



Micellization behavior of binary mixtures of amino sulfonate amphoteric surfactant with different octylphenol polyoxyethylene ethers in aqueous salt solution: Both cationic and hydrophilic effects



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ABSTRACT

The effect of different valent inorganic cations and the hydrophilic group of surfactant on the micellization behavior of binary surfactant mixtures constituted by an amphoteric surfactant, sodium 3-(*N*-dodecyl ethylenediamino)-2-hydropropyl sulfonate (C12AS), and three nonionic surfactants octylphenol polyoxyethylene ether (OP-*n*) with different numbers of oxyethylene glycol ethers (*n*), namely, OP-10, OP-7, and OP-4 was investigated in aqueous solution. These inorganic cations include Na⁺, K⁺, Mg²⁺, Ca²⁺, Ba²⁺, Al³⁺ and Fe³⁺. Both the tensiometry and the UV–vis spectrophotometry using pyrene as a probe were adopted to determine the critical micelle concentrations (*cmc*) of individual or mixed surfactants. Interaction parameters between two surfactants and other parameters were obtained based on the regular solution theory, the pseudophase separation model, Rubingh's model, etc. Thermodynamic parameters including Gibbs energy of micellization and thermodynamic stability were also calculated by both the equation proposed by Molyneux et al. and Maeda's treatment, respectively. The effect of different valent cations on both the mixed *cmc* of surfactant mixtures and the molar fraction of C12AS in mixed micelle (*X*₁) can be explained theoretically by the salting-out effect, electrostatic interaction and steric effect. For three binary surfactant mixtures, the chain length of hydrophilic group of surfactant results in different micellization behaviors. On adding salts, the interaction parameters show that there exists a synergistic effect between two surfactants, and the effect increases with increasing the ratio of valence (*Z*) and atom radius (*R*) of cation, especially, for the C12AS/OP-4 mixture. With increasing the *Z/R* value of cation, a deviation of *X*₁ from the ideal value shows a divergence for three binary surfactant mixtures because of different hydrophilicities of surfactant. Thermodynamic parameters indicate that the addition of cations with a large *Z/R* value can be contributive more effectively to the formation of stable mixed micelle than the case in the presence of cations with a small *Z/R* value.

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Introduction

In most practical applications, surfactant mixtures rather than an individual surfactant are used owing to their excellent properties to those with a single surfactant component [1–5], e.g., the stronger surface/interfacial activity, the lower critical micelle concentration (*cmc*), the more inexpensive cost, etc. In

view of this, surfactant mixtures containing binary or ternary combinations of different ionic and nonionic surfactants have been extensively investigated [1–9]. Amongst these investigations, because of their unique structural characteristics, polyoxyethylene-type nonionic surfactants are widely employed in both biochemical research and numerous technical applications [7,8,10]. However, the micellization behavior of mixtures containing polyoxyethylene-type nonionic surfactants and zwitterionic surfactants has been scarcely reported [3,11]. Sodium 3-(*N*-dodecyl ethylenediamino)-2-hydropropyl sulfonate (C12AS) developed by our group [1,3,4] is an amino acid-type amphoteric

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surfactant. In recent years, the properties of binary mixtures of C12AS with cationic, anionic, nonionic surfactants in aqueous solutions have been investigated by our groups [1,3,4,10–12]. Of course, the micellization of the mixture of C12AS with polyoxyethylene-type nonionic surfactants having different hydrophilic groups in aqueous solutions has also been reported in our previous literatures [3,11]. While the effect of inorganic salts on the micellization of surfactant mixtures has not yet been considered in our previous investigations, obviously, which does not accord with the practical occasions relating to surfactants. It is well known that different inorganic salts (including different valent cation or anion) are involved in water in many practical occasions, e.g., oil fields [5,13,14], etc. Therefore, it is very necessary to consider the effect of inorganic salt on the micellization behavior of surfactant mixtures, and it is of importance to the engineering application of surfactants in many fields. The cause may be from some aspects. First, the ionic type and their concentration in inorganic salt may change the optimum mixing ratio in surfactant mixture. Second, the inorganic salt may result in different interaction behavior between surfactant molecules. Third, once the concentration of inorganic salt in aqueous surfactant solution is more than a given concentration, some unexpected phenomena may happen, e.g., precipitate, haze, etc. These effects are very possible to lead to some disadvantages. Such as, the previous designed surfactant formula in aqueous solution without salt or with salts of low concentration will fail to use in some occasions relating to salts of high concentration or different ionic types. Then, the result of salt effect will help us to understand the micellization behavior of surfactant mixture, and then to design the surfactant formula suitable to use in many practical and engineering fields.

In this paper, the micellization of binary mixture constituted by C12AS with octylphenol polyoxyethylene ether (OP-*n*) with different numbers of oxyethylene glycol ethers (*n*), namely, OP-10, OP-7, and OP-4, was investigated. In particular, the major aim is to investigate the effect of inorganic salts on the micellization. In order to obtain some information, the *cmc* values of both an individual surfactant and binary surfactant mixtures in aqueous salt solution were determined by both the tensiometry and the UV–vis spectrophotometric method, and different mixing thermodynamic models were adopted to obtain some micellization parameters and thermodynamic parameters, and then the mechanism about the effect of inorganic salts and the hydrophilicity of surfactant on the micellization behavior was theoretically analyzed.

Experimental

Materials and solutions

The treated C12AS has a purity of over 99 wt% in mass fraction, measured with Vario EL III Automatic Elementary Analyzer made

by Germany Elementar Co. The nonionic surfactants OP-*n* (including OP-10, OP-7, and OP-4) and all inorganic salts (including NaCl, KCl, MgCl₂, CaCl₂, BaCl₂, AlCl₃ and FeCl₃) were analytical reagents, all of which have the purities of >99 wt% from Sinopharm Chemical Reagent Co., Ltd. Pyrene with a purity of 98 wt% was purchased from Aldrich Chemical Reagent Co. The chemical structure formulas of C12AS and OP-*n* and their representations are shown in Fig. 1. C12AS and OP-*n* were used as supplied, while all these inorganic salts were recrystallized three times using deionized triple distilled (DTD) water before use. In addition, pyrene was purified by recrystallization from the mixed cosolvents of ethanol and deionized triple distilled (DTD) water (the conductivity of 4.24 μS/cm at 298.15 ± 0.20 K measured by the DDSJ-318 conductometer made in China).

Solutions of C12AS, OP-*n* or their mixtures were prepared in water or salt water obtained with DTD water, respectively. For the convenience of investigation, all the concentrations of inorganic salts (including NaCl, KCl, MgCl₂, CaCl₂, BaCl₂, AlCl₃ and FeCl₃) in aqueous solution were fixed at 0.250 mol/L. The molar fractions of C12AS in bulk solution were uniformly designated to 0.561, 0.484, and 0.336 for the binary mixtures of C12AS/OP-10, C12AS/OP-7 and C12AS/OP-4, respectively, all of which were an optimum mixing fraction for each surfactant mixture in aqueous solution [11]. The pH values of all the surfactant solutions were found to be about 6.2 within the range of isoelectric point for C12AS, which agrees with our previous investigation [3,11]. In addition, the stock solution of pyrene was prepared as the method in the previous literatures [3,11,12,15,16].

Methods

Compatibility of surfactants in aqueous salt solutions

To observe the solubility phenomena of surfactants in aqueous salt solutions, the 1.000 g/L surfactant solution with the inorganic salt of 0.250 mol/L was prepared. After thorough mixing, the solutions were held in sealed tubes at ambient pressure, and then allowed to stand in water bath of 298.15 ± 0.20 K for 24 h. For all the specimens, the occurrence of precipitates in solutions can be visible to the naked eyes. Otherwise, the turbidimetry can help us to judge whether or not the precipitate or a haze occurs [3,15]. In this investigation, all the surfactants showed a good solubility in aqueous salt solutions.

Tensiometry and determination of *cmc*

Surface tension (γ) of the solutions was measured with a JK99C automatic surface tensiometer (made in China) by the Wilhelmy plate method. To obtain a constant temperature, all solutions in the conical flasks sealed with rubber plug were allowed to stand in water bath of 298.15 ± 0.20 K for over 50 min. Before measuring the surface tension of solution, the platinum plate washed with alcohol

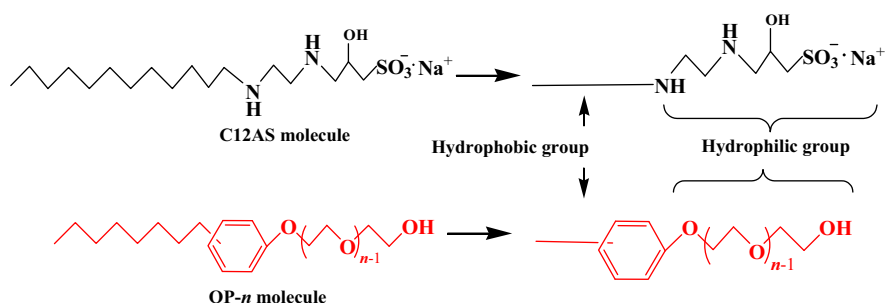


Fig. 1. Chemical structures of compounds (C12AS and OP-*n*) and their representations.

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