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Effect of Temperature on the Mobility of Nitroxide Probes in Cyclohexane and at the Alumina–Cyclohexane Interface

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Nitroxide spin probes have been widely used to study the behavior of surfactants in solution as well at solid–liquid interfaces. In this study the effect of temperature on the mobility of nitroxide spin probes in cyclohexane and at the alumina/cyclohexane interface is investigated in the presence of anionic aerosol-OT (AOT). The probe mobility in AOT micelles in solution is markedly dependent on the amount of solubilized water. The variation with temperature of the mobilities of adsorbed doxyl stearic acid with the nitroxide probe at the 5th, 10th, and 16th positions from the —COOH group has shed some light on the mechanisms of interaction of the probe with the solid surface as well as the molecular structure of the adsorbed layer. The results indicate that the adsorption of the probe occurs mainly through interactions of the —COOH group with the surface while the —NO group interacts only weakly with the surface. The adsorption of AOT causes changes in probe mobility with the changes being most significant when the nitroxide group on the stearic acid chain is farthest from the anchoring group. It is suggested that the adsorption of the surfactant causes an orientational rearrangement of the probe molecules. The relatively low-temperature effect on the probe mobility observed in the presence of surfactant is attributed to the compactness of the adsorbed layer which is found to be stable even at elevated temperatures.

Key Words: ESR; doxylstearic acid; nitroxide; non-aqueous; solid–liquid interface.

INTRODUCTION

The study of colloidal dispersions in nonaqueous media is of great importance to a number of industrial applications such as ceramic processing (1), paints, inks, pigments (2), electrophoretic image processing (3), and lubrication (4). Efficiency of these processes is dependent on the ability to control the dispersion stability by adjusting parameters such as adsorption density and molecular conformation.

Dispersions in nonaqueous liquids are usually stabilized by adsorption of surfactants or polymers on the particles to provide repulsive forces to counter the natural tendency of the particles to aggregate. The dispersive action of the surfactants can be due to electrostatic repulsion and/or a reduction of the attractive van der Waals forces via modification of the particle surface due to the presence of the adsorbed layer (5, 6). The electrostatic repulsion depends on the nature of the surfactant and its tendency to dissociate and develop residual charges on the particle surface. In contrast, the alteration of the van der Waals energy depends on the extent of surfactant adsorption and the microstructure of the adsorbed layer, i.e., the conformation and packing of the molecules at the solid–liquid interface. Indirect information on molecular orientation at the interface can be obtained from a detailed analysis of the adsorption isotherm as well as from measurements of thermodynamic parameters pertinent to the adsorption process. For example, Kipling and Wright in their work on the adsorption of fatty acids on different substrates deduced molecular orientation relative to the substrate surface from measurements of heats of immersion (7). Mills and Hockey discussed the possible variations in molecular conformations with adsorption from the heats of adsorption data as a function of surface coverage of *n*-fatty acids on silica (8). Such studies while providing some insight into molecular conformation are still inconclusive owing to the indirect nature of their observations. A number of spectroscopic techniques are now available that can be applied to obtain direct *in situ* information on the structure of the adsorbed layers. We have recently used fluorescence, electron spin resonance (ESR), Raman, infrared, and nuclear magnetic resonance (NMR) to study adsorption phenomena and to correlate changes in the adsorbed layer microstructure with variations in macroscopic properties such as wettability and hydrophobicity of the dispersions (9–11).

Spin probing using ESR spectroscopy is a sensitive technique which involves the incorporation of a suitable paramagnetic moiety into the system under investigation and measuring its response to changes in its environment. This technique has been successfully applied to study biological membranes (12) and membrane mimetic systems such as micelles or reverse micelles (13–15). This has also been employed to study the exchange kinetics and solubilization sites in water-in-oil microemulsions (16). Information on

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the micropolarity and microviscosity of the probe can be obtained from the ESR spectra and used to deduce structural information on its environment. This technique has been successfully employed to the study of adsorbed polymers and surfactants (17, 18). We have also shown, using ESR, that adsorption of water causes conformational changes in the adsorbed aerosol-OT layer at the alumina–cyclohexane interface (19). This observation was consistent with changes observed in the stability of these dispersions. Variations in probe mobility with temperature have been used in the past to understand structural changes in membranes and vesicles as well as to study diffusion of molecules in micelles and in adsorbed layers (20, 21).

In this study we use a series of nitroxide probes to understand the nature of interaction governing the adsorption and microstructural evolution of anionic aerosol-OT (AOT) on alumina in cyclohexane. The effect of temperature on the mobility of probes in solution and at the solid–liquid interface was monitored in the presence and the absence of the surfactant.

EXPERIMENTAL

Materials

Linde alumina of approximately 0.3 μm with a BET surface area of 14 m^2/g, purchased from Union Carbide, was used as the substrate for the adsorption studies. The surfactant used, sodium bis(2-ethylhexyl)sulfosuccinate (aerosol-OT), was purchased from Fisher Scientific and is purified by solubilization in methanol and recrystallization by solvent evaporation. Cyclohexane of spectroscopic grade was also purchased from Fisher Scientific and was dried by storing in molecular sieves. The amount of water present after drying, measured using Karl Fisher titration, was less than 5 mM. The spin probes used were a series of doxyl stearic acids with the paramagnetic nitroxide free radical attached to different positions along the stearic acid chain (n = 5, 10, 16). Another probe, 5-doxyl dodecane which has no terminal —COOH group was also used to investigate the effect of this functional group on probe adsorption (Fig. 1). All the probes were purchased from Aldrich Chemicals and used as received.

Methods

All ESR spectra were acquired using a Micronow 8300 X-band spectrophotometer, equipped with a temperature-controlled cavity, at a modulation frequency of 100 kHz. For isotropic spectra in the fast motion regime the rotational correlation times are calculated directly from the spectrum using the equation

$$\tau_B = 6.25 \cdot 10^{-10}\, \Delta H_0[(I_0/I_{-1})^{1/2} - (I_0/I_{+1})^{1/2}]\ \text{s},$$

where ΔH_0 = peak to peak distance of the central line in gauss, I_0/I_{-1} = ratio of the central to high field line peak heights, and I_0/I_{+1} = ratio of the central to low field line peak heights. For anisotropic spectra in the slow regime the application of the above equation leads to erroneous values of the correlation times. In such cases τ values were estimated using the following method of calculation (22).

$$\tau = a(\quad - S)^b,$$

where a and b are constants given in literature (23) and $S = A_{z'}/A_z$, where $A_{z'}$, is one-half the separation of the outer hyperfine extrema and A_z is the rigid limit value for the same quantity obtained from a frozen spectrum of the sample under consideration.

Sample Preparation

The alumina is dried by heating at 200°C for 6 h and cooling under vacuum to room temperature. Half a gram of the dried alumina is conditioned with 5 ml of a 10^{-4} M/liter solution of the probe in cyclohexane for 6 h. The slurry is then transferred to a narrow quartz capillary tube and introduced into the ESR cavity. For samples with adsorbed surfactant, the probe is initially adsorbed onto the alumina and the solvent removed by drying under vacuum. The solids are then contacted with AOT solutions of different concentrations for 6 h and the spectra recorded.

RESULTS AND DISCUSSION

Probes in Solution

A careful analysis of line broadening features of the ESR spectra can provide information on the rotational mobility of the nitroxide probe from which the characteristics of its environment can be deduced. A nitroxide radical tumbling isotropically in a non-viscous fluid will yield a characteristic sharp three-line spectrum. Immobilization of the radical causes line broadening and the resultant spectrum would have lost most of its details. If the molecule is rotating slowly then an intermediate spectrum is obtained.

Figure 2 shows the temperature variation of the rotational correlation time (τ_B) of 7-doxyl stearic acid in cyclohexane in the presence and absence of aerosol-OT micelles. The rotational correlation times are shown on a log scale against the reciprocals of the absolute temperature. The first point of interest is that at all temperatures the probe mobility is lower in the micellar solution. This has been reported previously and used to detect the onset of micellization in a variety of surfactant–solvent systems (15). Such an increase in τ_B is due to the incorporation of the probe molecules in the AOT reverse micelles, thereby restricting their rotational motion. The probe moves along with the micelle and the mobility measured now is a reflection of the micellar mobil-

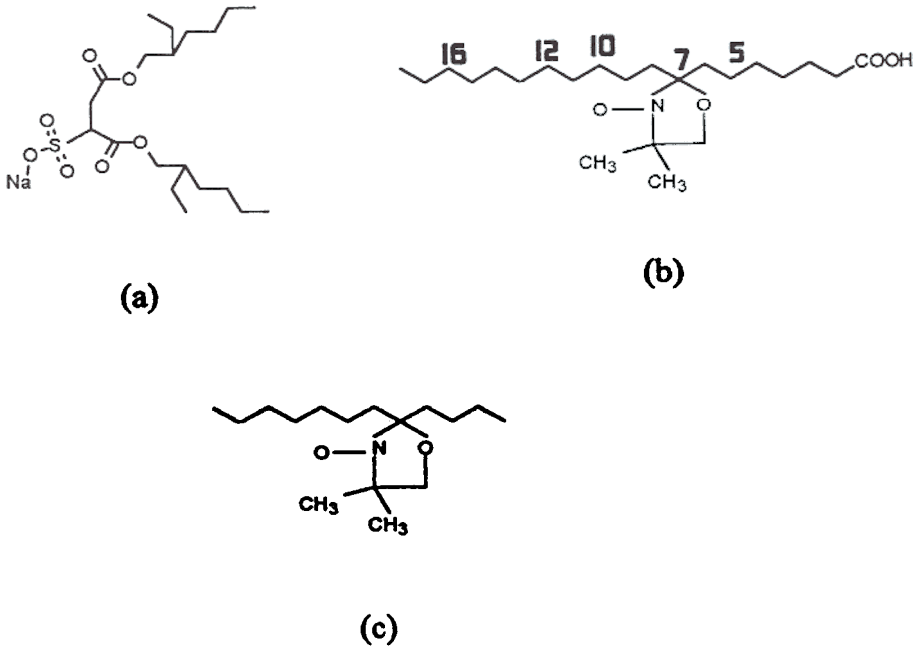

FIG. 1. Structure of (a) aerosol-OT, (b) *n*-doxyl stearic acid, (c) 5-doxyl dodecane.

ity in solution and the rotation of the probe within the micelle. The overall mobility is observed to increase (corresponds to a decrease in τ_B) with temperature in both the absence and presence of the AOT micelles. Such an increase in probe mobility may be attributed in both cases to changes in the medium viscosity. We have estimated also the activation energies (E_a) for the probe rotation from plots of log τ_B against $1/T$ for the various cases and the values obtained are -16 and -19 kJ/mol in the absence and presence of AOT micelles respectively. The similarity of these values suggests that nature of the probe rotation is similar in the two cases, and the lower probe mobility in the micelle is indeed due to the slower reorientational motion of the bulkier micelle in which it is incorporated.

The micelle size as well as the structure of the water in the micellar core is known to vary with the amount of solubilized water. Figure 3 illustrates the variation of τ_B with temperature in micellar solutions of AOT at different amounts of solubilized water ($w_0 = [H_2O]/[AOT]$). At room tempera-

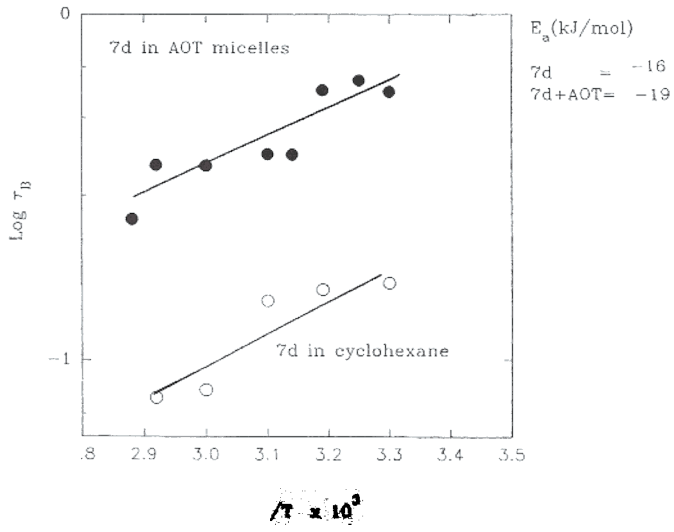

FIG. 2. Effect of temperature on the mobility of 7-doxyl stearic acid in cyclohexane and in AOT micellar solution in cyclohexane. Also shown are the activation energies (E_a) of probe motion under different conditions.

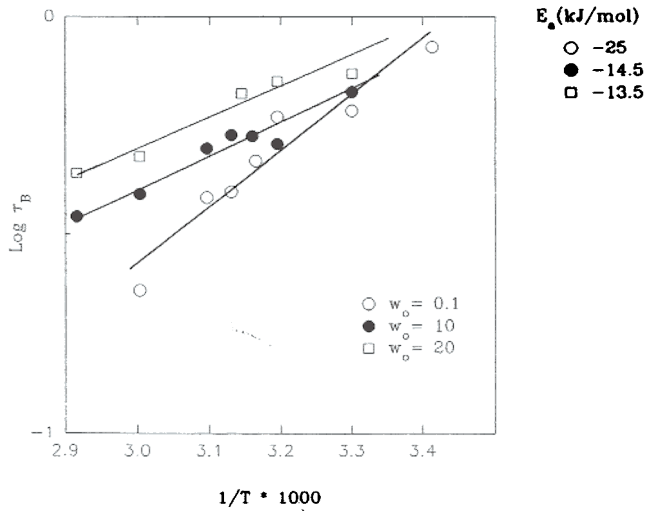

FIG. 3. Variation of probe mobility with temperature in AOT micelles at different levels of water content.

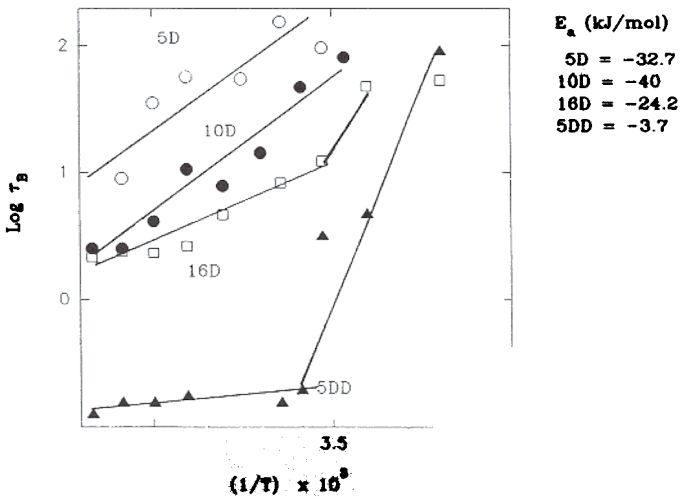

FIG. 4. Effect of temperature on the mobility of various probes adsorbed at the alumina–cyclohexane interface.

ture (T = 299 K) the mobility values decrease with increases in the water content. The micelles swell as they solubilize water, become bulkier, and hence their rotational motion is slowed down. For all the samples the mobility is seen to increase with temperature. The increase in mobility with temperature can be attributed to a change in the medium viscosity as well as increased exchange kinetics of the probe between the micelle and the bulk solution. The rate of increase in mobility is higher for the sample with the least amount of water. The E_a values for these cases are indicated in Fig. 3 and show that the activation energy for the probe motion decreases with increases in water content of the micelles. In the dry micelle the probe is presumably rigidly bound to the surfactant molecules via the trace amounts of water present. Earlier studies have also indicated that at low water contents the water in the reverse micelle is structured around the head groups of the surfactant molecule (24). In this case the probe rotation within the micelle is not significant and the probe mobility more or less accurately reflects the rotation of the micelle. However with increases in water content the micellar core becomes loose and the probe binding to the micelle becomes less rigid, and they start to have rotational freedom within the micelle.

Probes at the Alumina/Cyclohexane Interface

The spectrum of nitroxide probes adsorbed at the solid–liquid interface displays line broadening features characteristic of hindered motion. 5-, 10-, 16-Doxyl stearic acids and 5-doxyl dodecane were adsorbed onto the alumina surface from cyclohexane and the corresponding ESR spectra analyzed to estimate their mobility at the solid–liquid interface. Figure 4 depicts the variation of the interfacial mobilities of the different probes with temperature. It is observed that at room temperature, the mobility of the doxyl stearic acid probes increases in the order 5 < 10 < 16. This can be explained by a model for probe adsorption wherein the —COOH groups interact strongly with the alumina surface while the —NO group interacts only weakly with the surface. Thus the farther away the —NO is from the —COOH group the lesser its interaction with the surface, and hence 16-doxyl stearic acid exhibits higher mobility. All the doxyl stearic acid probes show an increase in probe mobility with temperature. This increase in mobility is due to a weakening of the interaction of the —NO group with surface. The E_a values shown in Fig. 4 indicate a low value for 16-doxyl corroborating the fact that this is more loosely bound to the surface. It should be noted that in all these cases there was no probe desorption detected even at the highest temperatures studied. It is to be noted that the 5-doxyl dodecane shows a different behavior. It shows very high mobility at the solid–liquid interface, and in this case the probe could be detected in the supernatant as well. This suggests that this probe adsorbs weakly onto the alumina surface, reiterating the fact that the —NO groups interact only weakly with the surface and cannot promote adsorption. The lower value of E_a estimated in this case further supports this fact. The 5-doxyl dodecane becomes immobile only at lower temperatures (below freezing point of cyclohexane) as can be seen from Fig. 4.

The adsorption of aerosol-OT causes interesting changes in the probe mobility. Figure 5 shows variation in probe mobility as a function of AOT concentration at the alumina/cyclohexane interface. While there is no significant change in the mobilities observed for 5- and 10-doxyl there is a dramatic increase in the mobility of 16-doxyl stearic acid. This can be schematically explained as shown in Fig. 6 where possible probe conformations in the presence and absence of AOT is shown for 5- and 16-doxyl stearic acid

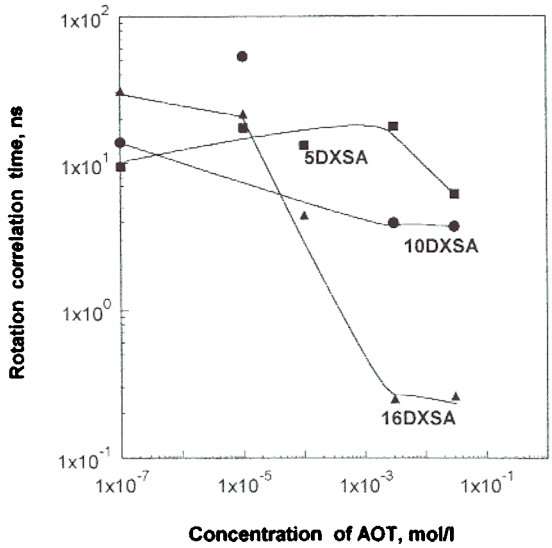

FIG. 5. Variation in probe mobility at the alumina–cyclohexane interface on surfactant addition.

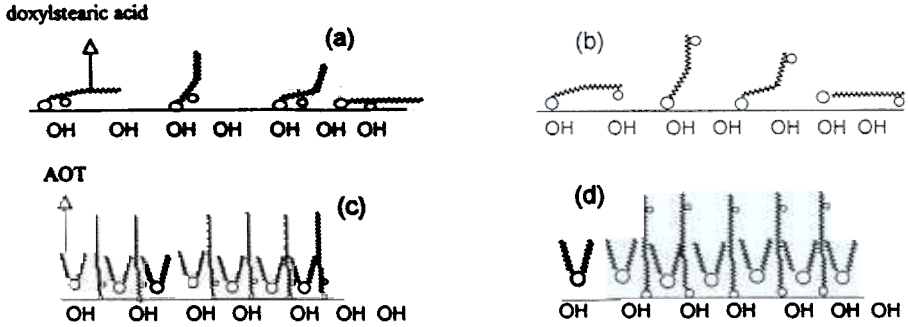

FIG. 6. Schematic diagram illustrating possible changes in probe conformation on surfactant addition (a) 5-doxyl on alumina surface, (b) 5-doxyl on alumina at monolayer coverage of AOT, (c) 16-doxyl on alumina, (d) 16-doxyl on alumina at monolayer coverage of AOT.

cases (18). The probe molecules are proposed to be pushed into a perpendicular orientation by the adsorbing AOT molecules. This is reflected as an increase in probe mobility in all three cases. However in the case of 16-doxyl the —NO group escapes the adsorbed layer of AOT which is approximately 10 $—CH_2$ chains long which explains the significant increase in mobility shown by the 16-doxyl stearic acid. In the other two cases the —NO group is still buried in the adsorbed AOT layer and continues to be motionally restricted.

The effect of temperature on the mobility of 5-doxyl in the presence and absence of surfactant is shown in Fig. 7 along with the activation energies involved. The activation energy estimated from the temperature dependence of the mobility is less in the presence of the surfactant, indicating that the probe is less rigidly bound to the surface in the presence of the surfactant. A similar observation is made for the case of 16-doxyl stearic acid where also the probe binding to the surface is less in the presence of the adsorbed surfactant (Fig. 8). These results also indicate that the AOT adsorbed layer is compact and stable even at elevated temperatures.

CONCLUSIONS

Temperature variation of mobility of nitroxide probes in cyclohexane and at the alumina–cyclohexane interface was studied using ESR. The temperature dependence in solution showed the probe binding to a micelle to vary as a function of the water content. The probe was found to be rigidly bound to the micelle at low concentrations of water and to become more loosely bound at higher water concentrations.

Adsorption of different nitroxide probes at the alumina–cyclohexane interface was also investigated. The probe adsorption was clearly shown to occur by interactions of the surface species with the —COOH group of the probe molecule. The —NO group while incapable of promoting adsorption by itself interacts weakly with the surface. The degree of interaction depends on the location of the —NO group relative to the anchoring —COOH group, with the interac-

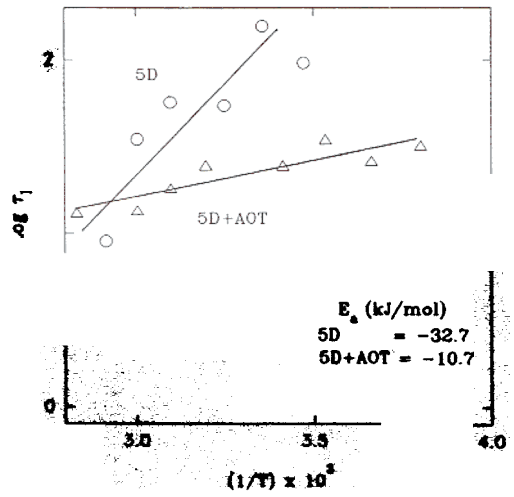

FIG. 7. Effect of temperature on the mobility of 5-doxyl stearic acid at the alumina–cyclohexane interface in the absence and presence of AOT.

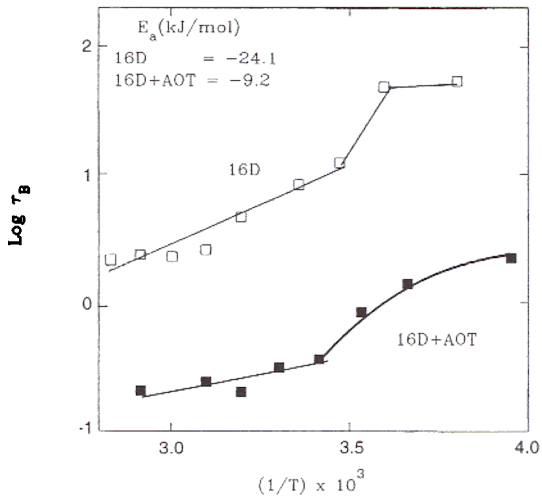

FIG. 8. Effect of temperature on the mobility of 16-doxyl stearic acid at the alumina–cyclohexane interface in the absence and presence of AOT.

tion weakening with increasing distance between these two groups. The interaction is also weakened by increases in temperature. An examination of the temperature dependence of probe mobility suggests that the 16-doxyl is indeed bound weakly to the surface compared to the 5-doxyl. Addition of aerosol-OT causes measurable changes in probe mobility, depending on the position of the —NO moiety. The adsorbing surfactant weakens the probe interaction with the surface and this fact is further illustrated by the temperature dependence of probe mobility in the presence of the surfactant. The surface pressure developed by the adsorbing AOT molecules is shown to cause the probe to orient perpendicular to the surface.

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