Spin Probes in Reversed Micelles. Electron Paramagnetic Resonance Spectra of 2,2,5,5-Tetramethylpyrrolidine-1-oxyl Derivatives in Benzene in the Presence of Dodecylammonium Propionate Aggregates

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Abstract: Hyperfine coupling constants and line widths of neutral 3-carbamoyl-2,2,5,5-tetramethylpyrrolidine-1-oxyl, cationic 3-ammonium-2,2,5,5-tetramethylpyrrolidine-1-oxyl, and anionic potassium 2,2,5,5-tetramethyl-1-pyrrolidinyloxy-3-carboxylate spin probes have been determined in water, in benzene, and in 0.10 M dodecylammonium propionate (DAP) solubilized water in benzene by electron paramagnetic resonance (EPR) spectroscopy. The neutral probe is somewhat soluble in benzene and exchanges among the environments provided by the reversed micelles. The exchange frequency is, however, $\geq 6 \times 10^6$ s^{-1}. Conversely, both charged spin probes favorably partition into water and their EPR data provide information on the microenvironments of these probes. The anionic radical is likely to be anchored at the water-hydrocarbon interface with the polar carboxylate group intruding into the surfactant solubilized water pool. The cationic radical, however, is situated in a less polar region, corresponding to that occupied by the ammonium head group of the surfactant. The microviscosities reported by the charged probes in 0.10 M DAP in benzene increase initially with increasing water concentration until maxima are reached at 0.40 M cosolubilized water concentration, when free water molecules begin to appear. Important consequences of these results are the required different environments for the surfactant cation head group and its counterion as well as the presence of more than one type of bound water molecule. The rate of quenching of the anionic radical by phenylhydrazine remained unaffected by micellar DAP but that by sodium ascorbate decreased if the concentration of the quencher is taken to be that dissolved in the surfactant solubilized water pool.

Introduction

Rates of many reactions are dramatically and specifically enhanced in surfactant solubilized water pools in organic solvents.[2-6] Concentration of the solubilized water, i.e., the size of the water pool, profoundly affects reactivities.[7-11] Depending on the amount of solubilized water, rate constants for the interaction of glycine on vitamin $B_{12}a$ in 0.20 M dodecylammonium propionate (DAP) in benzene at 24.8 °C varies, for example, between 6 and 100 M^{-1} s^{-1}.[10] The largest rate enhancement occurs in the smallest water pool. Under this condition one vitamin $B_{12}a$ molecule is surrounded by some 300 molecules of surfactant and all the available water is hydrating the surfactant head groups and/or glycine. The reaction site appears, therefore, to be the hydration shell of the reversed micelle where the reactants are somewhat immobilized. At the extreme, the reactants are so close that they need not diffuse together. The recently observed ultrafast excited state proton transfer ($k^*_{\text{protonation}} = (2.0 \pm 0.2) \times 10^{12}$ M^{-1} s^{-1}) at the hydration shell of DAP aggregates in benzene represents an example of this phenomenon.[12]

Information on the properties of surfactant aggregates in organic solvents and the water pool entrapped therein is vital for the rationalization of catalysis in reversed micellar systems. In the absence of additives, association of DAP in nonpolar solvents is of the

$$\text{monomer} \overset{K_2}{\rightleftharpoons} \text{dimer} \overset{K_3}{\rightleftharpoons} \text{trimer} \ldots . \overset{K_n}{\rightleftharpoons} n\text{-mer}$$

type.[13-18] In this system, the average aggregation number is rather small and is concentration dependent. Addition of a third component, particularly water, substantially alters the aggregation pattern of surfactants in organic solvents.[13] Using simple geometrical considerations, we have recently shown that the average aggregation number of 0.08 M DAP in cyclohexane increases from 5 to 115 as the stoichiometric concentration of cosolubilized water increases from 0.185 to 0.739 M.[19] Assuming four molecules of water hydration per DAP, numbers of bound and free water molecules had been assessed.[19] Interestingly, DAP aggregates having average aggregation numbers of 18 or less contained only bound water molecules. These calculations have been substantiated by determining the fluorescence polarization of 8-hydroxy-1,3,6-pyrenetrisulfonic acid in the DAP aggregates in benzene as a function of added water concentration.[19] The present work reports independent and additional data on the nature of surfactant solubilized water pools. Advantage has been taken of the sensitivity of spin probes to their environments and of the availability of information on their use in micelles.[20-30] Electron paramagnetic resonance (EPR) spectra of water-soluble neutral 3-carbamoyl-2,2,5,5-tetramethylpyrrolidine-1-oxyl, cationic 3-ammonium-2,2,5,5-tetramethylpyrrolidine-1-oxyl, and anionic potassium 2,2,5,5-tetramethyl-1-pyrrolidinyl-oxy-3-carboxylate have been observed in pure solvents and in benzene in the presence of DAP and different amounts of cosolubilized water. The nitroxide radicals used, in general, exhibit three-line spectra due to the contact hyperfine interaction between electron spin ($S = \frac{1}{2}$) and ^{14}N nuclear spin ($I = 1$). The hyperfine coupling constants depend on the local polarity whereas the line widths reflect the rate of molecular motion which is dependent on the local microviscosity.[30]

In addition to structural studies, we have observed micellar effects on rates of radical scavenging. Water-soluble sodium ascorbate and hydrocarbon soluble phenylhydrazine have been used as scavengers.

Experimental Section

Preparation, purification, and characterization of dodecylammonium propionate (DAP) were previously described.[2] DAP was dried for at least 12 h in vacuo and stored in a desiccator prior to the preparation of the solution. Benzene (Fisher, spectroanalyzed) was stored over preactivated Linde-type molecular sieve 4A for at least several days prior to use. Water was twice distilled from an all-glass equipment. Sodium ascorbate (Biochemical Laboratories) was used as received. Its purity was found to be satisfactory by absorption spectroscopy; observed ϵ_{265nm} 1.5×10^4 M^{-1} at pH 5.5, reported ϵ_{265nm} 1.6×10^4 M^{-1} cm^{-1} at pH 5.8.[31] Phenylhydrazine (Aldrich, 97% purity) was fractionally distilled through a 12-cm Vigreux column under reduced pressure and stored in the dark.

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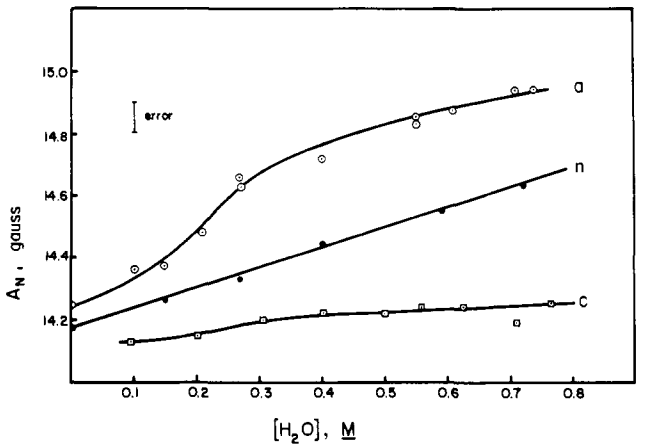

Figure 1. A plot of the hyperfine-coupling constants of the probes in 0.1 M DAP in benzene as a function of cosolubilized water concentration. a = anionic, n = neutral, and c = cationic probe.

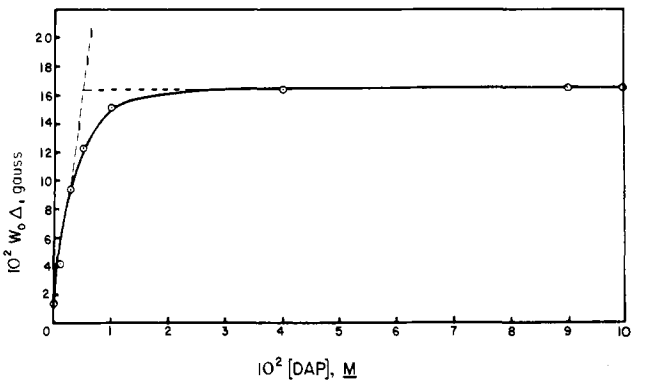

Figure 2. A plot of differential line-width broadening of the anionic probe as a function of DAP concentration in benzene. W_0 is the line width of the middle-field line and Δ is $(\sqrt{h_0/h_{-1}} - \sqrt{h_0/h_{+1}})$ where the designations of symbols are described in the text.

Table I. Hyperfine Coupling Constant of Spin Probes in Water, in Benzene, and in 0.10 M DAP in Benzene

	A_N, G		
spin probe	H_2O	benzene	0.10 M DAP/ benzene
neutral[a]	15.97 (16.27)[b]	14.17 (14.40)[b]	14.17
anionic[c]	16.16 (16.42)[b]	14.10 (14.36)[b]	14.25
cationic[d]	15.61	14.09[e]	

[a] 3-Carbamoyl-2,2,5,5-tetramethylpyrrolidine-1-oxyl. [b] Determined in ref 29, using benzosemiquinone as a standard. [c] Potassium 2,2,5,5-tetramethylpyrrolidinyl-3-carboxylate. [d] 3-Ammonium-2,2,5,5-tetramethylpyrrolidine-1-oxyl. [e] In "wet" benzene.

The neutral probe, 3-carbamoyl-2,2,5,5-tetramethylpyrrolidine-1-oxyl, and the precursor of the cationic probe, 3-amino-2,2,5,5-tetramethylpyrrolidine-1-oxyl, were prepared according to methods described in the literature.[32] The anionic probe, potassium 2,2,5,5-tetramethyl-1-pyrrolidinyloxy-3-carboxylate, was prepared by treating equivalent amounts of KOH and 2,2,5,5-tetramethyl-1-pyrrolidinyloxy-3-carboxylic acid in water. The acid radical (Eastman), recrystallized from chloroform/cyclohexane mixture and KOH, was of the best analytical grade. The alkali cation was replaced by hexadecylpyridinium ion for the kinetic experiments by treating an equivalent amount of potassium 2,2,5,5-tetramethyl-1-pyrrolidinyloxy-3-carboxylate with hexadecylpyridinium chloride (twice recrystallized from ethanol/ether mixture) in dried absolute ethanol. The precipitated alkali chloride was filtered off and the filtrate evaporated to dryness in a rotary evaporator. Dried cyclohexane was added to the resultant thick, viscous mass and the slightly cloudy solution was centrifuged. The clear, supernatant solution was carefully siphoned off and evaporated to dryness in a rotary evaporator. The resultant viscous mass was washed several times with ether and the last trace of ether was then pumped off with a vacuum pump. The resultant yellow solid, hexadecylpyridinium 2,2,5,5-tetramethyl-1-pyrrolidinyloxy-3-carboxylate, was used without further purification.

Absorption spectra were taken on a Cary 118C recording spectrophotometer. Electron paramagnetic spectra were obtained with a Varian E-6S spectrometer at room temperature (25 °C). In all line-width studies, the power was kept at or below 2 mW and the modulation amplitude at a level not exceeding 15% of the experimental peak to peak line width. The field was calibrated with Fremy's salt in saturated potassium carbonate solution where the distance between the two outermost lines is 26.182 G.[33] The hyperfine splitting constant (A_N) reported in this work is believed to have a maximum error of ±0.05 G. The line widths were carefully measured and the precision is ±0.01 G or even better in some cases. In all spin probe measurements, the probe concentration was kept at approximately 6×10^{-5} M concentration. The stock solution of the cationic probe was prepared from the amine radical by adjusting the pH of the solution to 5.8-6.0 by HCl. The stock solutions for the neutral and anionic probes were prepared directly from the solid with the appropriate solvents. The samples were carefully degassed on a vacuum line by means of repeated freeze-pump-thaw cycles.

Sodium ascorbate is insoluble in benzene. Stock solutions of this reducing agent were, therefore, prepared in degassed water at pH 5.8-5.9. Appropriate amounts of this stock solution and benzene were injected over weighted amounts of DAP just prior to the experiments. Phenylhydrazine solutions in benzene were also freshly prepared. These precautions were necessary since both the ascorbate ion and phenylhydrazine decompose on standing. Sample solutions containing the reducing agents and the radical were degassed simultaneously by repeated freeze-pump-thaw cycles prior to mixing. Peak to peak height of the middle-field line ($M = 0$) of the radical was measured as a function of time. The first measurement was usually made within 60-90 s after the mixing. A steady stream of N_2 was passed through the cavity throughout the experiment. The temperature variation was less than ±0.2 °C during the whole period of kinetic run.

Results

Hyperfine coupling constants of the three spin probes neutral 3-carbamoyl-2,2,5,5-tetramethylpyrrolidine-1-oxyl, anionic potassium 2,2,5,5-tetramethylpyrrolidinyl-3-carboxylate, and cationic 3-ammonium-2,2,5,5-tetramethylpyrrolidine-1-oxyl in water, in benzene, and in 0.10 M DAP in benzene are given in Table I. Differences between the present A_N values and those reported in the literature[29] are due to the different standards used to calibrate the instrument. For the anionic probe, the coupling constant in benzene in the presence of 0.10 M DAP is somewhat higher than that in neat benzene (Table I) indicating the increased polarity of the environment. Addition of water to the DAP-benzene system, i.e., increasing the size of the surfactant solubilized water pool, results in increased coupling constants for all three probes (Figure 1). There are significant differences, however, both in the rate and in the extent of increase of A_N values. Within the available range of added water (up to 0.8 M) the anionic spin probe experiences the greatest increase in coupling constant with increasing water concentration. Furthermore, the rate of increase in A_N values is more pronounced in the 0-0.30 M H_2O range than at higher concentrations of added water. A similar, although considerably less pronounced, trend is seen for the cationic probe. In contrast, the coupling constant for the neutral probe increases linearly with increasing size of the 0.10 M DAP solubilized water pool in benzene (Figure 1).

The differential line broadening (expressed as $W_0\Delta$, where $\Delta = \sqrt{h_0/h_{-1}} - \sqrt{h_0/h_{+1}}$, and h_{-1}, h_0, and h_{+1} are the heights of the $M = -1$, $M = 0$, and $M = +1$ lines, respectively) of the anionic probe in benzene as a function of DAP concentration is plotted in Figure 2. A pronounced break is observed at $(5.0 \pm 0.5) \times 10^{-3}$ M DAP concentration. Analogous, although less well defined, breaks in plots of the magnetically discrete proton magnetic resonance frequencies vs. surfactant

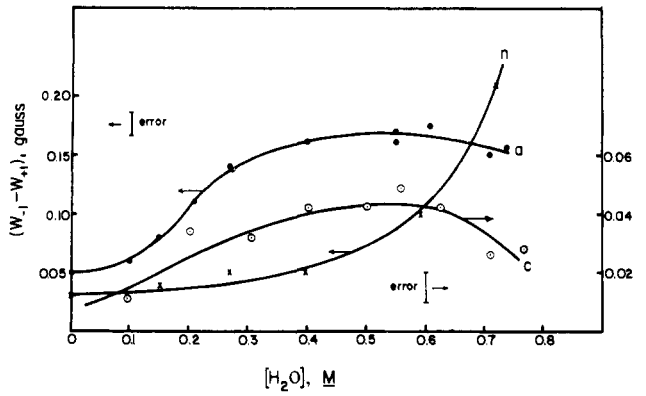

Figure 3. A plot of $(W_{-1} - W_{+1})$ of the probes in 0.1 M DAP in benzene as a function of cosolubilized water concentration. a = anionic, n = neutral, and c = cationic probe.

concentrations have been previously attributed to operational critical micelle concentrations.[34] Well-defined discontinuities in any physical parameter of the surfactant suggest the appearance of aggregates at a given concentration. This behavior can only be accommodated in terms of the accepted indefinite self-association of surfactants in organic solvents[13-18] if one or more of the association constants, $K_2, K_3, \ldots, K_n$, differ markedly from the others.

The ESR spectra were also observed as functions of added water. They are all sharp and symmetrical, suggesting that they fall within the fast, isotropic motion region. Differential line broadenings of all three spin probes in 0.10 M DAP aggregates in benzene solubilized with different amounts of water are as shown in Figure 3. Line-width contribution from Heisenberg spin exchange has been ruled out by taking EPR spectra in 0.10 M DAP-0.55 M H_2O-benzene system at different concentrations (all below 1.0×10^{-4} M of $R^{-}\cdot$). Differential line broadening was found to be independent of the radical concentration. The differential line broadenings are plotted as $W_{-1} - W_{+1}$ values, where W_{+1} and W_{-1} refer to the +1 and −1 lines in gauss.[35,36] Increasing the cosolubilized water concentration in 0.10 M DAP aggregates in benzene increases the differential line-width parameter up to a plateau, centered at 0.5 M H_2O, above which there is a slight decrease. Conversely, there is little change in the line-width parameter for the neutral probe in the 0.10-0.4 M water region but there is a rapid increase in $(W_1 - W_{+1})$ values above 0.5 M solubilized water concentration.

Solubility of the anionic probe, potassium 2,2,5,5-tetramethyl-1-pyrrolidinyloxy-3-carboxylate, in benzene was determined to be in the order of 10^{-6} M by EPR line intensity measurements. Line intensities were converted to concentrations by a calibration plot using known concentration of radicals. The anionic radical is, of course, highly soluble in water. The cationic radical, 3-ammonium-2,2,5,5-tetramethylpyrrolidine-1-oxyl, was partitioned between equal volumes of water and benzene. The concentration of the radical was determined in each phase by EPR and absorption spectroscopy. Less than 2% of the spin probe was found in the "wet" benzene phase. When the "wet" benzene was dried over Linde type 4A molecular sieve and calcium sulfate, no EPR signal could be detected under the normal experimental settings. This fact indicates the solubility of the cationic probe in benzene to be $\leq 10^{-6}$ M. Clearly both charged spin probes partition favorably into the surfactant-solubilized water pool. Conversely, 10% of the neutral radical, 3-carbamoyl-2,2,5,5-tetramethylpyrrolidine-1-oxyl, partitioned into benzene.

Sodium ascorbate[37-40] and phenylhydrazine[41] quench nitroxide-type radicals. Rate constants for quenching potassium 2,2,5,5-tetramethylpyrrolidine-1-oxyl spin probe by sodium ascorbate have been investigated in the present work. The height of the middle line of the spectra of the anionic radical was measured, as described previously,[38] as a function of time. Since there is no change in the line widths, line heights are good measure of the concentrations. In all kinetic runs, the concentration of the reducing agent was kept at least in a 100-fold excess over the concentration of the radical. Accordingly, pseudo-first-order rate dependency was observed. Plots of log h^0/h^t vs. time gave good straight lines, up to 90% reaction, from which the rate constants have been calculated in the usual manner. Table II summarizes the rate constants for radical scavenging in the different systems.

Table II. Effects of Medium on Rate of Reduction of the Anionic Radical[a]

reductant	medium	k_2, M^{-1} s^{-1}
sodium ascorbate	H_2O	0.14
	0.56 M H_2O + 0.1 M DAP	3.07[b]
	0.103 M H_2O + 0.1 M DAP	2.84[c]
phenylhydrazine	benzene	0.32
	0.55 M H_2O + 0.1 M DAP	0.33
	0 M H_2O + 0.1 M DAP	0.34

[a] Error as estimated from weighing, transferring of solution, and instrumental drifting was less than ±10% and the correlation coefficient for the pseudo-first-order plot was much better than 0.995 in all cases. The temperatures for the ascorbate and phenylhydrazine reduction experiments were 25.5 and 26.5 °C, respectively. [b] Stoichiometric sodium ascorbate concentration is 6.0×10^{-3} M. [c] Stoichiometric sodium ascorbate concentration is 3.0×10^{-3} M.

Discussion

Electron paramagnetic resonance spectroscopic investigations of spin probes provide information on their microenvironments. In a multicomponent system, such as reversed micelles, the differential line broadening may be due to changes in the microviscosity and/or to the modulation of the isotropic hyperfine splitting as a result of the exchange of the probe among the different environments.[42] In reversed micelles, one can a priori visualize exchange of the radical among the environments provided by the surfactant-entrapped water pool, the hydrophobic regions of the DAP aggregate, and the bulk benzene. The exchange contribution of the probe among these environments needs to be ruled out prior to interpreting the observed data in terms of the rotational behavior of the probe.

The appreciable partitioning of the neutral radical into benzene from water as well as the regular increase of the high-field line width (Figure 3) and the hyperfine coupling constant (Figure 1) with increasing cosolubilized water concentration in the DAP-benzene reversed micellar system is consistent with the exchange of this probe among different environments. Ordering of the spin probe does not contribute to differential line broadening since the high-field line remained symmetrical in all systems. The larger the size of the surfactant-solubilized water pool, the more pronounced the exchange effect becomes. It should be noted that the spectra in systems where the neutral probe is present in comparable quantity in the different pseudophases do not exhibit resolvable lines. Since the high-field line widths in benzene and in water are 1.24 and 1.15 G respectively, and $\Delta A_N \simeq 2$ G, the failure to resolve the spectra in DAP aggregates in benzene implies an exchange frequency of 6×10^6 or greater. In Aerosol-OT, sodium bis(2-ethylhexyl)sulfosuccinate, aggregates in heptane, on the other hand, two separate high-field signals were observed for the anionic spin probes at a solubilized water to surfactant ratio of 10.3.[29] On increasing the water to surfactant ratio, the two spectra collapsed to one. Lack of water solubility

Table III. Apparent Rotational Correlation Time of Spin Probes in Different Media at 25 °C

spin probe	medium	τ_r, [a] s	τ_r, [b] s
cationic	water		4.84×10^{-11}
	benzene (wet)		1.14×10^{-1}
	0.4-0.6 M H_2O and 0.1 M DAP	1.43×10^{-11}	3.17×10^{-11}
anionic	water		2.20×10^{-11}
	benzene		4.59×10^{-12}
	0.4-0.6 M H_2O and 0.1 M DAP	6.29×10^{-11}	1.67×10^{-10}

[a] Calculated from eq 1 based on direct line-width measurement. [b] Calculated from eq 1 based on "ratio of heights" method where the peaks were assumed to be Lorentzian and the peak to peak height of the first-derivative curve varies with the inverse square of the width.

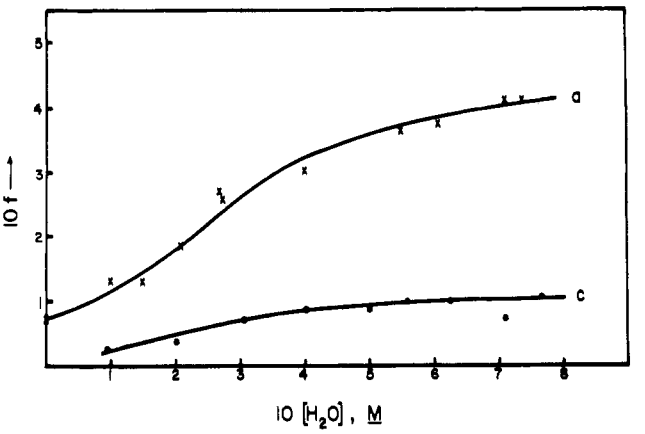

Figure 4. A plot of the polarity factor, f, for the anionic (a) and cationic (c) probes in 0.1 M DAP in benzene as a function of cosolubilized water concentration.

in DAP aggregates does not allow the investigation of the behavior of spin probes at conditions comparable to the Aerosol-OT system.

Conversely, there is no, or negligible, exchange contribution to the line-width broadening of the cationic and anionic spin probes in reversed micellar DAP. Negligible partitioning of these probes into benzene from water (see Results) supports this assumption. Furthermore, measurements in 0.10 and 0.40 M DAP in benzene of the cationic probe (in the presence of 1.6 M water) and of the anionic probe (in the presence of 2.4 M water) gave almost identical A_N and $(W_{-1} - W_{+1})$ values. If exchange effects were important, different proportions of the two phases would result in different EPR parameters.

In the absence of exchange effects the observed differential line widths, caused by the modulation of the anisotropic g tensor and electron-nuclear magnetic dipole interaction, can be related to the rotational correlation time of the radical (τ_r) by either eq 1 or 2[35,36]

$$\tau_r = \frac{\sqrt{3}\pi(\Delta\nu_{+1} - \Delta\nu_{-1})}{b\Delta\gamma B_0(0.5333 + 0.4u)} \quad (1)$$

$$\tau_r = \frac{\sqrt{3}\pi\Delta(\nu_{-1} + \Delta\nu_{+1} - 2\Delta\nu_0)}{b^2(0.25 - 0.05u)} \quad (2)$$

where

$$b = \frac{2}{3}[A_{zz} - \tfrac{1}{2}(A_{xx} + A_{yy})]\frac{g\beta}{\hbar}$$

$$\Delta\gamma = \frac{|\beta|}{\hbar}[g_{zz} - \tfrac{1}{2}(g_{xx} + g_{yy}]$$

$$u = 1/(1 + \omega_0^2\tau_r^2)$$

ω_0 = resonance frequency

$\Delta\nu_{+1}$, $\Delta\nu_0$, and $\Delta\nu_{-1}$ are the peak to peak line widths (MHz) of the low-, middle-, and high-field lines, respectively, and B_0 is the laboratory magnetic field (3400 G). A_{xx}, A_{yy}, and A_{zz} are the respective principal hyperfine coupling constants; g_{xx}, g_{yy}, and g_{zz} are the respective g-tensor elements, β is the Bohr magneton, and $\hbar$ is Plank's constant. Substitution of the observed line widths into eq 1 or 2 gave the rotational correlation times of the charged radicals in reversed micellar DAP (Table III). Rotational correlation times of $(6.29 \pm 0.63) \times 10^{-11}$ and $(1.43 \pm 0.36) \times 10^{-11}$ s were obtained from direct line-width measurements for the anionic and cationic probes, respectively, in 0.10 M DAP in benzene in the presence of 0.4-0.6 M cosolubilized water by using eq 1. Almost identical values were obtained on using eq 2.[43] In these calculations, values for the g and hyperfine splitting tensors were taken to be those available for 2-doxylpropane.[44] These values are not expected to change significantly with a gradual change in the medium since other factors, particularly molecular motion, have a considerably stronger effect on τ_r.[45] The rotational correlation times calculated here are only approximate because the line widths were not corrected for the hydrogen hyperfine splitting.[36] However, this does not affect the order of the relative magnitude in different systems. Furthermore, for the purpose of comparing the relative magnitude, it is sometimes more precise and convenient to obtain the apparent correlation times by the "ratio of heights" method[20,30] and the values in the fourth column of Table III were obtained by this method. The relatively large values of the rotational correlation time for the anionic radical suggest that its motion is more restricted in the surfactant aggregates. Correlation time ratios of the cationic to anionic probes (τ_r cationic probe/τ_r anionic probe) in neat water and in neat benzene are 2.2 and 2.5, respectively. The corresponding ratio in reversed micellar DAP in the presence of 0.40-0.60 M water is 0.19. These ratios further substantiate the restricted rotation of the anionic probe. The more restricted rotation of the anionic probe may originate in its association with the cationic head group of the surfactant which is attached to the long dodecyl chain. In contrast, the cationic probe associates with the much smaller propionate anion. Consideration of the polarity factor f ($f = (A_0 - A_b)/(A_w - A_b)$ where A_0, A_b, and A_w are the observed A_N values in the presence of DAP aggregates, in neat benzene, and in bulk water, respectively) as functions of water concentration in the DAP aggregates for the two charged spin probes implies, however, their locations in different environments. f values are seen to increase to a substantially higher value for the anionic than for the cationic probe (Figure 4). The predominant solubilization site of the anionic radical is, therefore, more polar than that of the cationic radical. Figure 5 illustrates the proposed interactions. The anionic spin probe is seen to be anchored at the water-hydrocarbon interface region with the polar carboxylate group intruding appreciably into the surfactant-solubilized water pool. Increasing the size of this water pool results in a greater degree of hydration of the carboxylate group and hence in more restricted rotation. The cationic radical, on the other hand, is most likely to be situated in a position similar to the ammonium head group of the surfactant. Comparison of the apparent correlation times of the cationic radicals in neat water and in (wet) benzene with those in the DAP-entrapped water system would suggest the microviscosity of the surfactant head group to be somewhere between that of water (0.89 cP) and (wet) benzene (0.61 cP).

There are two important corollaries of this model. Firstly, provided that there is a sufficient amount of cosolubilized water, the propionate head group of the surfactant is in a more polar environment than its counterion. Secondly, there are at

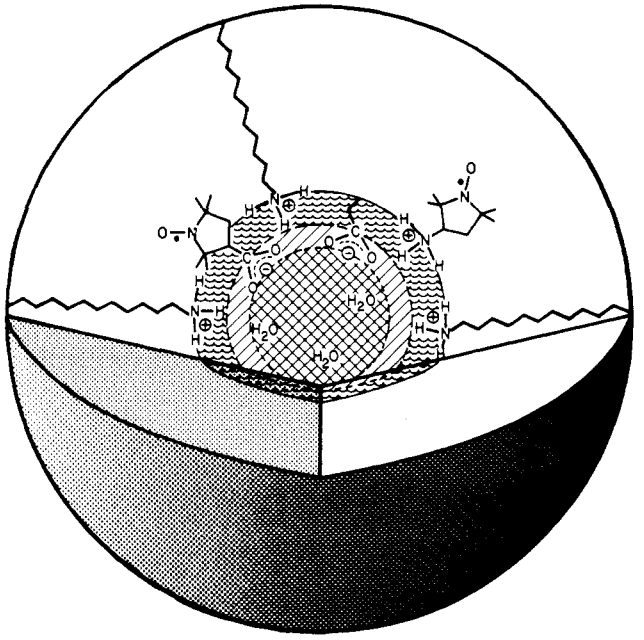

Figure 5. Schematic representation of the location of spin probes in the reversed micelle.

least two different types of bound water in reversed micelles: those around the ammonium and those around the more hydrophilic carboxylate head group. Figure 5 incorporates this refinement over the previously proposed model.[19] As the water concentration further increases free water molecules begin to appear. In 0.10 M DAP the appearance of free water occurs at 0.4 M stoichiometric water concentration. This concentration range corresponds to that observed previously by fluorescence[19] and thus provide an independent support for the proposed structure of DAP-solubilized water pools in benzene.

Superficially, sodium ascorbate quenches the anionic radical some 20-fold faster in the DAP-solubilized water pool than in bulk water (Table II). However, concentration of the reactants in the micellar phase, rather than that in the bulk water, needs to be considered for assessing true micellar effects on second-order reactions.[46,47] Since sodium ascorbate does not partition into benzene, its concentrations in the 0.103 and 0.561 M DAP-solubilized water pools are 1.35 and 0.56 M, respectively. Using these concentrations of ascorbate ion, the second-order rate constants become 6.3×10^{-3} and 3.3×10^{-2} M^{-1} s^{-1}, respectively. Thus, the rate constants for quenching the anionic radical by sodium ascorbate in the 0.561 and 0.103 M surfactant-solubilized water pool are factors of 4 and 22, respectively, slower than that in bulk water. The smaller the surfactant-solubilized water pool, the greater the rate retardation. This effect is entirely reasonable and can be rationalized in terms of electrostatic repulsions between the anionic radical and the negatively charged ascorbate ion. If these reactants are forced into greater proximity by decreasing the concentration of the surfactant-solubilized water pool, larger percentages of them are repelled from each other and consequently fewer percentages can undergo productive collisions. Since phenylhydrazine partitions into the benzene phase, its rate of quenching remains unaffected by micellar DAP.

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References and Notes

(1) On leave from the University of Malaya, Kuala Lumpur, Malaysia.
(2) J. H. Fendler, *Acc. Chem. Res.*, **9**, 153 (1976).
(3) J. Sunamoto and H. Kondo, *Yukagaku*, **26**, 389 (1977).
(4) K. J. Mollett and C. J. O'Connor, *J. Chem. Soc., Perkin Trans. 2*, 369 (1976).
(5) K. Kon-No, K. Miyazawa, and A. Kitahara, *Bull. Chem. Soc. Jpn.*, **48**, 2955 (1975).
(6) O. A. El Seoud, A. Martins, L. P. Barbur, M. J. da Silva, and V. Aldrique, *J. Chem. Soc., Perkin Trans. 2*, 1674 (1977).
(7) F. M. Menger, J.A. Donahue, and R. F. Williams, *J. Am. Chem. Soc.*, **95**, 286 (1973).
(8) C. J. O'Connor, E. J. Fendler, and J. H. Fendler, *J. Am. Chem. Soc.*, **96**, 370 (1974).
(9) C. J. O'Connor, E. J. Fendler, and J. H. Fendler, *J. Chem. Soc., Dalton Trans.*, 625 (1974).
(10) J. H. Fendler, F. Nome, and H. C. VanWoert, *J. Am. Chem. Soc.*, **96**, 6745 (1974).
(11) J. H. Fendler and L.-J. Liu, *J. Am. Chem. Soc.*, **97**, 999 (1975).
(12) J. R. Escabi-Perez and J. H. Fendler, *J. Am. Chem. Soc.*, **100**, 2234 (1978).
(13) A. S. Kertes and H. Gutmann, *Surf. Colloid Sci.*, **8**, 194 (1976).
(14) N. Muller, *J. Phys. Chem.*, **79**, 287 (1975).
(15) H. F. Eicke and H. J. Christen, *J. Colloid Interface Sci.*, **46**, 417 (1974).
(16) H. F. Eicke and H. Christen, *J. Colloid Interface Sci.*, **48**, 281 (1974).
(17) F. Y. Lo, B. M. Escott, E. J. Fendler, E. T. Adams, Jr., R. D. Larsen, and P. W. Smith, *J. Phys. Chem.*, **79**, 2609 (1975).
(18) K. Tsujii, J. Sunamoto, F. Nome, and J. H. Fendler, *J. Phys. Chem.*, **82**, 423 (1978).
(19) G. D. Correll, R. N. Cheser, III, F. Nome, and J. H. Fendler, *J. Am. Chem. Soc.*, **100**, 1254 (1978).
(20) A. S. Waggoner, O. H. Griffith, and C. R. Christensen, *Proc. Natl. Acad. Sci. U.S.A.*, **57**, 1198 (1967).
(21) N. M. Atherton and S. Strack, *J. Chem. Soc., Faraday Trans. 2*, **68**, 374 (1972).
(22) J. Oakes, *Nature (London)*, **231**, 38 (1971).
(23) J. R. Ernandes, H. Chaimovich, and S. Schreier, *Chem. Phys. Lipids*, **18**, 304, (1977).
(24) M. Aizawa, T. Komatsu, and T. Nakagawa, *Bull. Chem. Soc. Jpn.*, **50**, 3107 (1977).
(25) H. Yoshioka, *J. Colloid Interface Sci.*, **63**, 378 (1978).
(26) K. K. Fox, *J. Chem. Soc., Faraday Trans. 1*, **74**, 220 (1978).
(27) A. Kitahara, O. Ohashi, and K. Kon-no, *J. Colloid Interface Sci.*, **49**, 108 (1974).
(28) T. Masui, F. Watanabe, and A. Yamagishi, *J. Colloid Interface Sci.*, **61**, 388 (1977).
(29) F. M. Menger, G. Saito, G. V. Sanzero, and J. R. Dodd, *J. Am. Chem. Soc.*, **97**, 909 (1975).
(30) For a recent account of this subject, see P. L. Nordio in "Spin Labeling—Theory and Applications", L. J. Berlinger, Ed., Academic Press, New York, N.Y., 1976, pp 5–52.
(31) R. F. Morton, "Biochemical Spectroscopy", Vol. 2, Wiley, New York, N.Y., 1975, p 449.
(32) E. G. Rozantsev, "Free Nitroxyl Radicals", Plenum Press, New York, N.Y., 1970, Chapter IX.
(33) R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, **47**, 2462 (1967).
(34) J. H. Fendler, E. J. Fendler, R. T. Medary, and O. A. El Seoud, *J. Chem. Soc., Faraday Trans. 1*, **69**, 280 (1973).
(35) D. Kivelson, *J. Chem. Phys.*, **33**, 1094 (1960); P. W.Atkins and D. Kivelson, ibid., **44**, 169 (1966).
(36) G. Poggi and C. S. Johnson, Jr., *J. Magn. Reson.*, **3**, 436 (1970).
(37) R. D. Kornberg and H. M. McConnell, *Biochemistry*, **10**, 111 (1971).
(38) S. Schreier-Muccillo, D. Marsh, and I. C. P. Smith, *Arch. Biochem. Biophys.*, **172**, 1 (1976).
(39) H. Onishi and M. F. Morales, *Arch. Biochem. Biophys.*, **172**, 12 (1976).
(40) D. S. Cafiso and W. L. Hubbell, *Biochemistry*, **17**, 187 (1978).
(41) T. D. Lee and J. F. W. Keana, *J. Org. Chem.*, **40**, 3145 (1975).
(42) G. K. Fraenkel, *J. Phys. Chem.*, **71**, 139 (1967).
(43) The two separate methods of measuring "differential line broadening" are in fact the same method because

$$W_{-1} - W_{+1} = W_0\left(\frac{W_{-1}}{W_0} - \frac{W_{+1}}{W_0}\right) = W_0\left(\sqrt{\frac{h_0}{h_{-1}}} - \sqrt{\frac{h_0}{h_{+1}}}\right) = W_0\Delta$$

In Figure 2, ΔW_0 was used because each of the component lines is partially resolved (resolved from the hydrogen hyperfine splitting) and hence it is difficult to measure the line width precisely. It is more convenient to measure line heights instead. In Figure 3, no such problem exists for all the component lines are smooth (except at zero water concentration) and hence $(W_{-1} - W_{+1})$ was used. One can of course use ΔW_0 in Figure 3 but the conclusion is the same (although the τ values differ; see Table III). It should be realized that $(W_{-1} - W_{+1})$ is the exact and fundamental expression (it comes out directly in the derivation of eq 1) whereas $W_0\Delta$ is the derived expression which is based on the assumption that the lines are Lorentzian and therefore

$$\frac{W_{-1}}{W_{+1}}\sqrt{\frac{h_{+1}}{h_{-1}}}$$

(44) P. Jost, L. J. Libertini, V. C. Hebert, and O. H. Griffith, *J. Mol. Biol.*, **59**, 77 (1971).
(45) G. I. Likhtenshtein, "Spin Labeling Methods in Molecular Biology", Wiley, New York, N.Y., 1976, Chapter 1.
(46) L. S. Romsted in "Micellization, Solubilization and Microemulsions", K. L. Mittal, Ed., Plenum Press, New York, N.Y., 1977, p 509.
(47) K. Martinek, A. K.Yatsimirski, A. V. Levashov, and I. V. Berezin in ref 46, p 489.