Aggregation Behavior of Aerosol OT in Nonaqueous Solvents and Its Desorption—An ESR Study

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INTRODUCTION

Micelle formation by sodium bis-2-ethylhexylsulfosuccinate (Aerosol OT) has been studied widely by several investigators (1–4). Micelles of amphiphilic surfactants (having both polar and nonpolar groups) have inverse structure of micelles in aqueous solutions. Aggregation behavior of this surfactant in nonpolar solvents is considered to be a prerequisite for the formation of reverse micelles (6). However, Yu et al. in a recent paper have given evidence of water as an antimicellization agent in their study of the aggregation of sodium bis(2-ethylhexyl) phosphate in n-heptane (7).

The main driving force for the formation of reverse micelles is the polar interactions among the surfactant molecules and can be classified by the tendency of the molecules' inorganic ions to donate or accept electrons or to interact by polarization (8). The stability of the reverse micelles is also dependent on the nature of the solvent. It was found that among nonpolar solvents the more apolar the solvent is, the more pronounced is the aggregation tendency of the surfactants. Solvents with hydrogen bonding abilities like dioxane and ethyl acetate have a disaggregation effect on these amphiphilic surfactants (9). The size and shape of these micelles have also been well documented (10, 11). A number of detailed analyses have been carried out regarding the size and shape of these aggregates in different solvents and a good correlation has been obtained between the micelle size and the solubility parameter of the solvent which suggests that the latter may be the appropriate parameter for characterizing the solvent rather than its dielectric constant (12, 13).

Several techniques have been used to study the aggregation behavior of surfactants in nonaqueous media. Vapor pressure osmometry (14), light scattering (15), dye solubilization (16), and, more recently, positron annihilation technique (17) have been used to determine CMC of surfactants in nonaqueous media. Spectroscopic techniques like fluorescence spectroscopy have been previously used by several investigators to determine the CMC, aggregate size, and aggregation number of ionic and nonionic surfactants in aqueous and nonaqueous media (18–20). Electron spin resonance has been used to characterize the micropolarity and microviscosity of adsorbed surfactant layers (21) and micellar solutions of sulfate surfactants (22, 23). Nitroxide-labeled spin probes have also been used in the past to study the exchange kinetics and solubilization sites in water-in-oil microemulsions (24). By using a suitable probe that partitions into the surfactant aggregates it is possible to study the dynamics of the micellization and the behavior of micellar aggregates in solution. The rotational correlation time measured from the ESR spectrum is reflective of the probe mobility and can be used to study the formation of aggregates in solution. The change in probe mobility can often also yield useful information on the structure of such aggregates (25). The value of the hyperfine splitting constant is dependent on the polarity of the probe environment (26) and can be used to extract valuable information on the probe environment. The use of spin probing by ESR has the obvious advantage that in situ information on the different portions of the micellar interior can be obtained by choosing appropriate probes.

In this work, the behavior of 5-doxyl stearic acid, a commonly used ESR probe, was investigated in different organic solvents by measuring the rotational correlation time, \( \tau \), of a nitroxide labeled fatty acid probe (5-doxyl stearic acid) as a function of the surfactant concentration. These studies reveal that while Aerosol OT can form aggregates in low polarity (reverse micelles) and high polarity (regular micelles) solvents, they do not aggregate significantly in solvents of intermediate polarity. Also, water was not found to have any significant effect on the aggregation behavior of this surfactant in nonpolar solvents. A good correlation is obtained between the surfactant aggregation tendency and its desorption from alumina into different solvents.

ESR technique is used in this study to monitor the aggregation behavior of an anionic surfactant Aerosol OT in nonaqueous solvents by measuring the rotational correlation time, \( \tau \), of a nitroxide labeled fatty acid probe (5-doxyl stearic acid) as a function of the surfactant concentration. These studies reveal that while Aerosol OT can form aggregates in low polarity (reverse micelles) and high polarity (regular micelles) solvents, they do not aggregate significantly in solvents of intermediate polarity. Also, water was not found to have any significant effect on the aggregation behavior of this surfactant in nonpolar solvents. A good correlation is obtained between the surfactant aggregation tendency and its desorption from alumina into different solvents.
liquids. The ESR parameters analyzed in this work are $A_N$, the hyperfine splitting constant, and $\tau_B$, the rotational correlation time. The aggregation behavior of Aerosol OT in different nonaqueous solvents and the effect of water on the aggregation of Aerosol OT in cyclohexane is elucidated. Also, a correlation of the desorption of Aerosol OT from alumina surface into different solvents with the solubility parameters of the solvents is presented.

EXPERIMENTAL

Materials. The ESR probe, 5-doxyl stearic acid was purchased from Aldrich Chemicals and used as received. The surfactant, Aerosol OT was purchased from Fisher Scientific and purified following a procedure detailed in literature (27). All the organic solvents were bought from Fisher Scientific and dried by storing in molecular sieves when necessary. The alumina used in the desorption studies was bought from Union Carbide Corporation as Linde A. X-ray diffraction and chemical analysis of the powder have shown it to be a well-crystallized corundum of high purity ($>99\% \text{ Al}_2\text{O}_3$). Morphologically the powder consists of micron-sized aggregates composed of smaller particles of 300 nm and the measured nitrogen adsorption BET surface area is 14 m$^2$/g.

Methods. The ESR experiments were performed on a Micronow MN8300 X-band spectrometer. All the solution samples contained $2 \times 10^{-4} \text{ M/liter}$ of the probe and the requisite amount of surfactant and were deoxygenated by nitrogen bubbling prior to acquiring the spectrum. The water content of the solutions was measured by the Karl Fisher water titrimer. The hyperfine splitting constant $A_N$ and rotational correlation time $\tau_B$, $\tau_C$ were calculated from the ESR spectrum using procedures detailed in literature (26).

For the desorption experiments, the Aerosol OT was first adsorbed onto alumina from cyclohexane solutions of the surfactant. The solids were then separated by centrifugation and dried thoroughly. The alumina with the preadsorbed surfactant was then conditioned with the desired solvent. The Aerosol OT was analyzed by a two-phase titration technique where the surfactant is titrated against hexadecyltrimethylammonium bromide with dimidium bromide disulfine blue as the end-point indicator (28). All experiments were performed at room temperature ($22 \pm 2^\circ\text{C}$).

RESULTS AND DISCUSSION

Analysis of coupling constants. Figure 1 shows the hyperfine splitting constant $A_N$ for 5-doxyl stearic acid in different solvents as a function of the solvent dielectric constant. The observed variation of $A_N$ with solvent polarity is in accordance with previously reported data, with $A_N$ varying from about 13.7 gauss in cyclohexane (nonpolar) to about 15.8 gauss in water. Several relationships have been proposed to relate $A_N$ to the dielectric constant of the medium (29, 30). Figure 2 shows the variation of $A_N$ as a function of Aerosol OT concentration in three different solvents—cyclohexane, methanol, and water. While in the case of cyclohexane a gradual increase in $A_N$ is observed with AOT concentration, in the case of water there is a sharp decrease in the splitting constant at a certain AOT concentration ($8 \times 10^{-4} \text{ M/liter}$) and with methanol no significant change in $A_N$ is observed in the range of surfactant concentration studied. Both the change and the rate of change of $A_N$ give valuable information about the mechanisms bringing about the change. For cyclohexane the increase in $A_N$ corresponds to a transfer of the probe from the nonpolar solvent to the polar environment.
of the reverse micelles. The gradual change is proposed to be due to premicellar probe–surfactant interactions from which one can infer the existence of premicellar surfactant aggregates in solution. This is in good agreement with the widely accepted model of reverse micellization (31). The sharp decrease of $A_2$ in water corresponds to the CMC ($\sim 8 \times 10^{-4} \text{M/liter}$) and is due to the transfer of the probe from aqueous environment to the hydrocarbon environment of the micelle. However, no change in $A_2$ is observed in methanol, suggesting the absence of any aggregation or any probe–surfactant interaction.

Analysis of correlation times. Figure 3 shows spectra of 5-doxyl stearic acid in premicellar and micellar solutions of Aerosol OT in cyclohexane and water. In both cases line broadening is observed as a result of micellization. The variation of $\tau_B$ in cyclohexane, water, methanol, chloroform, and water–methanol mixture as a function of surfactant concentration is shown in Fig. 4. A sharp increase in the rotational correlation time was observed in cyclohexane and water at a concentration corresponding to the formation of reverse micelles and micelles, respectively. In the case of methanol no significant change in $\tau$ is observed, corroborating the absence of surfactant aggregation or probe–surfactant interaction. $\tau_B$ and $\tau_C$ values of 5-doxyl stearic acid in premicellar and micellar regions for cyclohexane and water are given in Table 1. It can be seen that there is almost an order of magnitude increase in correlation times due to the formation of surfactant aggregates. The probe is incorporated into the micelle (reverse micelle) by polar (hydrophobic chain) interactions and this restricts its motion, causing
TABLE I
Rotational Correlation Times of 5-Doxyl Stearic Acid
in Micellar and Premicellar Solutions of Aerosol OT

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Premicellar AOT (ns)</th>
<th>Micellar AOT (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_B$</td>
<td>$\tau_C$</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.097</td>
<td>0.065</td>
</tr>
<tr>
<td>Water</td>
<td>0.119</td>
<td>0.2</td>
</tr>
</tbody>
</table>

broadening of the ESR spectral lines. The premicellar probesurfactant interactions in cyclohexane may not be significant enough to produce a measurable change in $\tau_B$. Also shown in Fig. 4 are the rotation correlation times in chloroform and water–methanol mixture. In both cases there is no significant aggregation at low concentrations, although at higher concentrations the increase in correlation times suggests some micelle–aggregate formation.

$\tau_B$ for 5-doxyl stearic acid at different surfactant concentrations in cyclohexane is shown in Fig. 5a as a function of the water content of the solutions. At low surfactant concentrations (premicellar solutions) water has no effect on the correlation times, indicating that water does not induce any micellization in these systems. However, in micellar solutions there is an increase in $\tau_B$ with water concentration. At low water concentration the probe is tightly bound to the micelle and rotates isotropically with the micelle. The solubilization of water in the micelles makes the micelle bulkier and less mobile in general. The probe location in the micelle also changes with the concentration of water and in some cases spectral splitting may be observed due to probe exchange between different microenvironments (32). The probe motion also becomes more anisotropic with increase in water content as indicated by the increasing value of $\tau_C - \tau_B$ (Fig. 5b). This may be due to the fact that in the swollen micelle the probe may now have a motion independent of the micellar rotation, like lateral diffusion within the aggregate.

The desorption of preadsorbed Aerosol OT from alumina into different solvents is shown in Fig. 6a. It can be seen that as the solvent polarity (as indicated by the dielectric constant) is increased the desorption increases, goes through a maximum, and then decreases. Note that when the data of Fig. 6a are plotted against the solubility parameter of the solvent instead of the dielectric constant, the correlation is better (Fig. 6b). Also, the desorption data obtained using solvents of unusually high dielectric constants like formamide ($\epsilon = 109$) and $\lambda$-methyl formamide ($\epsilon = 182$) fit well into the curve shown in Fig. 6b when plotted against their solubility parameter. The forces causing adsorption from organic solvents are the same as those which induce micellization—namely dipole interactions between the polar moieties in the system. Little and Singleton, in their study on the aggregation of dinaphthylsulfonate in organic solvents, postulated that as the solubility parameters of the solvent and surfactant approach each other the surfactant aggregate becomes smaller and in the ideal limit tends to exist as monomers interacting with the solvent molecules when the solubility parameters match exactly (12). As the solubility parameter difference increases the surfactant forms aggregates the size and shape of which are such that the effective solubility parameter of the aggregate as seen by the solvent is similar to its own.

FIG. 5. (a) Diagram showing the effect of water on rotational correlation time of 5-doxyl stearic acid at different surfactant concentrations; (b) Effect of water on the rotational correlation time of 5-doxyl stearic acid in a micellar solution of AOT in cyclohexane.
value. This takes place by the formation of reverse micelles or regular micelles, depending on the nature of the solvent. In the present case in the low solubility parameter (also low dielectric constant) region the polar portion of the surfactant has a tendency to remove itself from the nonpolar solvent. This can be achieved by the formation of reverse micelles or by adsorption onto a polar surface through dipole interactions. As the solubility parameter is increased the dipole interactions between the solvent and surfactant increase, thereby decreasing surfactant–surfactant interaction as well. This is evident by the lack of surfactant aggregation in these solvents (ethanol and methanol) as seen from the ESR results. As the solubility parameter is further increased the solvent–surfactant interaction also decreases similarly, and the solid–surfactant interaction increases, leading to an increase in adsorption again. Based on this argument a solubility parameter of about 12–14 can be considered to be appropriate for Aerosol OT. Thus it can be concluded that in the lower solubility parameter region AOT adsorption on alumina is through dipole interactions with the surface, while in the higher solubility parameter region the surfactant interacts with the solid through its hydrocarbon chains.

CONCLUSIONS

1. Measurement of hyperfine splitting constant, $A_N$ and rotational correlation time, $\tau_B$ in ESR spectrum of 5 doxyl stearic acid in Aerosol OT solutions in different solvents shows aggregation of surfactant in solvents of low and high polarity. There is no significant aggregation in solvents of intermediate polarity.

2. Electron spin resonance studies reveal that Aerosol OT forms aggregates in solvents with which it has a significant solubility parameter difference.

3. In solvents with solubility parameter similar to that of the surfactant it exists possibly as monomers directly interacting with the solvent molecules.

4. Solubility parameter is more indicative of the surfactant-solvent interaction tendency rather than the solvent dielectric constant.

5. Adsorption in non-polar solvents is controlled by the same forces responsible for aggregation, namely the dipole interactions between the polar moieties in the system.

6. The solubility parameter difference (polarity difference) between the surfactant and the solvent determines the extent of adsorption. The more the difference the more is the adsorption.

7. As in aqueous systems, in polar organic solvents hydrocarbon chain interactions play a significant role in determining the adsorption.

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