Na⁺, since it has been shown that the strength of binding to SDS micelles increases in the order Li⁺ < Na⁺ < K⁺.¹³ One possible explanation for the apparent dependence of the radical exit rates upon the micellar volume comes from the work of Ulrich and Steiner¹⁴ who found that the rate of exit of thionine radicals from reverse micelles was inversely proportional to the micelle radius. This implies that it is simply the surface area to volume ratio which controls the rate of exit in this system. Even if this explanation is not applicable in the present case it

is clear that the factors which control the rate of radical exit and those which control the micellar volume are related.

The effect of added alcohols on micellar aggregation numbers has been extensively investigated in the past few years. The aggregation numbers of HDTBr (hexadecyltrimethylammonium bromide), HDTCl, and SDS micelles were found to be reduced upon the addition of ethanol or 1-butanol.⁷ Similar results were obtained for TTAB (tetradecyltrimethylammonium bromide) in the presence of <0.1 M butanol, pentanol, or hexanol.¹⁵ These effects were found to parallel the apparent microviscosity of the micellar systems.¹⁵ Addition of benzyl alcohol or 1,10-decanediol to the micellar solutions in the present systems increases the radical exit rates, which is in accord with a reduced micellar volume. The decreased cage effect and CIDNP ratios must be due to some extent to the increased radical exit rates; however, changes in the intersystem crossing rates in the presence of additives must also be considered likely. Moreover, it is again observed that the factors which control the micellar volume and the observed radical pair dynamics are related, and that the micellar volume concept serves as a useful tool in the understanding of the additive effects.

Conclusion

We have shown that the combination of steady-state product analysis, steady-state CIDNP, and time-resolved absorption studies can be used to investigate additive induced changes in micellar structure and intramicellar radical pair dynamics. The observed changes in the radical pair chemistry can be explained in terms of the changes in the micellar volume in the presence of the additives. The CIDNP polarization ratios provide an alternative method for determining the micellar aggregation numbers. It should be pointed out that dependence of our measurements on micellar volume represents a composite of several factors which are interdependent (i.e., intersystem crossing rates, exit rates from the micelle, radical pair separation). Experiments are currently in progress to identify and to separate such parameters, so that detailed discussion of the correlation of micellar volume with cage effects, CIDNP polarizations, and radical pair chemistry within micelles must await the results of these investigations.

Experimental Section

Time-resolved transient absorption experiments were performed with a Lambda Physik excimer laser (EMG 101, 308 nm, ca. 20 mJ, 15 ns fwhm) with a conventional transient absorption apparatus. The analyzing light was a pulsed 450-W Xe arc lamp (PRA Model 301 power supply, PRA Model 305 pulser) and was detected through an ISA H10 monochromator using 6 dynodes of an RCA 4840 photomultiplier tube. The signals were digitized with a Biomation 4500 digital oscilloscope. Data analysis was performed with a PDP 11/23 minicomputer.

Steady-state ¹H CIDNP spectra were obtained by using a Bruker WP-80 NMR with a modified light rod probe. An Oriel 1000-W Hg–Xe lamp filtered through a NiSO₄ solution provided the exciting light. The lamp output was focused directly onto the end of a Suprasil light rod which extended directly into the probe. For the CIDNP and cage effect measurements a ketone concentration of 0.002 M and a surfactant concentration of 0.07 M were employed. Each solution was purged with argon before the experiment.

Exit rates were measured at 27 °C by using degassed solutions of ketone (0.003 M) and sodium dodecyl sulfate (SDS, 0.05 M) in the presence of sodium carbonate (0.006 M) to stabilize the Fremy's salt. All additive concentration concentrations were 0.05 M except 1,10-decanediol (0.025 M).

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