

# Adsorption of Nitroxide Spin Probes at the Alumina/Cyclohexane Interface in the Presence of Aerosol OT

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Electron spin resonance has been recently applied to the study of adsorbed surfactant structures in aqueous solution. The extension of this technique to apolar media requires an accurate understanding of the adsorption behavior of the nitroxide probes used in this type of investigation and of their interactions with the adsorbed species. In this study, adsorption on alumina in cyclohexane was carried out for two types of nitroxide probes: Tempo derivatives (hydroxy and amino) and *n*-doxylstearic acids (*n* = 5, 7, 12, 16). All probes were found to adsorb on the mineral surface, but the addition of a surfactant, Aerosol OT, was found to affect the probe adsorption significantly. While the adsorbed layer of Aerosol OT solubilized the Tempo probes, it did not affect the adsorption of the 5- and 7-doxylstearic acids. Importantly, the molecular configuration of the 12- and 16-doxylstearic was found to be highly sensitive to the amount of surfactant adsorbed on the mineral. It is suggested that the configuration of these probes depends upon the surface pressure developed on the solid surface by the adsorbed surfactant species.

## Introduction

The conformation of molecules at the solid/liquid interface is of primary importance in understanding many interfacial processes such as aggregation/dispersion of colloidal suspensions, a phenomenon that controls the quality of pigment dispersions used as inks and paints,<sup>1</sup> and is important in magnetic tape processing<sup>2</sup> and in the cosmetic industry.<sup>3</sup> Structural features of molecules adsorbed at interfaces are also important in determining the efficiency of industrial processes such as flotation,<sup>4</sup> enhanced oil recovery,<sup>5</sup> waste water treatment,<sup>6</sup> and lubrication.<sup>7</sup> Among the methods used for studying the adsorbed surfactant layer, conventional adsorption experiments have yielded valuable basic information on the surface coverage by the adsorbates on various solids. On the basis of this information, molecular conformations have been postulated. For example, in their work on the adsorption of various fatty acids on different substrates,<sup>8</sup> Kipling et al. concluded on the orientation of the major axis of the molecule relative to the substrate surface. Adsorption experiments are particularly useful in providing information on the adsorbed surfactant layer at low surface coverage when they are coupled with other analytical methods such as electrophoresis,<sup>9</sup> bulk ion concentration determination,<sup>10</sup> or microcalorimetry.<sup>11</sup> However, certain changes in the adsorbed layer structure, especially those involving modifications at the molecular level, are not directly detected by adsorption experiments. The molecular configuration of polymers and surfactants is affected by their physicochemical environment (pH, ionic strength in aqueous solutions, nature of the solvent, presence of water in the case of nonpolar suspension). New methods are needed to follow in situ conformational changes of the surfactant molecules as their environment, especially at interfaces, is modified.

Recently, electron spin resonance spectroscopy (ESR) has been used to investigate the structure of the adsorbed layers in aqueous suspensions at a molecular scale.<sup>12</sup> Developed for microenvironmental studies of biological membranes<sup>13</sup> or membrane-mimetic systems such as micelles<sup>14</sup> or reverse micelles,<sup>15</sup> the spin-probing technique

has been extended to the study of adsorbed polymers and surfactants. Information was obtained on the fluidity profile in the adsorbed layer of dodecyl sulfate at the alumina/water interface by using doxylstearic acids probes.<sup>16</sup> Similarly, studies conducted with spin-labeled polymers have allowed estimation of the train-to-loop ratio of the adsorbed polymer chain and adsorbed layer thickness.<sup>17</sup>

For successful ESR investigation of interface structures, the selection of proper probes is a critical step. Two questions must be answered for the results to be meaningful: (1) Does the probe modify the adsorption characteristics of the adsorbate? (2) Can the information on

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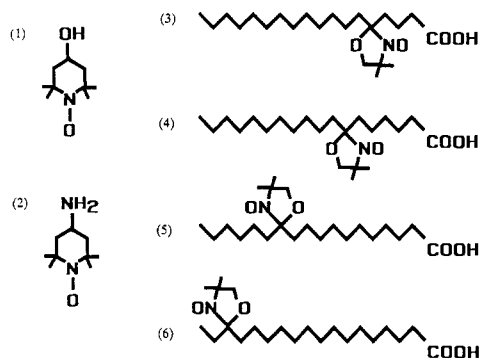
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**Figure 1.** Nitroxide spin probe structures: (1) 4-hydroxy-Tempo; (2) 4-amino-Tempo; *n*-doxylstearic acids with *n* = 5 (3), *n* = 7 (4), *n* = 12 (5), and *n* = 16 (6).

the probe environment given by its ESR spectra be used as a true representation of the environment constituted by the adsorbed molecules?

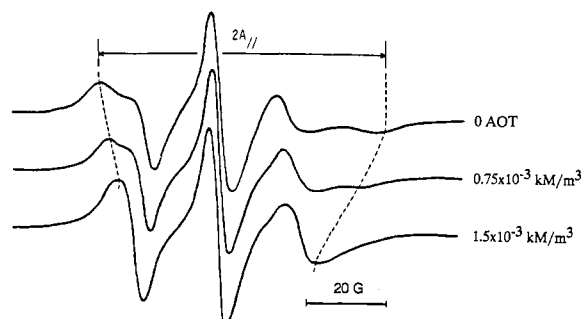
Nitroxide spin probes have been widely used in nonpolar media to study the structure of reverse micelles and W/O microemulsions, but we are unaware of reports of their behavior at the solid/nonpolar liquid interface. Furthermore, the use of this technique to study the physicochemical characteristics of the adsorbed layer requires a good understanding of the interactions between these probes and the coadsorbed surfactant species. In this paper, we report results obtained for two types of nitroxide probes at the alumina/cyclohexane interface and on the effects of the addition of a commonly used surfactant, Aerosol OT. The nitroxide probes chosen are 4-hydroxy- and 4-amino-Tempo (Tempo = 2,2,6,6-tetramethylpiperidinyl-1-oxy) and several doxylstearic acids (positions of the nitroxide free radical on the stearic acid alkyl chain: 5, 7, 12, and 16) (Figure 1). The use of Tempo derivatives was suggested by the extensive literature available on these probes, which have been often selected to investigate the structure of AOT reverse micelle and W/O microemulsions in nonpolar solvent.<sup>18</sup> The doxylstearic acids offer the unique possibility of collecting data profiles within the surfactant layer in reverse micelles as well as in the adsorbed state by monitoring the signal of the nitroxide radical in various positions along the alkyl chain of the stearic acid molecules.

### Experimental Section

**Materials.** The alumina used in the present study was of 99% purity (Linde A grade, Union Carbide Corp.). The particle size was 0.3  $\mu\text{m}$ , and the BET surface area was specified to be 15  $\text{m}^2/\text{g}$  by nitrogen adsorption. All the nitroxide spin probes were purchased from Aldrich Chemical Co. and used as received. Cyclohexane obtained from Fisher Scientific Co. was of certified ACS grade. The solvent was distilled and stored on Molecular Sieve 4A to avoid contamination by water. The surfactant used, Aerosol OT (sodium bis(2-ethylhexyl) sulfosuccinate) was obtained from Fisher Scientific Co. and was purified according to the procedure described in the literature.<sup>19</sup>

**Sample Preparation.** Samples were prepared by adding 15  $\text{cm}^3$  of cyclohexane solution of AOT containing approximately  $10^{-5}$  mol/L of the probe to 1 g of alumina previously desiccated at 200  $^\circ\text{C}$  for 4 h and allowed to cool in a desiccator connected to a vacuum pump using  $\text{P}_2\text{O}_5$  as desiccant. The suspension was conditioned for 24 h with a wrist shaker before being centrifuged.

**Methods.** The ESR spectra were obtained with a Varian E9 X-band spectrometer at a modulation frequency of 100 kHz using a quartz capillary tube. All experiments were performed at room



**Figure 2.** ESR spectra of 4-hydroxy-Tempo coadsorbed with different amounts of Aerosol OT on alumina in cyclohexane.

temperature. Both supernatant and sediment were used for the ESR experiments.

The Aerosol OT was analyzed by a two-phase titration technique where the surfactant is titrated against hexadecyltrimethylammonium bromide in chloroform with dimidium bromide disulfine blue as the end point indicator.

### Results and Discussion

**Adsorption of Tempo Derivatives at the Alumina/Cyclohexane Interface.** Analysis of the anisotropic features of the ESR spectra provides information on the rotational mobility of the nitroxide probe from which probe environment characteristics can be deduced. An isotropic spectrum characterized by a sharp three-line spectra is obtained when the nitroxide is tumbling in a nonviscous fluid. Immobilization of the probe leads to a line broadening and to a spectrum that has lost most of its details. If the molecule rotates slowly, an intermediate spectrum is obtained.

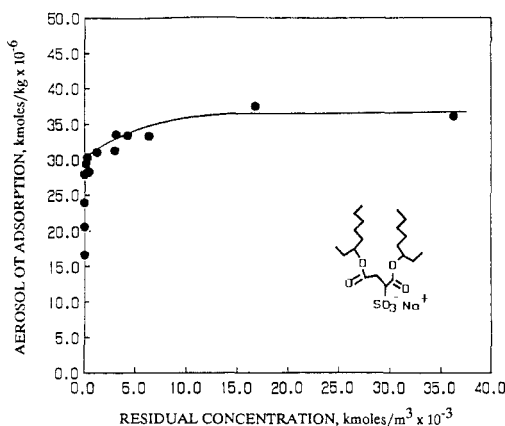
Changes in the ESR line shapes of the Tempo derivatives were studied as a function of the concentration of coadsorbed surfactant. When no AOT was added to the suspension, the probe was found to adsorb completely on the alumina surface. In this case, the spectrum obtained for the 4-hydroxy-Tempo (Figure 2) is typical of the probe in a "frozen state". Similar results were obtained with 4-amino-Tempo. The line broadening observed shows that rotational reorientations are not fast enough to average out anisotropies and that the rotational motion of the probe is strongly hindered by the presence of the solid surface. Since the hyperfine splitting constant  $A_{\perp}$  cannot be readily measured on this type of highly anisotropic spectrum, calculation of the empirical order parameter *S* (proportional to the difference in the hyperfine splitting constant  $A_{\parallel} - A_{\perp}$ )<sup>13</sup> is not a simple procedure. Accurate quantification of the probe mobility from its ESR spectrum would require a complete simulation of the spectrum. However, detection of modifications in  $2A_{\parallel}$  usually provides meaningful information, due to the fact that a decrease in  $A_{\parallel}$  implies a decrease in *S* and an increase in probe mobility. Furthermore, comparison of these changes with similar changes obtained by using experimental conditions at which molecular conformations and probe environment are well-known provides another way to obtain additional information on the probe environment and its effect on the ESR lineshape of the molecule.

**1. Effect of Surfactant Addition.** When the surfactant is added to the suspension, it coadsorbs with the nitroxide probe on the solid surface, affecting the mobility of the latter, a phenomenon that can readily be observed via the ESR technique. As the concentration of the surfactant is increased,  $A_{\parallel}$  decreases (Figure 2). This result is a clear indication that the probe mobility increases, suggesting that the probe molecule is solubilized into the surfactant adsorbed layer. Figure 3 shows the adsorption

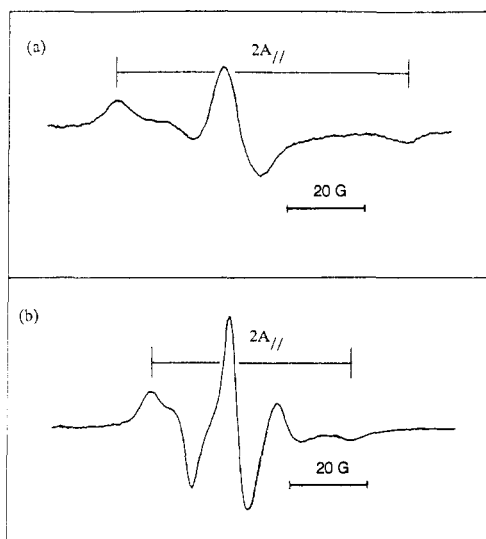
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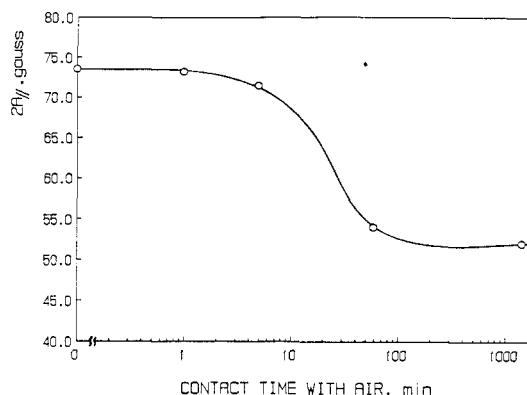
**Figure 3.** Equilibrium adsorption isotherm of Aerosol OT on alumina in cyclohexane.



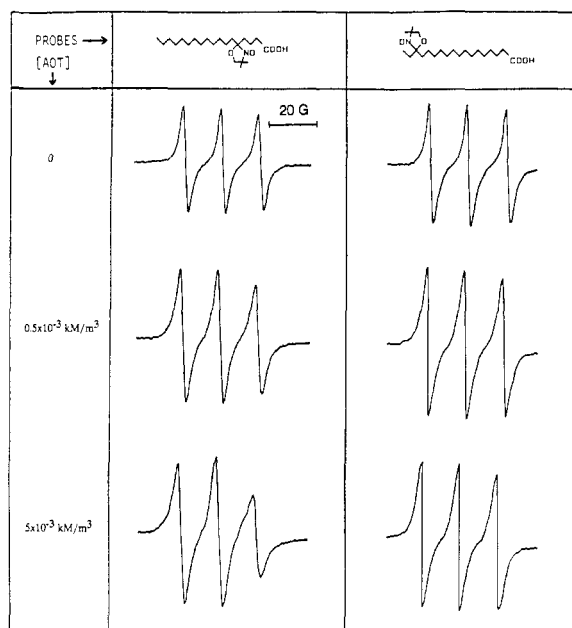
**Figure 4.** ESR spectrum of 4-hydroxy-Tempo adsorbed (a) on heat-treated alumina and (b) on as-received alumina.

isotherm of AOT on alumina in cyclohexane. The affinity of the surfactant for the alumina surface is rather high since the maximum absorption is reached before any residual surfactant concentration is detected in the supernatant. (Using a specific surface area of  $15 \text{ m}^2/\text{g}$  for the alumina and a parking area of  $70 \text{ \AA}^2$  for the AOT molecule, the maximum adsorption was found to correspond to the monolayer coverage.) Above the surfactant concentration corresponding to the monolayer coverage, the excess AOT remains in solution to form reverse micelles where the spin probe is also solubilized. Preferential partitioning of the nitroxide probe into the reverse micelles is apparently favored since the ESR signal of the supernatant does become increasingly stronger as the surfactant residual concentration in the supernatant increases.

**2. Effect of Water on the Probe Mobility.** The ESR response of the 4-hydroxy-Tempo was found to be very sensitive to the presence of water adsorbed on the alumina surface. The spectra obtained with the dehydrated alumina and with the alumina used as received were markedly different (Figure 4). The spectral anisotropy observed with the desiccated mineral was much larger (higher  $A_{||}$ ) than when the mineral was used without any pretreatment. The role postulated for the water present on the "as received" alumina surface was confirmed by leaving the desiccated alumina exposed to air for different intervals prior to the addition of the surfactant solution. In Figure 5, the hyperfine splitting constant  $A_{||}$  is plotted as a function of the time the desiccated solid is in contact with



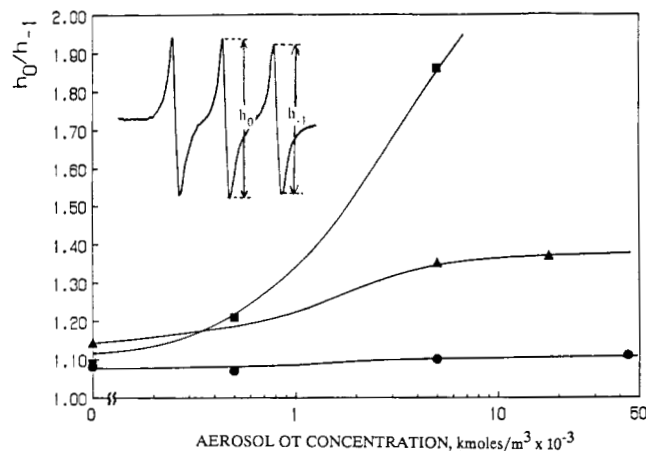
**Figure 5.** Variation of  $2A_{||}$  with the time of contact of the solid with air before the addition of the Aerosol OT solution ( $[AOT] = 5 \times 10^{-3} \text{ kM}/\text{m}^3$ ).



**Figure 6.** ESR spectra of 5- and 16-doxylosteic acid solubilized in cyclohexane with different AOT concentrations:  $0.5 \times 10^{-3}$  and  $5 \times 10^{-3} \text{ kM}/\text{m}^3$  are respectively below and above the surfactant cmc.

air (containing moisture). The line broadening observed at low water content decreases as the contact time with air is increased, indicating a change in the probe environment due to an increase in the amount of water adsorbed from the air on the mineral surface. Eventually, the mobility of the probe reaches a limiting value, which corresponds to the spectral anisotropy observed for the untreated alumina. These results confirm that the as received alumina contains adsorbed water which evaporates during the heating step but readsorbs when the sample is left in air.

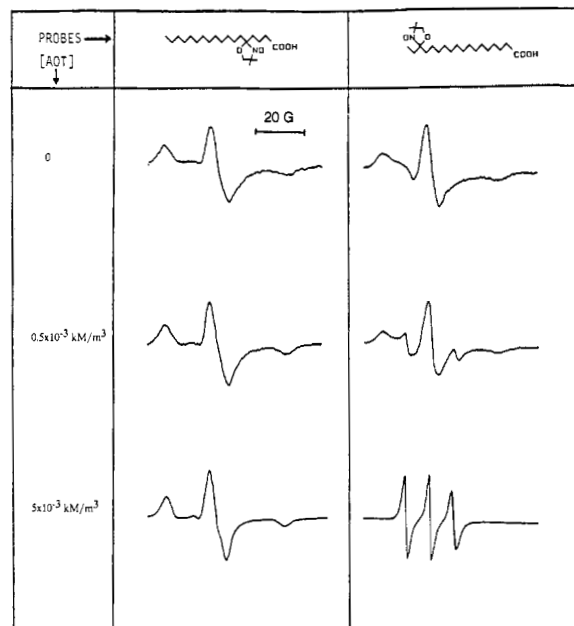
**Behavior of *n*-Doxylosteic Acids in the Alumina/AOT/Cyclohexane System.** Doxylosteic acid probes offer the unique possibility to collect information on structure profiles within the surfactant layer in reverse micelles as well as in the adsorbed state.<sup>12,16</sup> Figure 6 shows ESR spectra of 5- and 16-doxylosteic acid probes solubilized in cyclohexane in the presence of various amounts of surfactant. It can be seen that the spectral anisotropy varies with both the position of the nitroxide radical on the alkyl chain of the stearic acid molecule and the surfactant concentration. In Figure 7, the peak ratio  $h_0/h_{-1}$  is plotted as a function of surfactant concentration for various nitroxide positions on the probe. The central



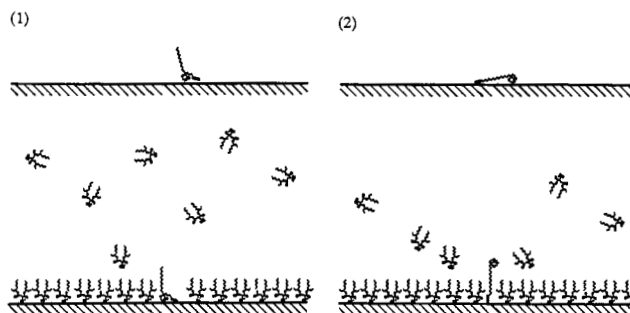
**Figure 7.** Changes in the peak ratio  $h_0/h_{-1}$  of the *n*-doxylstearic acid spectrum solubilized in cyclohexane as a function of surfactant concentration for different positions of the nitroxide probe on the alkyl chain of the stearic acid molecule: ■,  $n = 5$ ; ▲,  $n = 12$ ; ●,  $n = 16$ .

peak-to-peak line width being identical for all these probes, changes in the rotational correlation time of the probe are proportional to changes in the peak ratio  $h_0/h_{-1}$  ( $h_0$  and  $h_{-1}$  are respectively the heights of the central line and of the high field line). The use of the concept of the rotational correlation time as a measure of the probe mobility is justified only when the probe rotational motion may be considered as isotropic, an assumption valid in the case of doxylstearic acids in solution, even in the presence of surfactant. When the nitroxide free radical is very close to the polar head (5-doxylstearic acid), the spectral anisotropy increases sharply above the surfactant cmc (for AOT in cyclohexane, cmc =  $1.35 \times 10^{-3}$  kM/m<sup>3</sup>). This observation allows one to draw the conclusion that the stearic acid probe carrier is integrated into the reverse micelle, affecting the probe environment. No change in spectral anisotropy is observed with the 16-doxylstearic acid, suggesting that, although the probe carrier is integrated into the reverse micelles, the nitroxide free radical remains outside the surfactant shell of the micelle, because the length of the AOT molecule is equivalent to only about nine carbon-carbon bonds.

Figure 8 shows the spectra obtained for cases where the various doxylstearic acid probes are coadsorbed on the alumina surface with various amounts of coadsorbed surfactant. For the 5-doxylstearic acid, the spectra are characteristic of the probe in a frozen state, irrespective of the coadsorbed surfactant concentration. A similar phenomenon was observed with the 7-doxylstearic acid. This poor probe motion in these cases suggests that the probe is close to the surface, even when the coadsorbed AOT molecules cover the whole surface. The spectra obtained for 16-doxylstearic acid (Figure 8) and for 12-doxylstearic acid show the nitroxide in a frozen state when no surfactant is present. But, as the surfactant is added, a progressive shift toward an increased mobility is observed. This result may be interpreted as follows: at low surface coverages, interactions between the nitroxide radical of the 12- and 16-doxylstearic acids and the alumina surface lead to a bent configuration of the probe at which the rotational motion of the nitroxide is hindered, giving a characteristic frozen spectrum. These interactions are not strong enough to resist the "surface pressure" generated by the adsorbed surfactant as the concentration of coadsorbed surfactant increases. Under these conditions, the nitroxide probe is pushed away from the surface, allowing the stearic acid molecule to stand up in its stretched



**Figure 8.** ESR spectra of 5- and 16-doxylstearic acid probes coadsorbed on alumina with various amounts of AOT. The concentrations shown are the initial ones. An initial AOT concentration of  $0.5 \times 10^{-3}$  kM/m<sup>3</sup> gives incomplete surface coverage with no surfactant left in the supernatant;  $5 \times 10^{-3}$  kM/m<sup>3</sup> leads to a monolayer coverage with a micellar supernatant solution.



**Figure 9.** Effect of surfactant adsorption on the conformation of (1) the 5-doxylstearic acid molecule and (2) the 16-doxylstearic acid molecule adsorbed on alumina.

configuration. This hypothesis is in agreement with the results of Cadenhead et al. on the 12-doxylstearic acid configuration in a monolayer of dipalmitoyllecithin at the water/air interface.<sup>20</sup>

## Conclusions

Adsorption of various nitroxide probes on alumina in cyclohexane was studied by ESR. The effect of surfactant addition on the adsorption of the probes and their ESR response was investigated. Tempo derivatives and *n*-doxylstearic acids were found to adsorb on alumina when no surfactant was added to the system. The ESR spectra obtained in this case indicated that the rotational motion of the probes was hindered by the presence of the surface, suggesting that the nitroxide free radicals were close to the solid surface, in the case of all probes, including *n*-doxylstearic acids.

When Aerosol OT was added to the suspension, the behavior of the two types of probes differed. The decrease in spectral anisotropy observed for the Tempo derivatives shows the mobility of the probe to increase, possibly due to solubilization of the probe in the adsorbed surfactant

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layer. When the intensity of the ESR signal was used as a qualitative indication of the probe concentration and the surfactant concentration in the supernatant was measured, the result suggested that the probe stays preferentially in the adsorbed surfactant layer as long as the AOT concentration in the supernatant is not high enough to form micelle. When reverse micelles were present in the surrounding solution, the probe was preferentially solubilized into the micelles. Under adsorption conditions, the probe was found to be sensitive also to the presence of water on the alumina surface.

The behavior of the *n*-doxylstearic acids ( $n = 5, 7, 12,$  and  $16$ ) in the presence of surfactant was found to depend on the position of the nitroxide radical on the stearic acid alkyl chain. When the probe was close to the polar head of the carrier molecule ( $n = 5$  and  $7$ ), ESR was able to detect the presence of AOT reverse micelles. When the free radical was away from the carboxylic end of the carrier molecule ( $n = 12$  and  $16$ ), it was found to be less sensitive

to the surfactant concentration.

Changes in the ESR line shape of the *n*-doxylstearic acids were used in this investigation to monitor differences in the adsorption behavior of the *n*-doxylstearic acids when surfactant is added to the system. When the probe was adsorbed on alumina, the ESR response was found to depend upon the position of the nitroxide free radical. The nitroxide probe is pulled away from the alumina surface by the adsorbed surfactant only in the case of the 12- and 16-doxylstearic acids. It is suggested that the strength of nitroxide/alumina interaction depends upon the position of the spin probe along the alkyl chain of the carrier molecule.

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## The Role of Free Surfactant in Destabilizing Oil-in-Water Emulsions

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In a previous study, it was found that certain nonionic surfactants when present at a critical concentration above their cmc caused oil-in-water emulsions to rapidly cream. By analogy with polymers, this process was ascribed to flocculation induced by exclusion of surfactant micelles between approaching oil droplets. The present study was undertaken to determine the generality of this effect and its dependence on surfactant structure and to develop a deeper theoretical understanding of the process. A variety of paraffin oil-in-water emulsions having a controlled droplet size and a fairly narrow distribution were prepared. These emulsions were diluted and their stability and rheology determined as a function of surfactant concentration and structure. Three types of nonionic surfactants and one type of anionic surfactant were found to flocculate the emulsions when their concentration exceeds a critical value,  $C^*$ , that is roughly in the range 0.5–4 wt % in the aqueous phase. At surfactant concentrations above  $C^*$ , the emulsion rapidly creams and exhibits a dramatic change in rheology to become shear thinning. The value of  $C^*$  decreases with increasing droplet size and depends to some extent on surfactant structure. Emulsions with droplets larger than  $1 \mu\text{m}$  are particularly sensitive to small changes in surfactant concentration. Calculations obtained by using the osmotic model of Sperry (1982), adapted to micelles, account for most of the observed trends.

### Introduction

Emulsions are of considerable industrial importance in a broad range of applications and have been studied extensively. From the large body of literature it is clear that many factors control their stability (see for example ref 1–7).

Emulsions are subject to two common types of instabilities. *Flocculation*, which is generally a reversible aggregation of droplets, leads to separation in a gravity field, i.e., creaming. The droplets, however, retain their integrity. In contrast, *coalescence* is an irreversible fusion of droplets

resulting in separation of the emulsion into discrete bulk phases. Inversion is a special case of coalescence in which most of the droplets fuse at the same time.

In a previous study of emulsions made with nonionic surfactants, we<sup>8</sup> noted that both of these instabilities were sensitive to the concentration of emulsifier. In particular, when the emulsifier concentration exceeded a critical value, one of these processes dramatically accelerated. Flocculation predominated when the emulsifier was substantially water soluble, while coalescence predominated when the emulsifier had limited water solubility. Temperature has a significant effect since it controls the solubility of alcohol ethoxylates.<sup>9,10</sup>

The effect of emulsifier concentration on coalescence seems to be related to the formation of a surfactant phase at the phase inversion temperature (PIT).<sup>5,11</sup> The dependence on concentration may reflect either the variation

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