α-Sulfonato Palmitic Acid Methyl Ester–Hexaoxyethylene Monododecyl Ether Mixed Surfactant System: Interfacial, Thermodynamic, and Performance Property Study

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ABSTRACT: Interfacial, thermodynamic, and performance properties of aqueous binary mixtures of α-sulfonato palmitic acid methyl ester, $C_{14}H_{29}CH(SO_3Na)COOCH_3$ (PES), and hexaoxyethylene monododecyl ether, $CH_3(CH_2)_{11}(OCH_2CH_2)_6OH$ ($C_{12}E_6$), were investigated with tensiometric, conductometric, fluorimetric, and viscometric techniques. The critical micelle concentration (CMC), maximum surface excess, minimum area per molecule of surfactant at the air/water interface, and the thermodynamics of micellization and adsorption were determined. The CMC was very low for mixed systems, indicating probable use as a detergent with less effect on the environment because of surfactant biodegradability and less amount in the environment. The interaction parameter β^m, computed by using the theory of Rubingh and Maeda, indicated an attractive interaction (synergism) between the surfactant molecules, which was also confirmed by proton nuclear magnetic resonance studies in the mixed micelle. The micellar aggregation number (N_{agg}), determined by using a steady-state fluorescence quenching method at a total surfactant concentration of about ~10 mM at 25°C, was almost independent of the surfactant mixture composition. The micropolarity and the binding constant (K_{sv}) for the $C_{12}E_6$/PES mixed system were determined by the ratio of the intensities (I_1/I_3) of the pyrene fluorescence emission spectrum, and the local microenvironment inside the micelle was found to be polar. The viscosity of the mixed system at all mole fractions suggested that mixed micelles are nonspherical in nature. The cloud point of oxyethylene group-containing surfactants was increased by the addition of PES. Foaming was temperature dependent, and a 1:1 mixed system showed minimum foaming. All performance properties were composition dependent.

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KEY WORDS: Foaming, interaction parameter, micellization, mixed surfactant, viscosity.

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Abbreviations: α, degree of micelle ionization; A_{CMC}, area per molecule at CMC; A_{min}, limiting surface area per molecule; β^m, interaction parameter; γ, surface tension; Γ_{max}, maximum surface excess; $C_{12}E_6$, hexaoxyethylene monododecyl ether; CMC, critical micelle concentration; CP, cloud point; ε, dielectric constant; f_1, activity coefficient of surfactant 1 (PES) in the micelle; η, intrinsic viscosity; η_r, relative viscosity; K_{SV}, Stern–Volmer binding constant; N_{agg}, micellar aggregation number; NMR, nuclear magnetic resonance; N_{PES}, stoichiometric mole fraction of PES in mixture; PES, α-sulfonato palmitic acid methyl ester; σ, Traube's constant; X_1, mole fraction of ionic surfactant in the mixed micelle; X_{CMC}, CMC expressed as a mole fraction.

The association of surfactant molecules into finite-sized molecular aggregates such as micelles in aqueous solution is significant for their use in solubilization, catalysis, dispersion, and technological, biochemical, and pharmaceutical formulations (1,2). Mixed surfactants exhibit performance superior to that of single surfactants, and composition as well as concentration can be optimized for a particular application (3). Synergistic interactions between surfactant molecules in mixed surfactant systems may be exploited to reduce the total amount of surfactant used in a particular application, which ultimately can lead to a reduction in cost and environmental impact (4). Because of their distinctive behavior compared to single surfactants, mixed surfactant systems, such as nonionic–nonionic (5,6), nonionic–anionic (7,8), nonionic–cationic (9), and anionic–zwitterionic (10) combinations, have attracted attention in both theoretical studies and practical applications (11). Determination of various physicochemical properties of surfactant mixtures can provide a means to optimize their properties.

We have studied the physicochemical properties of α-sulfonato palmitic acid methyl ester (PES), an anionic surfactant, in the presence of hexaoxyethylene monododecyl ether ($C_{12}E_6$), a nonionic surfactant. Besides their ready availability from renewable plant material and good biodegradability, PES have superior detergency for fabrics and a high tolerance against calcium ions (12), indicating it can possibly be used in hard water. Moreover, the mixed system is expected to have low CMC values; hence, the amount required for use will be low. We are also interested in comparing properties of derivatives of various fatty acids (e.g., myristic, palmitic, and stearic acids) in mixed systems with $C_{12}E_6$ to determine which mixture will be a better detergent and to optimize biodegradability and minimize toxicity.

Physicochemical properties of binary mixtures of PES and $C_{12}E_6$ at different temperatures are reported here, including foaming, viscosity, and cloud point. Rubingh's regular solution theory (13) is used to estimate the composition of mixed aggregates, activity coefficients, and interaction parameters of the surfactants.

EXPERIMENTAL PROCEDURES

Materials. $C_{12}E_6$ and PES were obtained from Lion Corporation (Tokyo, Japan). PES was recrystallized from dry alcohol.