perature range 200–298 K. Although this is the expected magnetic moment for high-spin iron(IV), the formal oxidation state assignment is not proven. Thus, an alternate formulation could involve abstraction of the electron from a porphyrin-centered MO with subsequent strong coupling of iron(III) and the radical spins. This would leave a total of four unpaired electrons with electronic relaxation rates such that resolvable NMR signals might be expected. Such strong exchange coupling is apparent for copper(II) porphyrin π-cation radicals, which, as a result, exhibit a singlet ground state.[10] The site of iron porphyrin oxidation has not been elucidated, although some radical character of A_{2u} symmetry (large spin density at meso positions and little at β-pyrrole carbons) would serve to explain the unusually large phenyl proton isotropic shifts of oxidized FeTPP compounds.

Additional physical measurements are in progress using model compounds generated from doubly oxidized μ-oxo-bridged iron porphyrin dimers.

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(3) Cyclic voltammetry waves for the isolated product were identical with those of the iron(III) dimer, thus indicating no irreversible porphyrin modification. The oxidized product was also reducible by iodide titration. The possibility that these species are simply monomeric iron(III) porphyrin perchlorates is ruled out by a comprehensive ^{1}H NMR study of $Fe^{III}TPP\cdot ClO_4$: Goff H.; Shimomura, E., submitted for publication.

(4) ^{1}H NMR spectra were recorded at 90 MHz using a Bruker HX-90E instrument operating in the pulsed Fourier transform mode. The oxidized species were stable for longer periods of time than required for the ^{1}H NMR experiments as verified by separate experiments.

(5) Phenyl resonance assignments in ref 2 are reversed with respect to those reported here. Assignment by integration was complicated by availability of instrumentation with adequate sensitivity at the time of the earlier study.

(6) Assignments were made by titration with $Fe^{III}TPP\cdot Cl$ and concomitant monitoring of averaged signals. The para proton signal was readily assigned by evaluation of the $FeTPP(p\text{-}OCH_3)\cdot Cl)^+$ spectrum. The discrepancy between resonances observed for our oxidized product and those given in ref 2 can be accounted for by differences in temperature, solvent, and the likelihood that considerable unoxidized material was present in the earlier preparations. Likewise the optical spectrum of $FeTPP\cdot Cl(ClO_4)$ resembles that reported in ref 2, and an identical spectrum may be generated if some iron(III) material is added to the product.

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Kinetics of Penetration of a Probe Molecule into a Reversed Micelle

Sir:

Surfactant aggregates in apolar solvents, termed reversed micelles, have been the subject of recent increasing interest[1–5] owing to their industrial applications and to their ability to mimic biological membranes. 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 groups extend into and are surrounded by the bulk apolar solvent. They are capable of solubilizing a considerable amount of water and other polar molecules.[2–5]

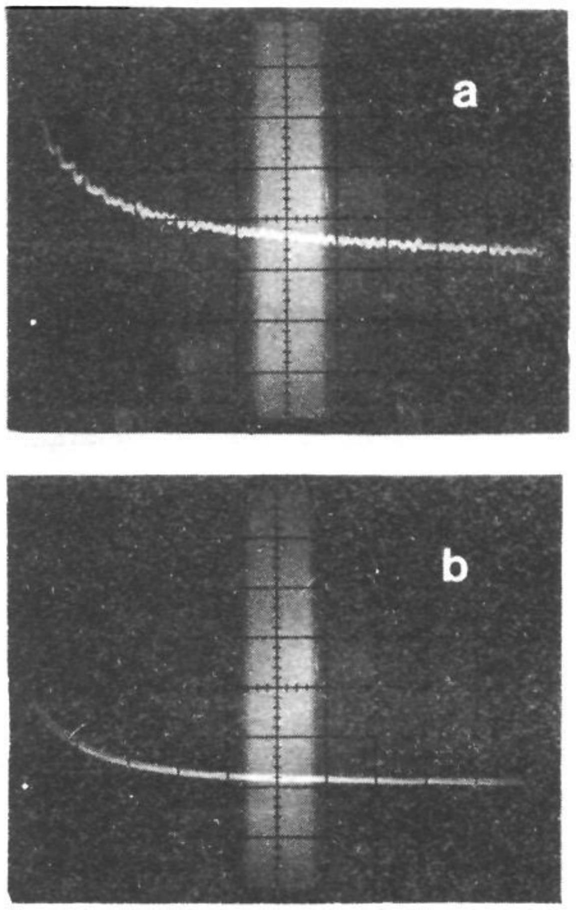

Figure 1. Time courses of a concentration-jump experiment carried out by mixing 2×10^{-5} M picric acid and 2×10^{-3} M Aerosol-OT solutions in benzene at 25 °C. Vertical scale: transmitted light intensity in arbitrary unit. Abscissa: (a) 20 ms/division; (b) 0.5 s/division. Wavelength of observation: 420 nm.

While there is a considerable accumulation of experimental results available about reversed micellar systems, as well as on their catalytic effects,[6] the information is incomplete. An unambiguous quantitative interpretation of micellar behavior is still missing. Even the basic concepts of the systems, such as the existence of critical micelle concentration (cmc), as well as the kinds of aggregates existing in solution, have been the object of controversy.[1,7–9] Especially much work is needed on the dynamic behavior of reversed micelles,[10] investigating the kinetics of their formation, and the solubilization of other molecules by the aggregates.

In the present communication we present kinetic results on the penetration of a probe molecule, picric acid, into reversed micelle of Aerosol-OT (di-2-ethylhexylsodium sulfosuccinate) in benzene containing 0.03% water. Aerosol-OT is a typical anionic surfactant forming reversed micelle in apolar solvent, the mean aggregation number of which is reported to be constant in a wide concentration range.[1,11] Picric acid is colorless in benzene, but it shows two characteristic absorption peaks at λ 345 and 420 nm in the presence of Aerosol-OT. The spectrum is similar to that of picric acid in water. The color change is apparently due to the dissociation of the indicator in and/or at the water pool of the micelle.

To investigate the rate of penetration of the indicator into the micelle, concentration- and solvent-jump[12] experiments were carried out using a stopped-flow apparatus that has already been described.[13] In a typical concentration-jump experiment the Aerosol-OT micellar solution (the surfactant concentration ranging from 2×10^{-4} to 1.6×10^{-2} M) was rapidly mixed (in 1 ms) with a benzene solution of picric acid (2×10^{-5} M) at a volume ratio of 1:1 at 25 °C. By monitoring the color change at λ 420 nm, two distinct rate processes can be observed. Representative oscilloscope traces are shown in Figure 1. Each of the rate processes was analyzed by fitting the curve to an exponential function. The time constant τ_1^{-1} of the faster process increases with the surfactant concentration until it reaches a constant value of 36 s^{-1} above 5×10^{-4} M Aerosol-OT. On the other hand, the time constant τ_2^{-1} of the slower reaction increases almost linearly from 0.9 to 2.8 s^{-1} with the

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surfactant concentration in the range of 2×10^{-4} to 3×10^{-3} M (after mixing).

In a series of solvent-jump experiments (performed in the same concentration ranges) where Aerosol-OT-picric acid solutions in benzene were rapidly diluted, no relaxation could be observed on a time scale of 10^{-3} to 5 s. This indicates that the solubilized indicator is too stable to be significantly perturbed by a twofold dilution.

Spectrophotometric data indicate that only two distinguishable forms of the picric acid exist in Aerosol-OT-benzene solutions. One is the undissociated picric acid and the other, which is responsible for the 345- and 420-nm absorption peaks, is the indicator solubilized (and probably dissociated) in the polar interior of the reversed micelle. Then the two rate processes observed may be ascribed to the solubilization of picric acid into the reversed micelle.

The concentration dependence of the larger time constant observed is similar to that reported by Robinson et al.[14] for the solubilization of acridine dyes into aqueous anionic micelles. Thus, the faster of our two rate processes may be interpreted analogously as follows. The solubilization mechanism consists of two steps involving a very rapid (close to diffusion controlled) adsorption of the indicator to an interior site of the micelle followed by a slow transfer to a more strongly binding site further in the interior of the micelle:

$$\mathrm{D} + \mathrm{Ms} \overset{K_0}{\rightleftharpoons} \mathrm{DMs} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{D^*M} \qquad (1)$$

where D is the indicator, Ms is the weaker binding micelle site, DMs is the adsorbed indicator at a weakly binding site, and D*M is the adsorbed indicator at a strongly binding site. Here DMs was considered to have the same spectroscopic character as D.

Since the formation of DMs is likely to be very rapid, the first step of eq 1 can be assumed to be in equilibrium at all times. Then, the rate-determining step of penetration will be the unimolecular conversion of DMs to D*M. The experimental conditions are such that [Ms] ≫ [D]. This enables us to interpret the rate processes as a concentration-jump relaxation. Under these conditions, the larger time constant can be shown to be

$$\tau_1^{-1} = k_1 K_0[\mathrm{Ms}]/(1 + K_0[\mathrm{Ms}]) + k_{-1} \qquad (2)$$

where K_0 is the equilibrium constant of the first step in eq 1. The above expression is in agreement with the concentration dependence of the observed time constant of the faster process; i.e., it increases with the surfactant concentration and finally reaches a constant value given by

$$\tau_1^{-1} \approx k_1 + k_{-1} \qquad (3)$$

when the condition of $K_0[\mathrm{Ms}] \gg 1$ is fulfilled. Since no relaxation was observed in the solvent-jump experiments, we can assume $k_1 \gg k_{-1}$. Thus, $k_1 = \tau_1^{-1} = 36\ \mathrm{s}^{-1}$ can be determined in experiments at high surfactant concentration.

The origin of the slower process observed is not clear at the present time. However, the concentration dependence of its time constant leads us to consider that it may be associated with an indicator-induced micelle formation, or a reconstruction of the indicator-solubilizing micelles to larger aggregates. The fact that relaxations were observed with a small amplitude also in the concentration range below the reported cmc values[1,4,7a,15,16] of the system supports the idea of the presence of premicellar aggregates proposed by Eicke et al.[7] Further kinetic and equilibrium studies are needed to answer the open questions.

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