Journal of Molecular Liquids 272 (2018) 380–386

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Micellization and interaction for ternary mixtures of amino sulfonate surfactant and nonionic octylphenol polyoxyethylene ethers in aqueous solution: 2 blending with nonionic surfactant with a longer or shorter hydrophilic chain

Zhao Hua Ren [a,*], Jing Huang [b], Yan Cheng Zheng [a], Lu Lai [a], Ping Mei [a], Xiao Rong Yu [a], Yan Ling Chang [a]

[a] College of Chemistry and Environmental Engineering, Yangtze University, Jingzhou 434023, China
[b] College of Management, Yangtze University, Jingzhou 434023, China

ARTICLE INFO

Article history:
Received 2 May 2018
Received in revised form 2 September 2018
Accepted 17 September 2018
Available online 23 September 2018

Keywords:
Amino sulfonate
Nonionic
Ternary mixture
Hydrophilic chain
Micellization

ABSTRACT

The micellization behavior of the ternary mixture of an amphoteric sodium 3-(*N*-dodecyl ethylenediamino)-2-hydropropyl sulfonate (C12AS) with two nonionic surfactants, octylphenol polyoxyethylene ether (OP-*n*, where *n* is the number of hydrophilic unit oxyethylene glycol ethers, $n = 4, 7, 10$), was investigated using both the tensiometry and the ^{1}H NMR technique. Also, the effect of the addition of nonionic surfactant with a longer or shorter hydrophilic chain, e.g., OP-10 or OP-4, on the micellization of the binary mixture of C12AS/OP-7 with a maximum synergism was probed. Based on the regular solution theory, thermodynamic models were adopted to obtain the composition, activity coefficient of mixed micelle and some thermodynamic parameters. The addition of OP-10 or OP-4 into the binary mixture of C12AS/OP-7 induces the change in the mixed critical micelle concentration, which can be explained by the change in the composition of mixed micelle and the effect of hydrophilic chain. Thermodynamic data show that the addition of OP-10 or OP-4 results in the change from the enthalpy overwhelming process of micellization to the entropy-driven process. The chemical shift of proton in the terminal hydroxy group of OP-*n* in binary or ternary surfactant mixture is also adopted to describe the obtained results. The findings will help with understanding the interaction behavior between molecules in the multicomponent mixture, especially, the effect of the addition of homologues or other components on the properties of surfactant formulation.

1. Introduction

In practical applications, the mixed surfactants are often used rather than pure surfactant. Because the mixtures can exhibit excellent properties, e.g., lower critical micelle concentration (*cmc*), better surface/interfacial activity, lower cost, etc., than their pure components [1–3]. It is attributed to the synergistic interaction between surfactants. In recent years, many investigations on mixed surfactant systems including the binary mixture of different ionic type surfactants, e.g., ionic/ionic [4–6], ionic/nonionic [7–9], even nonionic/nonionic [10,11], etc., have been made. Also, some thermodynamic models, e.g., the Clint's model [12], the Rosen's model [1], the Rubingh's model [13], etc., have been adopted successfully to analyze the experimental results of the binary mixtures and further to reveal the synergistic and antagonistic behavior between surfactants.

However, in many industrial situations, multiple combinations other than binaries prevail. It means that the surfactant mixture or formulation, namely, containing at least three components, even four components or more, is normally more than two components. In view of this, some investigations on ternary mixtures of surfactants have been carried out [14,15]. But, the detailed studies on the physiochemical properties for the ternary systems are fairly limited, which may be that such systems are complex [13]. Even so, considering the practical case for the surfactant formulation with multiple components in many industrial applications, the interaction behavior between surfactants for the ternary mixture is worthy to investigate in order to provide the foundational information and ultimately to properly design the surfactant formulation. Our previous investigations [2,9,16] focused on the properties for the binary mixture of an amphoteric sodium 3-(*N*-dodecyl ethylenediamino)-2-hydropropyl sulfonate (C12AS), which was developed by our group [18], and a nonionic octylphenol polyoxyethylene ether (OP-*n*, where *n* is the number of hydrophilic unit oxyethylene glycol ethers). Usually, it is well known that the nonionic surfactant OP-*n* as an industrial product is a mixture composed

* Corresponding author.
E-mail address: renzzzhuar@126.com (Z.H. Ren).

https://doi.org/10.1016/j.molliq.2018.09.088
0167-7322/

of homologues with different numbers of hydrophilic unit due to its manufacturing technique or cost and its industrial application. Regarding to this and as mentioned above, it is essential to probe the physicochemical properties for the multiple components systems composed of homologues of OP-*n*. In this work, the interaction behavior between surfactants for the ternary mixture of C12AS, OP-7 and OP-10 or OP-4 is investigated. Specifically, this work focuses on the effect of the addition of a nonionic surfactant OP-*n* with a longer or shorter hydrophilic chain (OP-10 or OP-4) on the molecular interaction for the binary mixture of C12AS/OP-7. In order to obtain some information about the molecular interaction, some thermodynamic models were adopted to calculate the parameters of micellization. And then, the interaction behavior is theoretically discussed. The chemical shift of proton in the ^{1}H NMR spectra also provide some information to discuss the interaction between surfactant molecules in mixed micelle.

2. Experimental

2.1. Materials

The amphoteric surfactant C12AS (>99.0 wt%) is developed by our group [17]. The nonionic surfactants OP-10, OP-7 and OP-4 are analytical reagents (>99 wt%) from Sinopharm Chemical Reagent Co., Ltd. and were used as received. In all the experiments, the deionized triple distilled (DTD) water with a conductivity of about 4.01 μS/cm at 298.15 K measured by the DDSJ-318 conductometer made in China was used to prepare all the surfactant solutions.

2.2. Tensiometry

Using a Wilhelmy platinum plate, the surface tension of surfactant solution was measured with a JK99C automatic surface tensiometer (Shanghai Zhongchen Digital Technic Apparatus Co., Ltd) at 298.15 ± 0.20 K. In the measurement, the ring used was cleaned by washing respectively with DTD water and alcohol followed by heating in an alcohol flame. To obtain the desired temperature of 298.15 ± 0.20 K, the solution was kept in thermostatic water bath for at least 50 min. The resulted value of surface tension is the mean value from three experimental values and has an uncertainty of ±0.2 mN/m.

2.3. ^{1}H NMR spectra

The samples were allowed to equilibrate at a desired temperature (298.15 ± 0.20 K) for at least 50 min prior to measurements. $CDCl_3$ was used as solvent instead of water in order to weaken the water signal. A Bruker AVANCE spectrometer with a proton frequency of 400 MHz was adopted in the NMR study with a TMS (tetramethyl silane) as the external reference.

3. Theoretical treatment

In the framework of the pseudophase separation model, the mixed critical micelle concentration (*cmc*) for ternary surfactant mixture and for binaries can be expressed respectively as [9,13]:

$$\frac{1}{cmc_{123}} = \frac{x_1}{f_1 cmc_1} + \frac{x_2}{f_2 cmc_2} + \frac{x_3}{f_3 cmc_3}$$

$$\frac{1}{cmc_{12}} = \frac{x_1}{f_1 cmc_1} + \frac{x_2}{f_2 cmc_2} \tag{1b}$$

where cmc_{123} and cmc_{12} are the mixed *cmc* of component *i* (*i* = 1, 2, 3) in ternary surfactant mixture and binaries, respectively; cmc_i is the *cmc* of individual surfactant *i*; x_i is the mole fraction of component *i* in bulk solution; f_i is the activity coefficient of component *i* in mixed micelle.

On the ideal mixing, $f_i = 1$. Then, the Eqs. (1a) and (1b) can be rewritten as:

$$\frac{1}{cmc_{123}^{ideal}} = \frac{x_1}{cmc_1} + \frac{x_2}{cmc_2} + \frac{x_3}{cmc_3}$$

$$\frac{1}{cmc_{12}^{ideal}} = \frac{x_1}{cmc_1} + \frac{x_2}{cmc_2} \tag{2b}$$

where $cmc_{123ideal}$ and $cmc_{12ideal}$ are the ideal mixed *cmc* for ternary surfactant mixture and binaries, respectively.

According to the regular solution theory (RST), the activity coefficient (f_i) for the multi-components mixture of surfactant can be expressed by the mole fraction (X_i) of component *i* in mixed micelle and the interaction parameters (β_{ij}) of binary surfactant mixture [13,15]:

$$f_i = \exp\left[\sum_{\substack{j=1 \\ j\neq i}}^{n} \beta_{ij} X_j^2 + \sum_{\substack{j=1 \\ j\neq i\neq k}}^{n} \sum_{k=1}^{j-1} (\beta_{ij} + \beta_{ik} - \beta_{jk}) X_j X_k\right] \tag{3}$$

For ternary surfactant mixture, the mole fraction (X_i) of component in mixed micelle can be calculated by the following equation set:

$$x_1 cmc_{123} = X_1 cmc_1 \exp\left[\beta_{12} X_2^2 + \beta_{13} X_3^2 + (\beta_{12} + \beta_{13} - \beta_{23}) X_2 X_3\right]$$

$$x_2 cmc_{123} = X_2 cmc_2 \exp\left[\beta_{12} X_1^2 + \beta_{23} X_3^2 + (\beta_{12} + \beta_{23} - \beta_{13}) X_1 X_3\right]$$

$$x_3 cmc_{123} = X_3 cmc_3 \exp\left[\beta_{13} X_1^2 + \beta_{23} X_2^2 + (\beta_{13} + \beta_{23} - \beta_{12}) X_1 X_2\right] \tag{4c}$$

As a constraint, the relationship can be given as:

$$x_1 + x_2 + x_3 = 1$$

$$X_1 + X_2 + X_3 = 1 \tag{5b}$$

Based on the RST, the free energy change ($\Delta_{mic}G$), the enthalpy change ($\Delta_{mic}H$) and the entropy change ($\Delta_{mic}S$) of micellization for

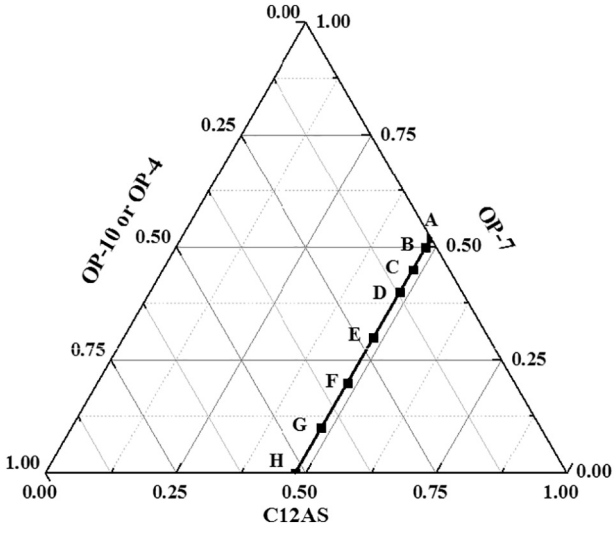

Fig. 1. The distribution point of composition for the ternary mixture of C12AS/OP-7/OP-10 or C12AS/OP-7/OP-4 in the equilateral triangle.