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Synergistic effect of binary mixtures contained newly cationic surfactant: Interaction, aggregation behaviors and application properties

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ABSTRACT

The synergistic effect in mixed different mole ratio of cationic with anionic, nonionic and zwitterionic surfactant binary systems are investigated, respectively, by surface tension, FTIR, DLS and TEM measurements. Besides the application properties of wetting, emulsification, foamability in binary systems of anionic or nonionic with addition of 1% or 3% cationic surfactant are also performed. Molecular interactions are characterized by the synergistic parameters β_m and the deviation between the ideal system and experimental results are also discussed. It shows the synergistic effects (evaluated by β_m) of investigated four systems has follow orders: cationic/anionic > cationic/nonionic (without ethoxylate unit) ≈ cationic/zwitterionic > cationic/nonionic (with ethoxylate unit). The aggregates size in cationic/anionic systems demonstrate cationic-rich mixtures easier forming large aggregates, but not vesicles observed in all investigated mole ratios. The wetting angle increased for anionic or nonionic surfactant with addition of 1% or 3% (weight percentage) $C_{16}NC_1$. Emulsification ability of mixed anionic enhanced but nonionic slightly decreased with addition of small amount of $C_{16}NC_1$. And the foam volume decreased for anionic/cationic systems, oppositely, an increasing in foam high for mixture of cationic/nonionic surfactant.

1. Introduction

Cationic surfactants are versatile in many aspects, including antibacterial, anti-electrostatic, bentonite inhibitor in oil field, corrosion inhibitor for metal, and act as structural and mesoporous template [1–4]. Industry applications of surfactants are universal involving mixtures of two or more surfactants. Therefore, it is highly important to identify the differences between applications properties and surface activity, in mixed binary surfactant systems of cationic and other surfactants.

Mixed binary surfactants systems containing cationic surfactants including: anionic/cationic, nonionic/cationic, zwitterionic/cationic, cationic/cationic, polymer/cationic, in which anionic/cationic systems are mostly investigated. The multiple phase behaviors including vesicles, wormlike micellar and liquid crystal structures, always combined with the synergism effect in anionic/cationic mixed systems. The foaming properties in different mole ratios of equal hydrophobic length of cationic/anionic surfactant mixtures are systematically investigated [5], founding that foam stability differ for different mixing ratio and relays on surface charge and surface layer composition, with excess anionic surfactants forming a stabilized foam film, but excess of cationic generally leads to formation of unstable foam. Synergism in mixed binary surfactant systems vary with the charge character of two surfactants. However, the foam ability and the detergent efficient are disagree with this trend [6], indicates the application properties in binary systems are different with synergism in surface active. The synergism effect in binary system of cationic-anionic systems is most strong [7–11], generally shows a sharply decreases in surface tension and critical micelle concentration (CMC) and more negative interaction parameter β, thus, contribute to formation precipitate [10,12]. Interaction in anionic-nonionic systems is moderate [13–15], cationic/zwitterionic systems is pH dependent [16,17], and the interaction in cationic-nonionic mixture is weak [18,19] due to the dipolar group, such as S=O or CH_2CH_2O, in which the electronegative oxygen atom easier being protonated, thus, leading partly positive charged of nonionic surfactant contained ethoxylate groups, hence, interaction more strong with anionic than cationic surfactants. But for alkylglycosides without ethoxylate groups, the slightly acidic of alkylglycosides (APG_{0810}) gift it weakly anionic character [20], hence interaction more strong with cationic surfactants than anionic ones. Generally, the application properties of mixed system probably have few been discussed, and binary surfactants systems containing cationic with newly counterion has never been reported.

To the research and development of cationic contained washing products, cationic surfactants cetyltrimethylammonium formate ($C_{16}NC_1$) was selected. Anionic surfactants: sodium dodecyl benzene sulfonate (LAS), alkylpolyoxyethylene sulphates (AES); nonionic surfactants: fatty alcohol polyoxyethylene ether (AEO_9) and green surfactants Alkyl poly glucoside (APG_{0810}) [21]; zwitterionic surfactant: dodecyl dimethyl betaine (BS_{12}) were selected, and one of which is mixed with $C_{16}NC_1$. In order to reveal relationship between surface active and

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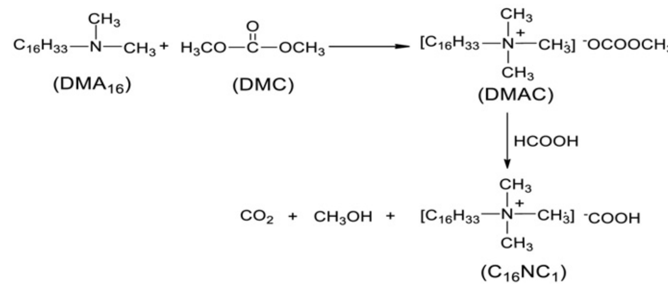
application properties in those compound systems, surface tension measurements and application properties, such as, emulsification, foaming, wetting and detergency ability were carried out.

2. Experimental section

2.1. Materials

Sodium dodecyl benzene sulfonate (LAS); sodium dodecyl ethers (AES) usually named alkylpolyoxyethylene sulphates; fatty alcohol polyoxyethylene ether (AEO_9) is nonionic ethoxylated surfactant with 9 ethoxylate units, business named Brij, CAS NO: 68131-39-5; (C_{8-10}) alkyl poly glucoside (APG_{0810}), CAS NO: 68515-73-1; dodecyl dimethyl betaine (BS_{12}), CAS NO: 683-10-3. Those molecular structures were shown in Fig. 1, all were commercial samples received from Shanghai Kay Chemical co., Ltd. And those surfactants used without further purified, with the average molecular weight respective was 348 g/mol, 386 g/mol, 582 g/mol, 370 g/mol, and 271 g/mol, and active substance corresponded to 78%, 70%, 99%, 50%, and 31.5%, respectively. Cetyltrimethylammonium formate ($C_{16}NC_1$) was synthesis by two steps routes [22,23] (Scheme 1), and purified with ethyl acetate to obtain a 99% purity. $C_{16}NC_1$ was characterized using nuclear magnetic resonance (^1H NMR) (in Fig. S1), Fourier transform infrared spectroscopy (FTIR) (Fig. S2) and element analysis by Perkin Elmer 2400 CHN analyzer. $C_{16}NC_1$ FTIR (KBr, cm^{-1}): 2910, 2850 v (C—H for —CH_3 or —CH_2—), 1609 v (C═O for carboxyl), 1487–1347 δ (C—H for —CH_3 or —CH_2—), 721 r (C—H for >CH_2). $C_{16}NC_1$ ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 0.79–0.83 (m, 3H, $\mathbf{CH_3}CH_2(CH_2)_{13}$) 1.19–1.29 (s, 26H, $CH_3CH_2\mathbf{(CH_2)_{13}}$), 1.64–1.69 (t, 2H, $N(CH_3)_3CH_2\mathbf{CH_2}$), 3.40–3.44 (m, 2H, $N(CH_3)_3\mathbf{CH_2}CH_2$), 3.34 (s, 9H, $N\mathbf{(CH_3)_3}$), 8.47 (s, 1H, COO**H**). Element analysis results: N (4.16%), C (73.17%), H (13.16%), O (9.54%), which is in accordance with theoretical results: N (4.25%), C (72.95%), H (13.07%), O (9.73%).



Scheme 1. Syntheses routes of cationic surfactant $C_{16}NC_1$.

2.2. Surface property measurements

Wilhelmy plate method was adopt for surface tension measurements, with a 19.9 mm in length and 0.2 mm in thickness of platinum plate and the measurement time Intervals fixed at 30 s in adjacent two point with maximum deviation is 0.2 mN/m. Tensiometer was corrected with doubly distilled water till the surface tension approximately to 72 mN/m before each operation. All samples were aged 24 h before detect and temperature kept at 25 ± 0.1 °C.

The surface tension as function of logarithmic sample concentration, from which the CMC and minimum surface tension (γ_{CMC}) were obtained. To calculate synergism effects in surface active. The theory for ideal mixed surfactant systems of both $ionic_1/ionic_2$ and nonionic/ionic were as follows. The prediction of critical micelle concentration for ideal

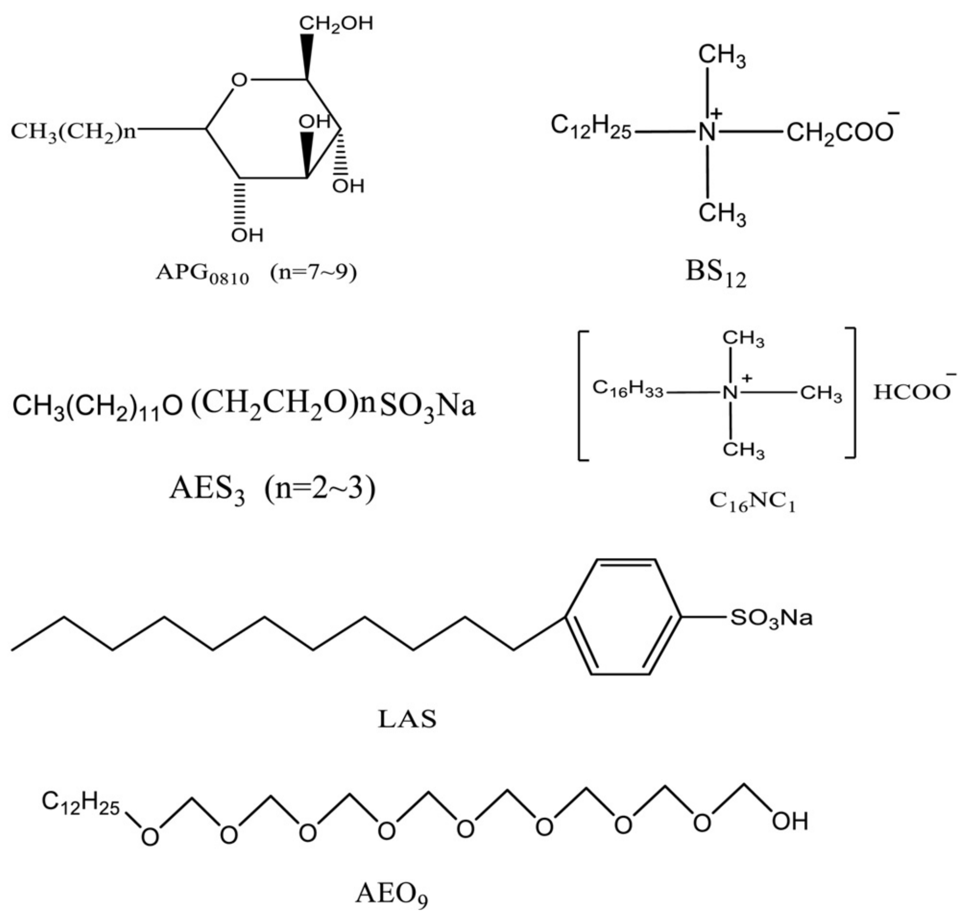


Fig. 1. Molecular structure for investigated surfactants.