

In Situ Kinetics Measurements of Surfactant Adsorption on Colloidal Alumina using ESR Spectroscopy

An electron spin resonance spectroscopy technique is employed to investigate *in situ* the kinetics of surfactant adsorption on colloidal particles. Using this technique, it was found that 40% of the adsorption of Aerosol OT at the alumina/cyclohexane interface takes place within 5 s after addition of the surfactant to the suspension. © 1990 Academic Press, Inc.

INTRODUCTION

The equilibrium adsorption of surfactant and macromolecules at solid/liquid interfaces has been extensively investigated experimentally as well as theoretically (1, 2). These studies have led to a better understanding of the mechanism controlling adsorption, have provided practical means to determine the amount of material adsorbed under various conditions, and have identified the physicochemical parameters controlling adsorption. In contrast to the well-documented aspects of equilibrium adsorption, the field of adsorption kinetics has been neglected despite its practical significance. This situation is largely due to a lack of reliable experimental techniques capable of monitoring the fast adsorption process in solid-liquid systems. The kinetics of adsorption at the solid/liquid interface is usually studied by flowing a solution through a packed bed of adsorbent and monitoring changes in the composition of the liquid phase (3). However, these methods are useful for the study of only relatively slow adsorption processes since the residence time of the solution in the packed column does not allow collection of information during the first minutes of the adsorption process (between 1 and 300 s). Similarly, conventional depletion technique is also limited to the same time range because the concentration in the liquid phase can only be determined once the liquid phase is separated from the solid particles, i.e., after a centrifugation or filtration, which also takes tens to hundreds of seconds.

Spectroscopic techniques inherently possess two main advantages over these techniques for studying short-term kinetics of adsorption: (1) *in situ* changes are monitored directly at the interface where surfactant adsorption takes place; (2) a wide flexibility is available in the experimental conditions employed, which allows measurements under conditions close to the realities of a slurry. In this note, we report results obtained using electron spin resonance spectroscopy (ESR) to monitor the adsorption of a surfactant, Aerosol OT, on a suspension of colloidal alumina in cyclohexane using the spin probe 12-doxyl stearic acid to probe the surfactant adsorption.

EXPERIMENTAL

Materials

The alumina used for the present study was purchased from Union Carbide Corp. as Linde Alumina Polishing Powder Type A. X-ray diffraction and chemical analysis of the powder shows the mineral to be a well-crystallized corundum of high purity (>99% Al_2O_3). Morphologically, the powder is constituted of micrometer-sized aggregates composed of smaller particles (between 200 and 500 nm). Nitrogen adsorption at 77 K using a Quantasorb apparatus leads to a specific surface area of $13.4 \text{ m}^2/\text{g}$ for this powder. The absence of hysteresis on the adsorption/desorption isotherm suggests this material to be essentially nonporous.

The surfactant, Aerosol OT (sodium bis-(2-ethylhexyl) sulfosuccinate), was obtained from Fisher Scientific. It was purified following a procedure described in the literature (4). Cyclohexane, also obtained from Fisher Scientific, was of certified spectroscopic grade. The nitroxide spin probe used for this work, 12-doxyl stearic acid, was purchased from Aldrich Chemical Co. and was used as received.

Methods

The ESR experiments were performed on an IBM Bruker Model 100D X-band spectrometer using the experimental setup shown in Fig. 1 which allows the colloidal suspension to flow continuously through the cavity of the ESR spectrometer. 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. All experiments were performed at room temperature.

Sample Preparation and Experimental Procedure

The samples were prepared using the following procedure: (1) desiccation of the alumina powder at 200°C for

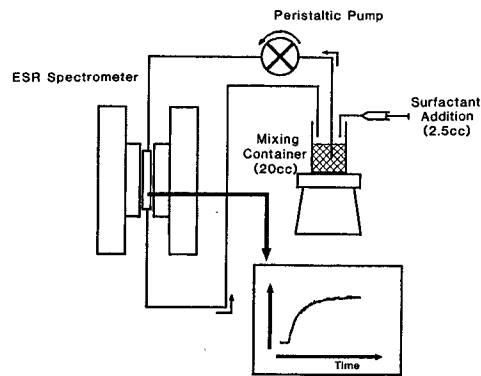


FIG. 1. Experimental setup used for continuous ESR measurements.

6 h followed by a cooling period (2 h) at 25°C in a vacuum desiccator, (2) preparation of a cyclohexane solution containing the probe, 12-doxyl stearic acid (250×10^{-6} mol/liter), (3) addition of 20 ml of the solution to 3 g of alumina in a vial, and (4) conditioning of the sample (tumbling) for 24 h at room temperature. At the end of this procedure, the alumina surface became ESR sensitive. The probe was then ready to record changes occurring in its surroundings when surfactant molecules adsorbed at the alumina/cyclohexane interface.

For the kinetics experiments, 2.5 ml of surfactant solution was injected into 20 ml of suspension which flowed continuously through the cavity of the spectrometer as shown in Fig. 1. As a control experiment, a dye solution was added to the suspension in place of the surfactant solution and confirmed that the mixing between surfactant solution and suspension is fast (under 1 s) and that the suspension in contact with the surfactant solution reaches the ESR cavity within 2 s after the surfactant addition. Equilibrium adsorption data were obtained using the same experimental procedure but, in this case, the dry powder was directly mixed with surfactant solutions of known concentration. No difference in the ESR signal of the final equilibrium adsorption system was detected, whether the probe was preadsorbed on the alumina surface prior to surfactant addition or added with the surfactant solution to the suspension.

RESULT AND DISCUSSION

In Fig. 2, the adsorption isotherm of Aerosol OT on alumina is plotted together with the corresponding ESR spectra obtained using 12-doxyl stearic acid as a probe. Due to the high affinity of Aerosol OT for the alumina surface in cyclohexane solution, the maximum adsorption was reached before any residual concentration was detected in the supernatant. However, under conditions where no change in the equilibrium surfactant concentration can be detected in the supernatant, the spectra obtained change

gradually from conditions where the probe is adsorbed alone on the surface to maximum surfactant adsorption density where the probe is coadsorbed on the alumina surface with a monolayer of Aerosol OT (5). 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 probe is tumbling in a medium of low viscosity; 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. The interpretation of the ESR response of 12-doxyl stearic acid coadsorbed with Aerosol OT at the alumina/cyclohexane interface led us to suggest recently that the conformation of the probe at the interface was very sensitive to the presence of coadsorbed surfactant (6). Without the surfactant, the anisotropic ESR spectrum obtained indicates that the rotational motion of the nitroxide radical is very slow, suggesting that the probe is adsorbing in a flat conformation. This structure is to be expected since both the carboxylic group and the polar nitroxide radical have a high affinity for the polar alumina surface. In the presence of a coadsorbed surfactant, interactions between the adsorbed probe and the surfactant molecules yield to a spectrum consistent with a model where the probe is adsorbed in a stretched dangling configuration, possibly due to the pressure created by the adsorbed surfactant molecules surrounding it.

As seen in Fig. 3, among other changes on the spectrum, a third peak appears and progressively increases in intensity as the surfactant adsorption density increases. This peak corresponds to the highly mobile population of probe molecules stretched dangling in solution by the coadsorption of surfactant around them. It was arbitrarily selected as an indicator of the surfactant adsorption since its changes

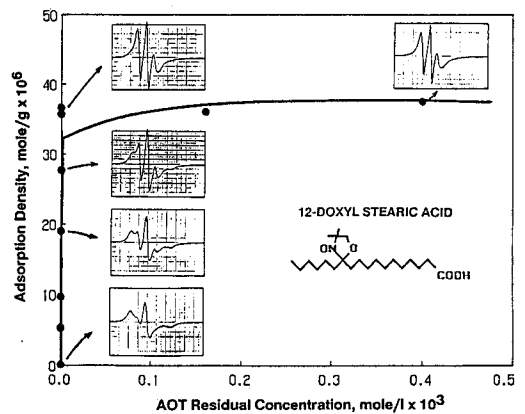


FIG. 2. Adsorption isotherm of Aerosol OT on alumina in cyclohexane and corresponding ESR spectra obtained using 12-doxyl stearic acid as a probe.

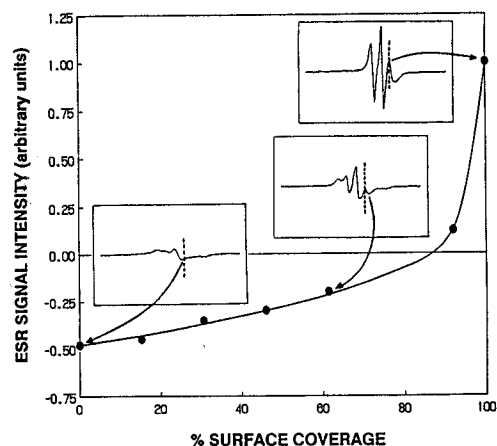


FIG. 3. Intensity of the ESR peak (indicated by the dotted line on the spectra in inserts) as a function of surface coverage estimated from the adsorption isotherm data.

during surfactant adsorption are very significant. Thus, by setting the magnetic field of the ESR spectrometer at an intensity corresponding to this peak, indicated in Fig. 3 by the dotted line, it is possible to monitor continuously the surfactant adsorption as a function of time by following the changes in the signal intensity. The intensity of this peak as a function of surface covered by surfactant (defined as $\Theta = \Gamma/\Gamma_{\max}$) is plotted in Fig. 3. The overall adsorption phenomenon is relatively fast as can be seen from Fig. 4 where the adsorption process is shown to be complete in 1.5 to 2 h. In Fig. 5, typical results are given for two different initial concentrations (both lead to a monolayer coverage

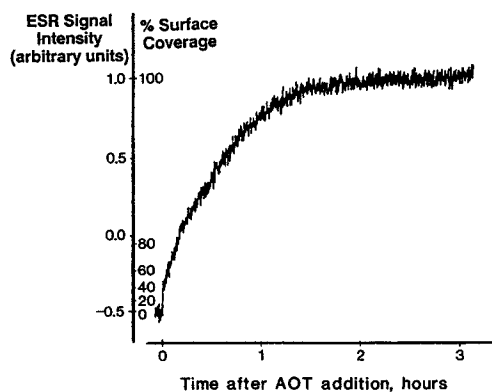


FIG. 4. Changes in the signal intensity as a function of time after the addition of a surfactant solution to the slurry continuously flowing through the cavity of the spectrometer. The signal intensity is monitored at the position indicated by the dotted line in Fig. 3. $[\text{AOT}]_{\text{init}} = 5.0 \times 10^{-2}$ mol/liter.

Journal of Colloid and Interface Science, Vol. 137, No. 2, July 1990

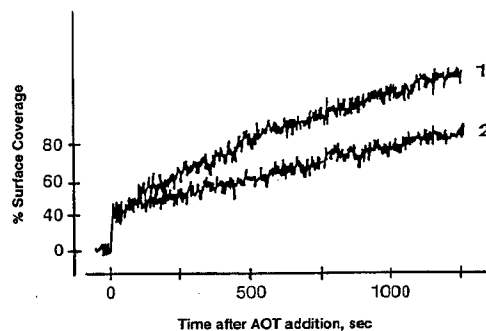


FIG. 5. Effect of surfactant concentration on the short-term kinetic of surfactant adsorption. (1) $[\text{AOT}]_{\text{init}} = 5.0 \times 10^{-2}$ mol/liter and (2) $[\text{AOT}]_{\text{init}} = 1.2 \times 10^{-2}$ mol/liter.

of adsorbed surfactant). These data correspond to the first 20 min of the adsorption process. Both curves show a sharp discontinuity in the signal intensity occurring 3 to 5 s after the addition of the surfactant solution to the suspension. When the data from Fig. 3 are used to calibrate the change in signal intensity in terms of adsorption density and surface coverage, it is found that this jump in the signal intensity corresponds to 40% of the total adsorption, which thus occurs within the time required for the suspension in contact with the surfactant solution to reach the cavity of the ESR spectrometer. After the 3 to 5 s necessary for mixing and circulation which constitute the lowest time scale limit of the technique, the remaining adsorption process is clearly concentration-dependent.

CONCLUSION

Based on changes in the ESR signal intensity of 12-doxyl stearic acid as a function of surfactant adsorption on colloidal alumina, an experimental technique has been developed to study the short-term kinetics of surfactant adsorption. Using this technique, it was found that 40% of the total adsorption of Aerosol OT at the alumina/cyclohexane interface occurs in less than 5 s after the addition of the surfactant. Compared to conventional approaches, this technique allows one to study the short-term aspects of adsorption kinetics under conditions similar to practical ones where a slurry is conditioned with a solution of additives. This technique can provide a practical means to measure quantitatively adsorption rates of polymers and surfactant in colloidal systems.

ACKNOWLEDGMENTS

We acknowledge the financial support of the NSF under Contracts MSM-86-17183 and CBT-86-15524, IBM Corporation, the New York Mining and Mineral Resources Research Institute (C.A.M. and P.S.), as well as the Air Force Office of Scientific Research (N.J.T.).

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Received August 11, 1989; accepted November 2, 1989

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