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Properties of quaternary ammonium surfactant with hydroxyethyl group and anionic surfactant mixed systems

Jun Li, Yunling Li *, Yongbo Song, Zhifei Wang, Qinghong Zhang

China Research Institute of Daily Chemistry Co., Ltd., Taiyuan 030001, PR China

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ABSTRACT

The surface activities and application properties for the mixtures of cationic surfactant didecylmethylhydroxyethylammonium acetate (DEAQ) and anionic surfactant sodium fatty alcohol ether carboxylate (AEC_9-Na) were studied systematically. The interaction parameters and thermodynamic micellization parameters of DEAQ/AEC_9-Na mixtures were evaluated. Results showed that the mixed systems have higher surface activity, lower contact angle and better wetting ability than either component due to the synergistic effect and there are attractive interactions between molecules for the surfactant mixtures at the mixed micelles and the air/liquid interfaces. The thermodynamic parameters indicate that the micellization of the mixtures is an entropically driven process. When the mole fraction of DEAQ (α_{DEAQ}) is 0.608, the emulsifying capacity for liquid paraffin and soybean oil of DEAQ/AEC_9-Na mixtures is the best among the mole ratios studied, and the emulsifying capacity of the mixtures is stronger than that of AEC_9-Na except $\alpha_{DEAQ} = 0.509$. For the mixed systems, the foaming ability is the best when $\alpha_{DEAQ} = 0.608$, whereas the foam stability is the best when $\alpha_{DEAQ} = 0.280$. And there were greater foaming abilities and foam stabilities for mixed systems than those of DEAQ.

1. Introduction

Surfactant mixed systems are always widely used rather than single surfactants for practical applications, either because commercial surfactants are always mixtures due to the raw materials used and method of manufacture or because mixtures of surfactants often show better performance properties than individual ones [1–5]. The Mixed binary surfactants systems containing cationic surfactants can be formed by cationic/anionic [6–9], cationic/cationic [10], cationic/nonionic [11], and cationic/zwitterionic surfactant systems [12], in which anionic/cationic systems are mostly investigated.

It has long been well known that the mixtures of cationic and anionic surfactants exhibit the stronger synergistic effects under some special conditions, as evidenced by the lower surface tension and critical micelle concentration (cmc). Such synergetic effects mainly arise from electrostatic interactions between two surfactant molecules with oppositely charged head groups [13,14]. They are important for a wide range of applications in industries such as oil recovery, printing industry, wastewater treatment, textile wetting, froth flotation, pharmaceutical production and so on [15–17]. However, it is easy to precipitate or flocculate with the increasing of surfactant concentration. For some anionic/cationic mixed systems, the solubility of mixtures is so small that the precipitation concentration is lower than the cmc value [18–21], which limited the thorough study of such systems. Researchers have found that to introduce oxyethylene (EO) units into the hydrocarbon chain or hydrophilic groups of surfactant molecules can greatly improve the solubility of cationic/anionic mixed systems [22,23], which made it possible to extend research work to mixtures of anionic and cationic surfactants with relatively long chains.

Fatty alcohol polyoxyethylene ether carboxylates (AEC) combine the advantages of both anionic and nonionic surfactant types, which are mild, safe, and biodegradable. The existence of oxyethylene units can improve solubility. Moreover, AEC shows excellent compatibility with other different types of surfactants [24–27]. In the past several years, lots of researchers have investigated the effect of adding hydroxyethyl groups (CH_2CH_2OH) to the hydrophilic group of quaternary ammonium salts. Wang et al. [28] synthesized a series of quaternary ammonium salts containing hydroxyethyl group, and discovered that the surface activity increases with increasing the number of hydroxyethyl groups on hydrophilic groups of surfactants. Sun [29] also synthesized a new quaternary ammonium salt with two alkyl chains and a hydroxyethyl group and concluded that this quaternary ammonium salt with hydroxyethyl group exhibits high surface activities and good bactericidal efficacy. According to the reports on the aggregation properties of quarternary ammonium type cationic gemini surfactants containing dihydroxyethylamino headgroups [30], we can found that these surfactants can form both micelles and vesicles in aqueous solution, and the hydroxyethyl groups are a dominant factor in the determination of these unique aggregation

* Corresponding author at: 34# Wenyuan Str., Taiyuan, Shanxi Province 030001, PR China.
E-mail address: lyunl0068@sina.com (Y. Li).

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behaviors. Zhang and his coworkers [31] had characterized a cationic surfactant with a Guerbet-type branched tail and hydroxyl-decorated head group and made a conclusion that the introduction of hydroxylated hydrophilic head was proposed to be responsible for the outstanding performances of the new amphiphilic material. In a word, quaternary ammonium salts with hydroxyethyl groups have some special properties.

Didecylmethylhydroxyethylammonium acetate (DEAQ) is a new type quaternary ammonium salt cationic surfactant, which with a hydroxyethyl group, two alkyl chains and a novel counterion. Researches on mixtures of DEAQ and other surfactants were little. So in our work, we aim to exploring the synergetic behaviors of mixtures of DEAQ and sodium fatty alcohol ether carboxylate (AEC_9-Na).

In this paper, we added DEAQ to AEC_9-Na with different mole proportions and the interaction behaviors and various physicochemical properties for the mixtures of DEAQ with AEC_9-Na were investigated. The wetting ability, emulsify capacity and foaming properties of the mixed systems were also evaluated. The important results about the mixed systems may provide a theoretical and technical support for broadening their applications in detergent formula and life cleaning.

2. Experimental section

2.1. Materials

Didecylmethylhydroxyethylammonium acetate (DEAQ) and sodium fatty alcohol ether carboxylate (AEC_9-Na, carbon length is 12–14, was synthesized by oxidation process) were supplied by the China Research Institute of Daily Chemistry Co., Ltd. Their structures were showed in Scheme 1. Liquid paraffin was purchased from Tianjin University Chemical Reagents Co., Ltd. Soybean oil marked with Arawana was purchased by Qinhuangdao, Hebei province.

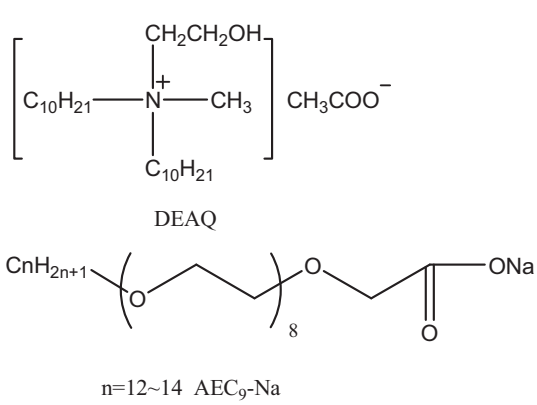
2.2. Properties

2.2.1. Surface tension measurement

The surface tensions of samples were measured from a series of aqueous solutions with a platinum ring using a Biolin Sigma 700 Processor Tension meter at 25 ± 0.2 °C. The surface tension of double distilled water was measured to calibrate instruments, which was generally 72.00 ± 0.50 mN/m. Every sample solution was prepared with the double-distilled water which was stabilized for 5 min in the instrument before measurements and was repeated three times to reduce the error.

2.2.2. Contact angle test

Contact angle test was carried out to measure the spreading of surfactant solutions on a Drop Shape Analyzer DSA255 (Krüss Company, Germany) equipped with a CCD camera at room temperature (298 K), using parafilm as a solid substrate. Each experiment was repeated at least three times to ensure the accuracy of results.



Scheme 1. Chemical structures of DEAQ and AEC_9-Na.

2.2.3. Wetting ability

The wetting abilities of samples were measured by canvas sedimentation [32]. Different aqueous solutions with the concentration of surfactant mixtures of DEAQ and AEC_9-Na being 1.5 g/L were prepared in advance into 1000 mL beakers. A canvas was immersed to the surfactant solution at room temperature, after some time, the canvas was permeated by surfactant solutions and began to sink. We generally record the period from immersion to sinking to evaluate the wetting ability. The above operation was repeated three times. The average value is wetting time of surfactant solution. The wetting ability is in negative correlation with the wetting time.

2.2.4. Emulsifying capacity

Emulsifying test was operated in glass-stoppered measuring cylinder of 100 mL at room temperature [33]. Liquid paraffin or soybean oil (40 mL) and aqueous solution of surfactant mixtures of 1.5 g/L (40 mL) were added and emulsified by shaking vigorously for five times every 1 min. After the last shaking, the measuring cylinder was kept standing and the demulsification process was observed. Time was recorded during which 10 mL water was separated from the emulsion. The longer time it takes, the better emulsifying capacity the surfactant has.

2.2.5. Foaming properties

The foaming properties were tested using the Modified Ross-Miles method at 50 °C [34]. First, 50 mL aqueous solution of surfactant mixtures of 1.5 g/L was poured into the bottom of a flask. Then, 500 mL of the solution in a funnel was placed into the flask from the top of the apparatus. After the solution had run out of the funnel, the time and foam volume were recorded at 30 s, and 3 min. Foaming ability was determined by the foam volume after 30 s. Foam stability was determined by ratio of the foam volume at 3 min and 30 s in the Ross-Miles apparatus.

3. Results and discussion

3.1. Surface tension measurements

The surface activity of the single surfactants and binary surfactant mixtures (DEAQ/AEC_9-Na) was investigated by surface tension measurements at 298 K. The plots of surface tension (γ) versus concentration of the surfactant mixtures at various mole fractions of DEAQ (α_{DEAQ}) were depicted in Fig. 1.

From Fig. 1, we can infer that the mixed systems show better surface activity than either component due to the lower critical micelle

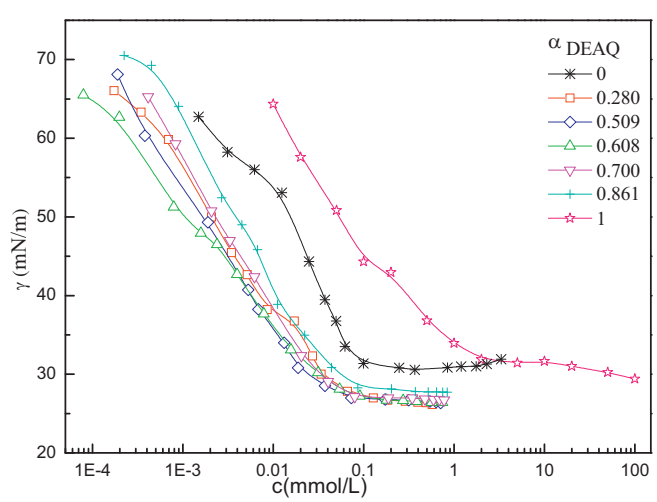


Fig. 1. Surface tension vs. concentration for DEAQ/AEC_9-Na mixtures at various α_{DEAQ} at 298 K.