

Self-Aggregation of a Cationic–Nonionic Surfactant Mixture in Aqueous Media: Tensiometric, Conductometric, Density, Light Scattering, Potentiometric, and Fluorometric Studies

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Self-aggregation of tetradecyltrimethylammonium bromide (TTAB, $[\text{CH}_3(\text{CH}_2)_{13}\text{N}^+(\text{CH}_3)_3\text{Br}^-]$) and polyoxyethylene 23 lauryl ether (Brij-35, $[\text{CH}_3(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_{23}\text{OH}]$) binary surfactant mixture in aqueous medium was studied using tensiometric, conductometric, density, quasielastic light scattering, potentiometric, and fluorometric measurements. The binary surfactant mixture was studied well above the Krafft temperature, which was evaluated by conductance measurements. Rubingh's nonideal solution theory predicted nonideal mixing and attractive interaction between the constituent surfactants in the mixed micelle. Moreover, attractive interaction between the two surfactants in the mixed micelle is explained by assuming that water acts as a bridge between the hydrophilic polar groups of the surfactant molecules. The chain-chain interaction among the surfactant does not seem to be high in this case. The partial specific volume of pure as well as binary surfactant mixtures was also evaluated, and it was inferred that the mixed micelles are more hydrated compared to individual components. The excess Gibbs free energy of mixing was evaluated, and it indicated relatively more stable mixed micelles for this binary combination. Surface tension measurements indicate an existence of a second state of aggregation for the mixed surfactant system, which is supported by the break in conductance–concentration of surfactant profile. The Krafft temperature of TTAB decreases as the nonionic surfactant content increases in the mixed system. Quasielastic light scattering studies suggest an increase in the hydrodynamic radius of the micelle in the mixed surfactant system.

Introduction

Surfactant comprises a hydrophilic and a hydrophobic group. The different interactions of these two moieties with water is an important cause for surfactants to aggregate into micelles and other nanometer scale structures in aqueous solution.¹ Due to widespread uses and application of surfactants as well as their micellar aggregates in chemical, biochemical, pharmaceutical, and industrial fields, detailed investigation on the fundamentals of aggregation of existing conventional and newer amphiphiles are in progress.² The micelles composed of mixed surfactants occur in biological fluids and are very often used in industrial application, pharmaceutical, and medicinal formulation for the purpose of solubilization, suspension, dispersion, etc.^{3,4} Extensive reports exist in the literature on studies of different combination of mixed surfactant system viz. cationic–cationic,⁵ nonionic–nonionic,^{5,6} anionic–cationic,⁷ anionic–nonionic^{8,9}

etc. Ionic–nonionic surfactant mixtures are important from fundamental as well as application point of view as they exhibit highly nonideal behavior on mixing and also their behavior can be complementary in the mixed micelle causing the cmc to decrease.¹⁰ Cationic surfactants are useful as antifungal, antibacterial, and antiseptic agents and have attracted recently more attention with reference to their interaction with DNA and lipids,¹¹ whereas the nonionic surfactants are useful as detergents, solubilizers, and emulsifiers.⁶

To characterize the micelle formation of ionic–nonionic binary surfactant mixture, we are reporting a detailed investigation of physicochemical properties of binary cationic–nonionic surfactant mixture (TTAB/Brij35). The physicochemical properties were characterized by adopting tensiometry, conductometry, fluorometry, potentiometry, and quasielastic light scattering measurements. Moreover, we have also discussed the evidence of existence of second state of surfactant aggregation for the mixed surfactant combination by employing tensiometric and fluorometric techniques that have been further corroborated by conductance measurements in the absence of any additive.

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