Dynamic Surface Tension Behavior of Hexadecanol Spread and Adsorbed Monolayers

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Received August 2, 1993. In Final Form: September 20, 1993®

The spread monolayer tension behavior of hexadecanol at 25 °C was linked to the adsorption dynamics from sprinkled particles or from dispersions in saline. The dynamic tension was measured with the Langmuir trough (Wilhelmy plate) method, the pendant drop method, and the bubble method. The rate of adsorption was found to be proportional to the surface area of particles spinkled on the surface. Moreover, the size and concentration of dispersed particles close to the surface affected strongly the rate of tension drop for 1500 ppm dispersions. When the dispersed crystallites were melted, broken to smaller particles, and refrozen, the rate of adsorption increased drastically. The bubble method was used in the constant area mode and in the pulsating area mode at 1–80 cycles/min, at 25 and 37 °C. The tension amplitude during pulsation increased with increasing frequency and decreased with decreasing particle size. The constant area data were compared to the predictions of a simple diffusion-controlled adsorption model with an effective diffusion length which represents the contribution of the particles as the source of molecules available for adsorption.

1. Introduction

The dynamic adsorption and surface tension behavior of soluble surfactant systems have been widely studied as a function of concentration and in developing models for diffusion-limited, adsorption-limited, or mixed-kinetics conditions.[1-8] However, the dynamic behavior of insoluble surfactant systems has received little attention. There are two common ways of studying an insoluble surfactant. One is to use spread monolayers on a trough, which yields the surface pressure–area (Π–A) isotherms. The other method, which is to use sprinkled or suspended solid surfactant particles on a clean surface, gives the rate of release of molecules from the solid particles to the aqueous surface.[9-15] Insoluble surfactants have many applications. They are used in helping retardation of evaporation of lakes.[16-18] Many detergents are also used above their solubility as dispersed microcrystallites, liquid microcrystallites, or even liquid emulsions (surfactants above their cloud point). Another possible application area is the stability and rheology of soap lather.

In this paper, hexadecanol is studied as a model system of a nearly insoluble surfactant. Its solubility in water at various temperatures below its melting point of 49 °C has been reported by several researchers using different techniques.[19-21] Krause and Lange[19] used isotopically labeled hexadecanol at 33 °C to measure the solubility of 3.3×10^{-8} M (0.008 ppm) with ±10% uncertainty. Radioactive hexadecanol was spread on the water surface and was equilibrated for 1–2 weeks. Then, its concentration in the bulk water was determined. Hoffman and Anacker[20] analyzed by gas chromatography saturated solutions prepared by a procedure based on that of Krause and Lange. They reported the solubility at 43 °C to be 6.4×10^{-10} M (0.000 155 ppm). Robb[21] prepared a saturated solution by stirring hexadecanol powder with water for 24 h at 25 °C and filtering twice to remove particles (filter pore size 350–1000 Å). He determined the solubility to be $1.7 \times 10^{-7} \pm 0.2 \times 10^{-7}$ M (0.04 ppm) by comparing the surface properties of recovered hexadecanol spread monolayer to the standard Π–A isotherm. The discrepancies are probably due to the solubility being quite small. Resolving the discrepancies is clearly a nontrivial task. Some material can be lost due to the adsorption on the container surfaces. The solubility can be overestimated if small submicrometer suspended particles are present. Nonetheless, the solubility of hexadecanol in saline at 25 °C can be safely taken to be smaller than 1.7×10^{-7} M (0.04 ppm). Thus, hexadecanol is nearly insoluble in water at 25 °C. The solubility is expected to be of the same order of magnitude at 37 °C, either in water or in saline. No information is available on whether it forms micelles. Because of the small solubility, we consider this possibility unlikely. The suspended phase is crystalline.

Hexadecanol has been chosen for study because it is sparingly soluble in water, is chemically stable without the hydrolysis problem of ester-type lipids, and is used in many practical household and pharmaceutical products. Moreover, hexadecanol (or other higher alcohols) is used as a key ingredient in controlling the respreadability and dynamic surface tension behavior of a successful commercial lung surfactant replacement drug called Exosurf[22-24] and marketed by Burroughs Wellcome, Co.,

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® Abstract published in *Advance ACS Abstracts*, November 15, 1993.

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0743-7463/93/2409-3640$04.00/0