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parameter. If ζ varies linearly with n_c and if the individual binary mixtures are thought of as differing only in this parameter, then the analytic theory predicts that ΔT and Δp are both proportional to $\Delta n_c^{3/2}$.

Figure 3a shows the upper- and lower-critical-end-point temperatures t_u and t_l as a function of n_c and Figure 3b is a plot of $(\Delta t)^{2/3}$ against n_c . The cusplike variation of the end-point temperatures is in accord with the analytic theory and the linearity of $(\Delta t)^{2/3}$ with n_c demonstrates that, certainly to a first approximation, n_c is proportional to ζ .

The tricritical point is located at the intersection of the LCEP and UCEP curves, which from Figure 3b corresponds to $n_c \approx 17.6$, and experiments currently under way with the quasi-binary system ethane + (*n*-heptadecane +

n-octadecane) confirm this. Thus, limited miscibility should not be found in binary mixtures of ethane with normal alkanes below octadecane.

Although the phase rule restricts tricritical points to systems of at least three components, occasionally one can find a true binary mixture that lies close to a tricritical point. This appears to be the case in ethane + *n*-octadecane: all three coexisting phases appear opalescent throughout the 160-mK wide three-phase region. Light-scattering investigations of this fascinating system are being pursued.

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ARTICLES

Hydrated Electrons in Surfactant Solubilized Water Pools in Heptane

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Hydrated electron (e_{aq}^-) formation has been observed in the laser photoionization of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and dodecylammonium propionate reversed micelle solubilized phenothiazine, 8-hydroxy-1,3,6-pyrenetrisulfonate, and potassium ferrocyanide in heptane. Changes in the H_2O/AOT ratios, ω_0 values, were found to affect substantially e_{aq}^- lifetimes and spectra. Decreasing ω_0 values or the temperature resulted in increasing lifetimes and in narrowing the absorption spectra of e_{aq}^- . These results are rationalized in terms of increasing viscosities with decreasing ω_0 values.

Introduction

Surfactant solubilized water pools in apolar solvents, referred to as reversed micelles, provide unique microenvironments for reactions and interactions.¹⁻³ A variety of microscopic polarities can be attained by altering the water-to-surfactant ratios, i.e., the size of the water pools.⁴⁻⁸ The ability of reversed micelles to organize molecules in compartments of controlled hydrophobicities has been exploited in a variety of processes including photochemical energy conversion.⁹⁻¹⁴ Employing photochemical and

photophysical techniques has allowed, in turn, the deduction of structural information on organized assemblies.^{12,13,15} Pulse radiolysis of reversed micellar sodium bis(2-ethylhexyl) sulfosuccinate (AOT) in heptane has provided, for example, useful information on the properties of this system.¹⁶ The behavior of hydrated electrons, produced radiolytically or photolytically, strongly depended on the water content of the micelles.^{16,17} Decreasing the size of the water pools resulted in decreased hydrated electron yields. Hydrated electron formation was not observable, in fact, below a critical size of AOT-solubilized water pools.¹⁷

Properties of hydrated electrons, formed by laser photoionization of AOT and dodecylammonium propionate (DAP) solubilized phenothiazine, trisodium 8-hydroxy-1,3,6-pyrenesulfonate (pyranine), and potassium ferro-

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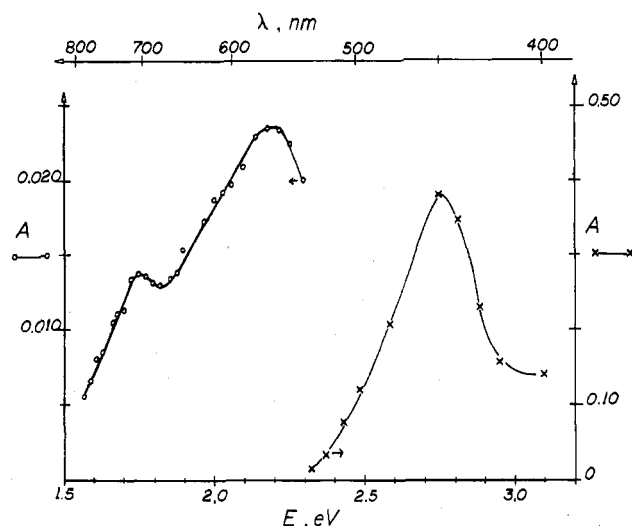


Figure 1. Transient absorption spectrum of 1.0×10^{-4} M phenothiazine in 0.075 M AOT reversed micelles in heptane in the presence of 0.375 M H_2O ($\omega_0 = 5$) at 10°C immediately after the laser pulse.

cyanide are reported in the present work. Lifetimes and spectra have been determined as functions of the size of the water pools and temperature.

Experimental Section

n-Heptane (Fisher spectral grade) was twice distilled from CaH_2 . Sodium bis(2-ethylhexyl) sulfosuccinate (AOT (Sigma)) was purified by column chromatography on activated charcoal (Fluka). Activated charcoal, packed in a 1.0-m long, 2.0-cm wide (i.d.) column, was washed with 2.0 L of 1:5 (v/v) methanol/cyclohexane. AOT (100 g) dissolved in 1.0 L of 1:5 (v/v) methanol/cyclohexane was passed through the column at a rate of one drop per minute. The solvent was rotary evaporated, and the pure AOT was dried at 50°C in vacuo to constant weight (2 days). Phenothiazine (Sigma) was recrystallized from 1:2 (v/v) methanol/butanol and dried in vacuo. Dodecylammonium propionate (DAP) and trisodium 8-hydroxy-1,3,6-pyrenetrisulfonate (pyranine) were prepared and purified as previously described.¹⁸ Reagent-grade potassium ferrocyanide and sodium nitrate, high-purity Ar, N_2O , and SF_6 were used as received.

Triply distilled water was used to adjust the concentration of reversed micelles. Water contents of solutions were determined by gas-liquid partition chromatography on a Porapak column.¹⁹

Flash photolysis was carried out by using the third harmonic (353 nm) of a Quanta-Ray DCR Neodymium-Yag laser, delivering ~ 5 –6-ns pulses at 25–100 mJ per pulse. The excitation energy was varied by changing the amplifier and by introducing filters. Samples, placed in a thermostated 1.0-cm quartz fluorescence cell, were continuously bubbled with argon (or with SF_6 or N_2O when appropriate). The 450-W Oriel xenon lamp analyzing beam, passed through the cell 90° to the laser beam, was focused into the entrance slit of a 25.0-cm Jarrel-Ash monochromator. Light absorption was detected by a R-924 Hamamatsu PM-tube operated at 750–800 V, connected to a Tektronix 7834 storage oscilloscope (7A13, 7B801, and 7B85 plug-ins) or to a Tektronix 7912 digitizer. A 7D12-M2 plug-in was used to monitor I_0 values (500 ns before the laser flash). Corrections have been made for changes in the pulse-to-pulse laser intensities by monitoring them with a Hew-

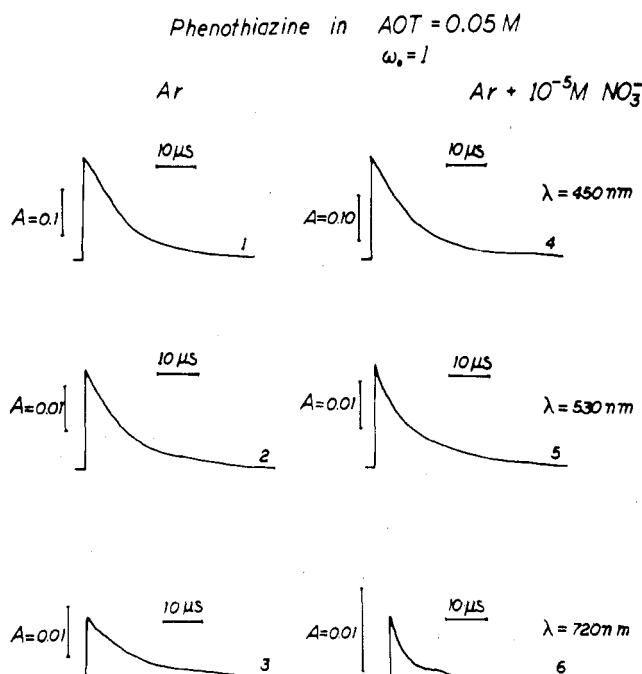


Figure 2. Temporal behavior of the transient generated by laser photolysis of 1.0×10^{-4} M phenothiazine in 0.05 M AOT, containing 0.05 M cosolubilized water ($\omega_0 = 1$) in heptane at 450, 530, and 720 nm in argon-saturated solutions (1–3) and in argon-saturated solutions containing 1.0×10^{-5} M NaNO_3 (4–6). Absorbances and time scales are as indicated.

lett-Packard 2-4220 diode. Appropriate cutoff filters (20% NaNO_2 and a series of Corion glass filters) were used to protect the samples against photolysis and to prevent stray light from entering the monochromator. To avoid the buildup of photoproducts, we changed samples frequently (typically after exposure to 10–30 shots).

Results and Discussion

Laser photolysis of a 1.0×10^{-4} M phenothiazine in 5.0×10^{-2} M AOT reversed micellar solution in heptane containing different amounts of cosolubilized H_2O resulted in the development of a transient spectrum with absorption maxima at 450, 720, and 530 nm (Figure 1). This spectrum is entirely consistent with the phenothiazine triplet, the phenothiazine cation radical, and the hydrated electron (e_{aq}^-) having absorption maxima, respectively, at 450, 530, and 720 nm.^{20–24}

Evidence for e_{aq}^- formation has been obtained by quenching experiments. Addition of NaNO_3 , SF_6 , and N_2O , known electron quenchers, decreased the lifetime of the 720-nm absorption without affecting those at 450 or 530 nm. Figure 2 illustrates the effects of NaNO_3 on the decay of transient absorbances at 450, 530, and 720 nm following phenothiazine photoionization in 5.0×10^{-2} M AOT– 5.0×10^{-2} M H_2O reversed micelles in heptane. The half-lifetimes in argon-saturated solutions were found to be 8, 5, and 5 μs at 450, 530, and 720 nm, respectively. Of these, only the decay of the 720-nm absorption is seen to decrease to 2 μs by the addition of 1.0×10^{-5} M NaNO_3 (Figure 2).

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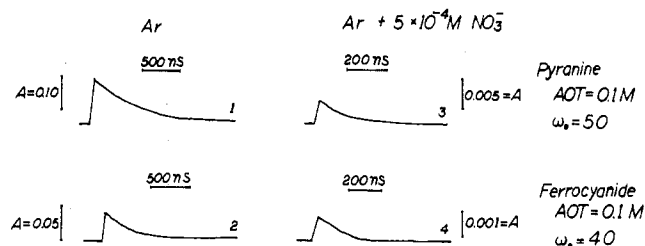


Figure 3. Decay of transient absorbances at 720 nm following laser photoionization of 1.1×10^{-4} M pyranine and 8.0×10^{-4} M potassium ferrocyanide in 0.1 M AOT reversed micelles in heptane containing 5.0 M ($\omega_0 = 50$) and 4.0 M ($\omega_0 = 40$) cosolubilized water. Traces 1 and 2 represent argon-saturated solutions while traces 3 and 4 show argon-saturated solutions in the presence of 5.0×10^{-5} M NaNO_3 . Absorbances and time scale are as indicated.

Yields of e_{aq}^- , phenothiazine triplet, and cation radical were found to increase linearly with increasing laser intensities up to saturation at high intensity (not shown). Although phenothiazine photoionization in acetonitrile²⁵ and aqueous micelles²⁴ has been discussed in terms of monophotonic processes, the present data in reversed micelles are insufficient for allowing a distinction between monophotonic and biphotonic ionizations.²⁶ Increased e_{aq}^- yields with increasing laser intensities were paralleled by decreased lifetimes and by a change from first- to second-order kinetics of electron decay. This is due, of course, to the increased prevalence of electron-electron annihilation at high laser intensities. All subsequent photoionizations were carried out at minimum laser energies (~ 30 mJ/pulse) when the e_{aq}^- decay followed strictly first-order kinetics. Under this condition e_{aq}^- decayed by reacting with the surfactant and other species present. Decreasing the temperature resulted in exponentially decreasing electron yields and increasing lifetimes. A similar situation has been found for phenol photoionization.²⁷ An activation energy of 3.5 ± 0.3 kcal mol⁻¹ has been calculated for e_{aq}^- decay in 0.05 M AOT-0.03 M H_2O reversed micelles in heptane obtained from data at -2.5 , -7.5 , and -15 °C. The good agreement between this activation energy and that determined for e_{aq}^- reactions with substrates (3.5 ± 0.5 kcal mol⁻¹) further substantiates our assigning the 720-nm transient to e_{aq}^- .

Laser excitations of $\text{K}_4\text{Fe}(\text{CN})_6$ and pyranine in 0.1 M AOT reversed micelles in heptane containing 5.0 and 4.0 M cosolubilized water, respectively (Figure 3), as well as that of phenothiazine in 0.25 M DAP-0.75 M H_2O reversed micelles in heptane (Figure 4) have also resulted in photoionization. The observed quenching of the 720-nm transient by electron scavengers substantiated the assignments of e_{aq}^- to this absorption. No detailed investigations were carried out, however, in these systems.

Since the solubility of phenothiazine in heptane is appreciably increased by AOT, it must be taken up by reversed micelles and be partially exposed to water molecules of hydration. This area is the likely site, therefore, for electron hydration. Quenching of e_{aq}^- in the smallest surfactant solubilized water pool ($\omega_0 = [\text{H}_2\text{O}]/[\text{AOT}] = 0.3$, $R_H \sim 14$ Å (ref 8)) by 5.0×10^{-5} M NaNO_3 is hardly surprising. The half-life of e_{aq}^- in this system (5 μs) is decreased to 2 μs in the presence of 5×10^{-5} M NaNO_3 .

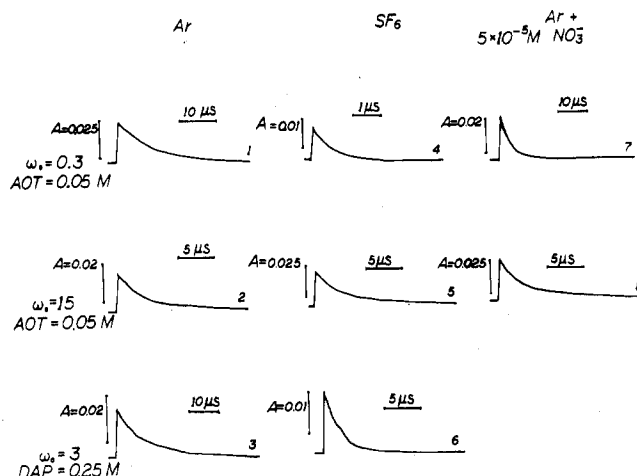


Figure 4. Decay of transient absorbances at 720 nm following laser photoionization of 1.0×10^{-4} M phenothiazine in 0.05 M AOT reversed micelles in heptane in the presence of 0.015 M H_2O , $\omega_0 = 0.3$ (traces 1, 4, and 7), and 0.75 M H_2O , $\omega_0 = 15$ (traces 2, 5, and 8). Traces 3 and 6 show the decays of the 720-nm transients following laser photoionization of 1.0×10^{-4} M phenothiazine in 0.25 M DAP containing 0.75 M H_2O , $\omega_0 = 3$. Effects of SF_6 (traces 4-6) and 5.0×10^{-5} M NaNO_3 (traces 7 and 8) are illustrated. Absorbances and time scales are as indicated.

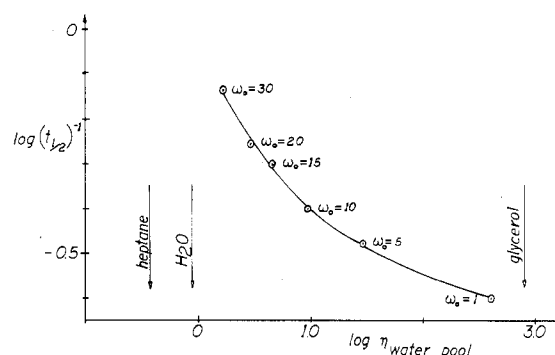


Figure 5. Plot of the logarithm of reciprocal e_{aq}^- lifetimes (in μs) against the logarithm of the viscosities (in cP) of AOT solubilized water pools in heptane. Viscosities have been calculated from rotational correlation times, determined in ref 29, by means of equations $\tau_c = 1/6D$ and $D = kT/8\pi\eta R^3$ (where τ_c is the rotational correlation time, D is the diffusion coefficient, η is the viscosity, k is Boltzmann's constant, T is the absolute temperature, and R is the radius of the rotating molecule, water, taken to be 1.3 Å). Water-to-AOT ratios, ω_0 values, are shown for each e_{aq}^- decay. Arrows indicate the viscosities of heptane, water, and glycerol.

(Figure 4). Effective quenching by SF_6 implies the close proximity of heptane (the solvent for SF_6) to e_{aq}^- . Such proximity is not unreasonable for reversed micelles whose diameters do not exceed 25 Å and whose constituent surfactants are fairly mobile.¹ The half-lifetime of e_{aq}^- in SF_6 -saturated AOT reversed micelles in heptane at $\omega_0 = 0.3$ is 500 ns (Figure 4). Increasing the size of the water pool resulted in decreased quenching efficiencies. At the extreme, the lifetime of e_{aq}^- was found to be unaffected by NaNO_3 or SF_6 (Figure 4). In reversed micelles with $\omega_0 > 15$, there are considerable amounts of free water molecules in addition to those hydrating the surfactant headgroups. These free water molecules are the predominant sites of electron hydration.¹⁷ Nitrate ions, on the other hand, are likely to form ion pairs and higher aggregates with the sodium counterions in close proximity to the inner core of reversed micelles and are unable, therefore, to quench e_{aq}^- before its decay. Similarly, in large water pools e_{aq}^- decays before having the opportunity of encountering

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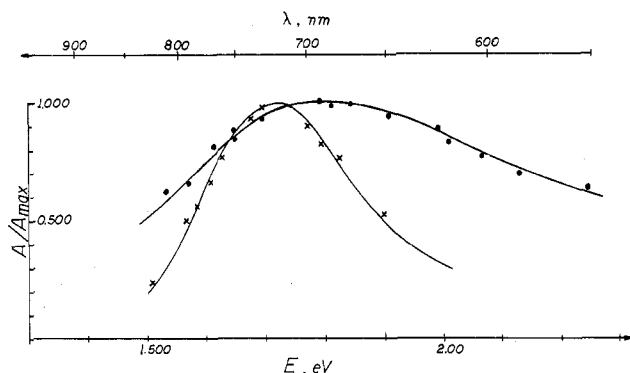


Figure 6. Spectrum of e_{aq}^- in 0.05 M AOT reversed micelles in heptane at $\omega_0 = 5$ and 20° (crosses) obtained by laser photoionization of 1.0×10^{-4} M phenothiazine. For the sake of comparison, the spectrum of e_{aq}^- has also been obtained in water by laser photoionization of potassium ferrocyanide (points). Solid lines are drawn by using eq 1 and 2.

SF₆, located in the heptane phase.

Increasing the size of AOT entrapped water pools in heptane has resulted in decreased lifetimes of e_{aq}^- . This behavior can be rationalized in terms of viscosity effects. In very small micelles ($\omega_0 < 15$) e_{aq}^- reacts within the viscous hydration shell of the surfactant. Consequently, it encounters fewer collisions than in bulk water.²⁹ This results in longer lifetimes and smaller rate constants. With increasing cosolubilized water concentration, the viscosity of the reaction site decreases. This, in turn, leads to an increased number of collisions and hence to increased rates. A good correlation has been obtained between the lifetime of e_{aq}^- and the viscosity of AOT reversed micelle entrapped water pools, calculated from published rotational correlation times³⁰ (Figure 5). A similar behavior has been recently reported for the reaction of solvated electrons, e_{aq}^- , with phenanthrene in alcohols.³¹ A plot of the logarithm of the rate constant for this reaction was shown to decrease

with logarithmically increasing viscosities.³¹ A two-step process was invoked to rationalize the viscosity dependence. In the first step, the reactants were considered to approach each other from an inactive zone by a diffusion-controlled process. Advance into the reaction zone and completion of reaction were assumed to occur in a somewhat slower second step.³¹ In reversed micelles at small ω_0 values, the inactive zone vanishes and e_{aq}^- dissipates entirely within the relatively viscous reaction zone. This results in longer e_{aq}^- lifetimes than that observed in larger, less viscous, surfactant solubilized water pools.

Solvated-electron spectra were determined by least-squares fitting of experimental points to Lorentzian and Gaussian shapes using the following equations:^{32,33}

$$A/A_{\max} = \{1 + [(E - E_{A_{\max}})/l]^2\}^{-1} \quad (1)$$

$$E > E_{A_{\max}}$$

$$\ln(A/A_{\max}) = -[(E - E_{A_{\max}})/g]^2 \ln 2 \quad (2)$$

$$E < E_{A_{\max}}$$

where A_{\max} is the maximum absorbance, $E_{A_{\max}}$ is the energy at the band maximum, and l and g are the portions of the width at half-height on the Lorentzian and Gaussian sides, respectively.

The spectra of e_{aq}^- at different ω_0 values also substantiate the uniqueness of the microenvironments provided by AOT reversed micelles. Decreasing the size of surfactant solubilized water pools as well as decreasing the temperature resulted in pronounced narrowing of the absorption spectrum (Figure 6). The spectrum in AOT reversed micelles corresponds, in fact, to that obtained in ice at -194°C .³⁴ Narrowing of the e_{aq}^- spectra is taken to indicate more ordered environments^{17,32,33} in accord with the present results.

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Querles Concerning Local Models for Hydrogen Uptake in Metal Hydrides

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A new prescription based on models of local environment is given for generating pressure-composition isotherms for pseudobinary metal hydrides. However, it is shown that for pseudobinaries such as $\text{Zr}_{1-x}\text{Ti}_x\text{Mn}_2$ the amount of H uptake as a function of x around ambient conditions can be explained predominantly as a result of the α - β phase transition rather than by local models.

Introduction

This paper deals with why in such systems as $\text{Zr}_{1-x}\text{Ti}_x\text{Mn}_2$ there is a threshold value for x for there to be a significant increase in hydrogen uptake according to $\text{Zr}_{1-x}\text{Ti}_x\text{Mn}_2\text{H}_2$. Also, it will be shown in section that a

model^{1,2} accounting for the "maximum" amount of hydrogen uptake ("saturated" β phase) in pseudobinary in-

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