THE EFFECT OF DISSOLVED OILS AND ALCOHOLS ON THE CMC OF SYNTHETIC
AND PETROLEUM SULFONATES

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The CMC of sodium dodecyl benzene sulfonate was determined using surface tension, light scattering and electrical conductivity measurements. It is shown that the presence of alcohol or oil decreases the CMC. The decrease in CMC depends on the chain length of dissolved alcohol or oil. For oils of different chain length, it was observed that the higher the chain length of oil, the greater is the decrease in CMC.

Using light scattering and osmotic pressure measurements, the CMC of a petroleum sulfonate (TRS 10-80) in 1% NaCl solution was found to be 0.005%. However, upon equilibration with n-octane, the CMC in the equilibrated aqueous phase was found to be 0.05% using light scattering and osmotic pressure measurements. The interfacial tension in TRS 10-80 solution/n-octane was found to be minimum (≈ 1 millidynes/cm) at 0.05% surfactant concentration. The electrophoretic mobility of oil droplets was also found to be maximum at 0.05% TRS 10-80. It is proposed that upon equilibration with oil, the higher equivalent weight species partition preferentially in the oil phase whereas lower equivalent weight species remain preferentially in the brine phase. Thus, after equilibration with oil, the average weight of the surfactant remaining in the aqueous phase is considerably less than the average equivalent weight of the original surfactant. This interpretation explains why the CMC increases ten-fold for TRS 10-80 upon equilibration with n-octane. A unified theory is presented to account for the observed effects.
of several variables on partition coefficient and the effective CMC of a surfactant, which in turn, influence the surface concentration of surfactant, surface charge density and solubilization of oil or brine in each other. These parameters influence the magnitude of interfacial tension at the oil/brine interface.

INTRODUCTION

Various techniques have been used to determine the critical micelle concentration (CMC) of surfactants. The most commonly used methods are surface tension, dye absorbance, light scattering and electrical conductivity measurements. It is well recognized that the CMC value obtained by one method may be slightly different from that determined by other techniques.

For a pure surfactant, the concentration of monomers increases with the increase of surfactant concentration until CMC is reached. Above the CMC, it is assumed that monomer concentration remains constant in pure surfactant solutions, if micellization process is,

\[ n(\text{monomers}) \xrightarrow{+} (\text{micelle})^n \]

where the right hand side showing a micelle with aggregation number \( n \). If the aggregation number changes with concentration of surfactant, then monomer concentration will change above the CMC.

In the case of petroleum sulfonates, with broad equivalent weight distribution, the surface concentration of surfactant depends greatly on the micellization process in the bulk phase. Surfactants of longer chain length may be adsorbed first at the surface and then be solubilized into the micelles formed by surfactant of shorter chain length. By this process, the long chain molecules at the surface can be gradually replaced by molecules of shorter chain length. The effectiveness of surfactant molecules to decrease the surface tension depends on their chain length. Hence, the surface tension of petroleum sulfonate solutions may increase after a minimum is reached. The CMC determined using this minimum in surface tension is actually the concentration at which the concentration of monomers is maximum. By the same reasoning, we can say that the structure and composition of the micelles in such a broad distribution surfactant system should undergo a constant change in composition as the surfactant concentration increases. Since petroleum sulfonates consist of a broad distribution of equivalent weights, we used light scattering and membrane osmometry techniques to determine the CMC. Both these techniques would mea-