Colloids and Surfaces A: Physicochem. Eng. Aspects 504 (2016) 131–138

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Effect of isopropanol on the micellization of binary mixtures containing amino sulfonate amphoteric surfactant in aqueous solution: Mixing with octadecyltrimethyl ammonium bromide

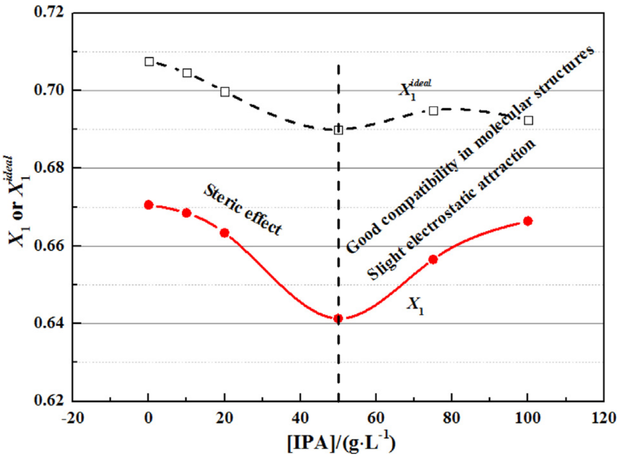
Zhao Hua Ren[a,*], Jing Huang[b], Yue Luo[a], Yan Cheng Zheng[a], Ping Mei[a], Wei Chu Yu[a], Lu Lai[a], Yan Ling Chang[a], Fan Xiu Li[a]

[a] College of Chemistry and Environmental Engineering, Applied Chemistry Research Centre for Oil and Gas Fields, Yangtze University, Jingzhou 434023, China
[b] College of Management, Yangtze University, Jingzhou 434023, China

HIGHLIGHTS

- Cosolvent effect on the micellization of amino sulfonate (C12AS) with cationic surfactant.
- The change in the conformation of C12AS.
- An abnormal dependence of component's fraction in mixed micelle on cosolvent.
- Electrostatic interaction between two surfactants.
- Molecular and thermodynamic mechanisms are presented.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 March 2016
Received in revised form 16 May 2016
Accepted 22 May 2016
Available online 24 May 2016

Keywords:
Amino sulfonate
Cationic surfactant
Micellization
Cosolvent effect

ABSTRACT

In aqueous solutions containing isopropanol (IPA), within the range of 0–100 g/L, the micellization behaviors of binary surfactant mixtures of amphoteric sodium 3-(*N*-dodecyl ethylenediamino)-2-hydropropyl sulfonate (C12AS) and cationic octadecyltrimethyl ammonium bromide (OTAB) were investigated by three techniques including tensiometry, conductometry and isothermal titration microcalorimetry (ITC). Based on extant theories and models (such as, the regular solution theory, the pseudophase separation model, the Rubingh's model, etc.), the effects of IPA on the molar fraction of components in mixed micelles, the interaction parameters between the two surfactants, and associated thermodynamic parameters have been discussed. The addition of cosolvent IPA results in a change in the conformation of C12AS, as well as affecting the interaction behavior between the two surfactants and a decrease in the hydrophobic effect. The synergistic effects between the two surfactants varies partly with the concentration of IPA. The observations can be used to explain the cause for the abnormal

---

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

http://dx.doi.org/10.1016/j.colsurfa.2016.05.063

dependence of the molar fraction of components in mixed micelles and the interaction parameters on the concentration of the cosolvent IPA. Thermodynamic parameters further show the effect of IPA on the entropy-driven process of micellization.

1. Introduction

In many industrial and commercial practical applications, surfactant mixtures, rather than a pure surfactant, are used. This results from the fact that the mixtures can usually form mixed micellar aggregates that frequently exhibit remarkably different characteristic properties and have superior performances to their components [1–3]. Then, a synergistic effect is defined as the case in which the properties of the mixture are better than those observed for the sum of the individual components [1–4]. In some cases, the synergism can be observed due to the attractive interaction between surfactants. The interaction parameter (β_{12}) in some representative models [1–4] (e.g. Rosen's model, Rubingh's model, etc.) were adopted to discribe the synergistic behavior between surfactants. A negative value of β_{12} indicates some synergism between surfactants, whereas a positive value denotes the antagonism between surfactants. β_{12} value near to zero reveals that there is little or no interaction between surfactants.

By applying these theoretical models, many binary mixtures of ionic/ionic, ionic/nonionic, and nonionic/nonionic surfactants have been investigated in aqueous solution without other additives [1,5–7]. Some investigations have considered the effect of different additives on the mixed micelle or the aggregates of mixed surfactants [8–10], and different measurement techniques [1–3,8–11], including tensiometry, UV–vis spectrometry, conductometry, neutron scattering, etc. have been used. Indeed, the formation of aggregates and their properties with mixed surfactants depend partly on environmental factors (e.g., temparature, different additives, etc.) [1,12–14]. In many practical situations, some cosolvents (e.g., short-chain alcohols.) are frequently added to modify the solubility of components of surfactant formulations in solution [1,15,16]. To date, many investigations have dealt with cosolvent effect on the formation of mixed micelles in ionic/ionic or ionic/nonionic surfactant mixtures [17–21], which helps with understanding the micellization behavior in polar organic solutions. Also, some investigations have reported that the addition of high concentration of cosolvent (even to 30vol% ethanol [10] or 50 wt% glycol [22]) may influence the micellization behavior in aqueous solution, which may be important in considering the consolvent effects on the formation of mixed micelles. However, it is well known that the concentration of cosolvent in some surfactant formulations (e.g., oil-displacing agents employing surfactants [15,16]) is very small, less than 10 wt% (or 100 g/L). To date, the cosolvent effects on micellization with surfactant mixtures containing zwitterionics has not received much attention. In our previous investigations [16,23,24], surfactant formulations containing amino sulfonate amphoteric surfactants and other surfactants have been used successfully to enhance oil recovery in some field tests. And, in the enhanced oil recovery field, cationic surfactants are sometimes used as sacrificial agents to modify the properties of rock surfaces in a reservior. Consequently, cationics may possibly be mixed with other ionic or nonionic surfactants injected later, which may result in some problems, e.g., the occurrence of a precipitate on mixing cationic with anionic or zwitterionic surfactants, the reduction of interfacial activity, and so forth. Therefore, based on the cases mentioned above, the micellization behavior of surfactant mixtures containing the amino sulfonate amphoteric surfactant, sodium 3-(*N*-dodecyl ethylenediamino)-2-hydropropyl sulfonate (C12AS), which belongs to a green chemical developed by our groups [12,23,24] and a cationic surfactant, octadecyltrimethyl ammonium bromide (OTAB), was investigated, especially, to consider the effect of a low concentration of a cosolvent in aqueous solution. The structures of the two surfactants are depicted in Fig. 1. Amongst cosolvents, isopropanol (IPA) is frequently regarded as a common cosurfactant in representative surfactant formulations [15,16]. The branched chain IPA relative to the straight chain propanol, owing to the difference in their molecular structures, can to a larger extent influence the volume (v) occupied by the hydrophobic group in the micellar core and the cross-sectional area (a_0) occupied by the hydrophobic group in the micelle-solution interface, and then influence the process of micellization [1]. The parameters v and a_0 are usually used to calculate the critical packing parameter $P_c = v/(a_0 l_c)$ which quantitatively characterizes the micellization behavior of a surfactant [1], where l_c is the length of the hydrophobic group in the micellar core. Therefore, this investigation was carried out in a water-IPA (not exceeding 100 g/L) mixed solvent media. In addition, considering the Krafft point or the limited solubility of OTAB and C12AS at room temperature, the temperature of 40 °C was selected to ensure good solubility of the mixed surfactants in aqueous solution.

In this work, the main aim was focused on the cosolvent effect on the interaction between two surfactant molecules and their synergistic properties so as to provide the basic data for designing surfactant formulations, and eventually to achieve the application of these formulations in field tests. To obtain information, the critical micelle concentrations (abbr. *cmc*) of the individual surfactants and their mixtures were measured by tensiometry, conductometry and isothermal titration microcalorimetry (ITC), micellization parameters were calculated using different thermodynamic models, and the interaction behavior between the two surfactant molecules was theoretically considered.

2. Experimental details

2.1. Materials and solutions

C12AS was synthesized in two steps as previously reported [25]. The purified product of C12AS developed by our group [12,23] has a purity of over 99 wt%, measured with a Vario EL III Automatic Elementary Analyser (Germany Elementar Co.). Both OTAB and IPA are analytical reagents with a purity of 99% from Sinopharm Chemical Reagent Co., Ltd. The chemical structural formulas of C12AS and OTAB are depicted in Fig. 1. All these materials were used as supplied. Deionized triple distilled (DTD) water was used to prepare the surfactant solutions in this study.

Solutions of binary mixtures of C12AS and OTAB were prepared with DTD water in the absence and presence of a given concentration of IPA. For all the binary mixtures of C12AS/OTAB, the molar fraction of C12AS (x_1) in bulk solutions were uniformly fixed at 0.670, which was the optimum mixing fraction in aqueous solution to obtain the maximum synergism between the two surfactants [23]. The pH values of all the solutions were near 6.2 within the range of the isoelectric point of C12AS, which agrees with our previous investigations [3,12,23].