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Unusual Dynamics of Micellized Radical Pairs Generated from Photochemically Active Amphiphiles

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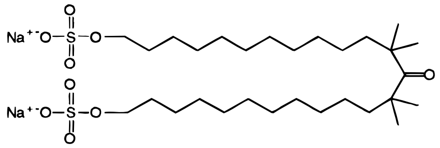
Photochemical reactions in heterogeneous media such as micelles have been under intense study in recent years.[1] These involve reactions of several types: (1) those where a probe molecule is dissolved in the interior of the micelle and the photochemical reaction takes place between the probe and the surfactant making up the micelle,[2] (2) those which occur between the probe and a water soluble molecule on the exterior of the micelle,[3] and (3) those which are unimolecular but are initially confined to the micelle.[4] Magnetic field effects are often observed in micellar radical reactions due to the presence of an exchange interaction (J) between the members of the radical pair (RP).[5] This exchange interaction has also been observed directly by time-resolved electron paramagnetic resonance (TREPR) spectroscopy,[6] and its observation is the basis for a well-established theory of chemically induced electron spin polarization known as the spin-correlated radical pair (SCRP) mechanism.[6,7]

To learn more about the magnitude of J in confined systems, and to understand the effect of micellar dynamics on the RPM and SCRP spin polarization mechanisms, we have synthesized the surfactant molecule **1**. The details of the synthesis, purification, and characterization of this and other amphiphilic ketones will be published separately.[8] From small-angle neutron scattering (SANS) experiments, we have determined that **1**, when dissolved in triply distilled and deionized water at concentrations of 0.02−0.2 M, forms elliptical micelles with a diameter along the major axis of 60 Å and along the minor axis of 30 Å.[9] The aggregate numbers vary from 24 to 45 depending on concentration, and the critical micellar concentration was determined to be approximately 6×10^{-5} M from measurements of surface tension as a function of concentration.[10] In the experiments reported here, the aggregate number was approximately 42 (0.17 M aqueous solution of **1** at room temperature).



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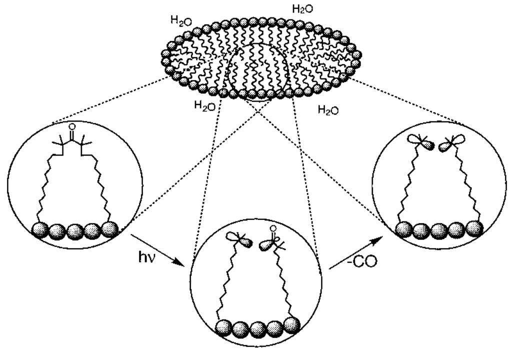
Scheme 1



The goal of our TREPR experiments[11] on micelles formed from **1** was to create RPs where both members of the pair would retain their amphiphilic character after the photochemistry had taken place. By doing this, the relative rate of diffusion of the radical centers and their exit rates from the micelle might be altered significantly from any of the previously studied micellar RP systems. The photochemistry is depicted in Scheme 1. From our knowledge of the concentration, the micelle structure and the rather poor absorbance of the carbonyl moiety, we can safely conclude that only one RP per micelle is produced per laser flash.

The TREPR spectra obtained upon photolysis of micelles make up of **1** are shown in Figure 1. Figure 1A shows spectra from photolysis of the pure surfactant, while Figure 1B shows spectra obtained when a solution containing a mixture of **1** and sodium *n*-dodecyl sulfate is photolyzed. There are several noteworthy features in these spectra. At early delay times they clearly show an intensity pattern indicative of the RPM, that is emmissive/absorptive (E/A) about the center of the spectrum. However, at later delay times, each line in the spectrum appears to be split into E/A doublets, which is the classic manifestation of SCRP polarization with a small exchange interaction. The time dependence of these patterns is an unexpected observation. In all other TREPR studies of micellized RPs, it is the SCRP pattern that is observed first, then the RPM.[6] The accepted explanation for these previous observations is that confinement of the radicals at early times leads to SCRP polarization, but after some time escape processes take place and radicals exit the micelle, either to free solution or to other micelles which contain no free radicals. The resulting noninteracting radicals retain the RPM polarization which was generated in the geminate pair. The RPM pattern is not observed in the confined, interacting pairs because it is usually much weaker in overall intensity than the SCRP spectrum.[6]

A possible explanation of the reverse phenomenon reported here is that the dynamics of the micellized radicals prevent the observation of the SCRP until later delay times. In all previous publications of micellar TREPR spectra, the systems were of either two types: (1) RPs produced by hydrogen atom abstraction by a triplet state of a molecule such as benzophenone or (2) RPs produced by cleavage of a triplet state molecule resulting in two smaller radicals. In both cases there is at least one

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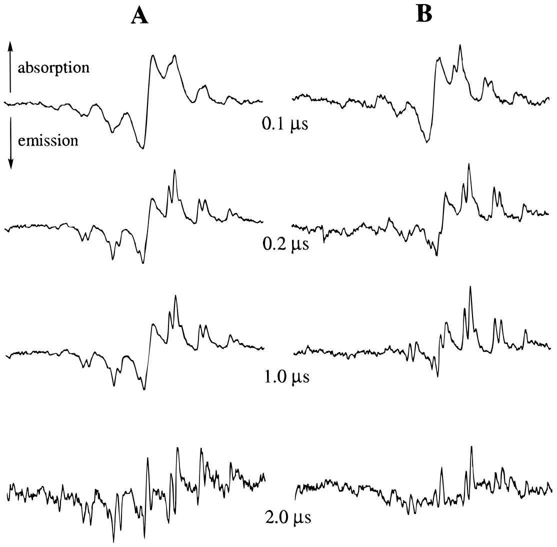

Figure 1. X-band TREPR spectra at the delay times indicated from photolysis of aqueous solutions of surfactant **1**: (A) [**1**] = 0.17 M, (B) [**1**] = 0.17 M, [SDS] = 0.7 M. The center field is 3375 G with a width of 200 G in all spectra. The photolysis wavelength was 308 nm.

component of the RP that is small and therefore quite mobile. Exit rates for many such radicals have been measured and are usually on the order of 10^6 s^{-1}.[12] This mobility has consequences in the appearance of the SCRP and RPM spectra. As has been pointed out by Norris and co-workers,[13] a manifestation of this mobility in TREPR spectroscopy is that RPM polarization will be large in systems where J can be modulated between large and small values on an appropriate time scale. Theoretical support for this in free solution TREPR spectra comes from the work of Pedersen and Freed[14] and Adrian and Monchick,[15] who independently examined and found a strong dependence of RPM polarization magnitude on the diffusion coefficient. In particular, they found stronger RPM in more viscous solutions.

Recently, theoretical attention has been paid to the effects of diffusion on spin polarization mechanisms in restricted geometries such as micelles. In numerical calculations by Hore and Hunter,[16] the strong RPM dependence on diffusion coefficient was found, as expected. However, they found no large dynamic effect on the amplitude of the SCRP polarization. They arrived at this result because they used a so-called "static approximation" of spectral contributions from individual RPs in their analysis. This point has recently been discussed in a more rigorous theoretical treatment of micellar EPR spectra by Shushin,[17] who found, using an analytical solution to the problem, that both the amplitude and line shape of the SCRP spectrum in micellar systems can be extremely sensitive to the dynamics of the RP. Independently, Adrian has recently reported a similar theoretical treatment.[18]

There is experimental evidence that modulation of the exchange interaction can strongly affect the SCRP polarization pattern and can adversely affect our ability to observe the SCRP spectrum altogether.[19] We have recently shown in two separate types of flexible biradical that SCRP polarization can be significantly altered due to line broadening from J modulation caused by temperature-dependent conformational motion, and we have demonstrated how it can be accounted for as a T_2 relaxation process.[20] These cases all involved a large average J coupling (larger than the hyperfine interactions) being modulated over a fairly wide range of values. If the time scale for J modulation is just right, it may be possible to remove the SCRP spectrum almost completely, and this is a possible explanation of the spectra shown in Figure 1.

The previously mentioned RPM theories, along with the model for SCRP proposed by Shushin and Adrian, may account for this unusual time dependence. There are two parameters relevant to our discussion which need to be defined. One is the splitting between the SCRP doublets, $\langle 2J \rangle$, and the other is the line width, which for the purposes of demonstration we will assume is dominated by modulation of the J coupling by motion of the RP. We will call this parameter ΔJ. Diffusion to regions of larger interradical distance will lead to smaller values of $\langle 2J \rangle$, which in turn leads to increased overlap of the emissive and absorptive lines of each SCRP doublet. In this case, the splitting between any two E/A doublets is no longer just $\langle 2J \rangle$ but is a more complicated function of $\langle 2J \rangle$ and ΔJ. The overall amplitude of the SCRP signal will in general be smaller due to collapse of the doublets. By this mechanism, the RP dynamics can dramatically alter the amplitude of the SCRP spectrum. While this is somewhat speculative, the observed effects are accounted for qualitatively by theories of Shushin and Adrian.[21] It should be emphasized that the slower dynamics can enhance the RPM while simultaneously suppressing the SCRP. We cannot say at present which effect is dominant in this system.

In Figure 1, it is interesting to note that the appearance of the SCRP polarization takes place on the same time scale as decarbonylation. It is possible that the carbonyl group, being more polar, remains closer to the outer shell of the micelle. After decarbonylation, both radicals are more hydrophobic and more mobile and therefore may move quickly toward the micelle interior. A slight increase in temperature increases the rate of appearance of the SCRP polarization, which supports this hypothesis.

We also ran the experiments with a mixture compound **1** and sodium *n*-dodecyl sulfate (SDS). The SDS was present in a much larger concentration, and thus, we can again conclude that only one ketone per micelle is absorbing the light. This experiment was run to show that the structure and time scale of surfactant motion are important in determining the relative ratios of RPM to SCRP at a given delay time. From Figure 1B it is clear that adding SDS changes the rate of appearance of SCRP polarization, which supports the hypothesis that micellar dynamics are affecting the amplitude of the two spin polarization mechanisms.

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