A novel fluorinated quaternary ammonium salt cationic surfactant \( \text{N,N,N-trimethyl-2-\{[4-\{[3,4,4,4-tetrafluoro-2-\{1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl\}-1,3-bis(tri-fluoromethyl)-1-buten-1-yl\}oxy\]-benzoyl\}amino\}-iodide} \) (FQAS) was synthesized successfully, and its structure was characterized by FTIR, \(^1\)H-NMR, \(^{19}\)F-NMR, and MS. The surface activities of FQAS and the effect of temperature, electrolyte, and combination with hydrocarbon surfactant were investigated. The results showed that FQAS exhibited excellent surface activity and combination with hydrocarbon surfactant.

1. Introduction

A surfactant is an amphiphilic molecule bearing both hydrophobic and hydrophilic parts. The fluorinated surfactants have generated much interest for high surface activity, chemical resistance, thermal stabilization, and low critical micelle concentration. Cationic fluorinated surfactants were generally used in coatings [1–3], paints [4], inks [5, 6], waxes, additives for etching, leather, firefighting foams [7, 8], and other applications [9–16].

The most known are perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) (Scheme 1). However they are persistent in the chemosphere, toxic, bioaccumulable pollutants and can be transferred into the environment such as soil and water as well as in the animal body through the food chain [17]. The US Environmental Protection Agency launched the PFOA Stewardship Program to decrease the production of PFOA and PFOS. However, decomposition of perfluorooctanoic acid photocatalyzed by \( \text{TiO}_2 \) was reported recently [18]. Hexafluoro propylene oligomers are an important class of compounds which can be used to prepare useful PFOA and PFOS replacements fluorinated anionic, cationic, nonionic, and amphoteric surfactants [19, 20].

In this paper, we describe a new fluorinized quaternary ammonium salt cationic surfactant \( \text{N,N,N-trimethyl-2-\{[4-\{[3,4,4,4-tetrafluoro-2-\{1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl\}-1,3-bis(tri-fluoromethyl)-1-buten-1-yl\}oxy\]-benzoyl\}amino\}-iodide} \) (FQAS) using the \( 4\text{-\{[3,4,4-Tetrafluoro-2-\{1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl\}-1,3-bis(tri-fluoromethyl)-1-buten-1-yl\}oxy\]-benzoyl\}amino\}-iodide \) (Scheme 2). The surface activity of FQAS, such as surface tension and critical micelle concentrations (cmc), the effect of temperature and electrolyte on the surface activity of FQAS, and the surface activity of FQAS mixed with nonionic hydrocarbon surfactant polyethylene glycol 400 (PEG400) were investigated in detail.

2. Results and Discussion

2.1. Surface Tension. Unlike many fluorinated surfactants, the branch fluorinated cationic surfactant (4) (FQAS) exhibits excellent solubility in water at room temperature; thus, it could be employed to reduce the surface tension of water. The curve of surface tension was obtained by Wihemlmy (Figure 1). It can be seen in Figure 1 that the cmc value of FQAS in water is \( 6.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1} \) at 293 K and the
2.2. Effect of Temperature on FQAS Surface Tension. Temperature is a significant effect factor for the surface tension of ionic fluorinated surfactant.

At $1.2 \times 10^{-5}$ mol·L$^{-1}$, the surface tension of FQAS decreased from 67.0 mN·m$^{-1}$ to 54.8 mN·m$^{-1}$, when the temperature was increased from 293 K to 313 K (Figure 2). The present data shows that the effect of temperature was small when the concentration of FQAS is high ($\geq 1.3 \times 10^{-4}$ mol·L$^{-1}$). This phenomenon can be explained by the following facts. The fluorinated surfactant tends to be adsorbed at the interface, driving the system to a thermodynamically more stable state. The effect of adsorption form both sides at the vapor/liquid interface was considered simultaneously. The result is a reduction in Gibbs energy, thereby a decrease in surface tension [23–25].

2.3. Effect of Electrolyte on the Surface Tension of FQAS. The FQAS exhibited lower surface tension at different electrolyte

surface tension of the aqueous solution is 21.1 mN·m$^{-1}$ at the cmc. However, the value of cmc for hexadecyl trimethyl ammonium chloride (HTAC) is $1.6 \times 10^{-3}$ mol·L$^{-1}$, and the surface tension is 42.3 mN/m at the same temperature (in the literature Applied Surfactants, John Wiley & Sons Inc.). The cmc value of branch fluorinated cationic surfactant FQAS is remarkably lower than that of the hydrocarbon surfactants HTAC for the C-F group introduced [21, 22]. We infer that the decrease results from the formation of a closely packed film of fluorinated cationic surfactant caused by further adsorption of the surfactant to the air/aqueous solution interface.

**Figure 1:** Surface tension of FQAS versus logarithm concentration/mol·L$^{-1}$ (lg C).
concentrations of NaCl (1.0 g·L⁻¹ and 5.0 g·L⁻¹) aqueous solution (Figure 3). It can be seen in Figure 3 that the effect of electrolyte on the surface tension of FQAS is small. That shows FQAS has good salt resistance. The electrolyte remains in many aspects enigmatic. Although the phase at which the solution is at equilibrium does neither attract nor repel electrolytes, the solutes absorb either positively or negatively depending on their nature. It has strong attraction with just one water molecule under ions free. In double-layer terminology, they should be classified as “indifferent.” Rather, their hydration with more water molecules keeps them out of the surface region. The observed ionic specificities are relatively minor and do not exhibit a clear ionic trend. According to general expectation, bigger ions would dehydrate more easily than the smaller ones and hence are more inclined to enrich the surface [26, 27]. However, the Ca²⁺ and Mg²⁺ may vary dramatically with changes in the solubility of FQAS, which can make the surface activity poor.

2.4. Combination with Hydrocarbon Surfactant. The different mass ratio nonionic surfactant PEG600 was mixed with FQAS. Surface tension was measured for mixed surfactant solution of different concentrations at 293 K (Figure 4). The surface tension was decreased with the increase in the total concentration and the mass ratio of FQAS of combined surfactants. This suggests that when micelles begin to from at the critical micelle concentration, the impurity becomes soluble in the micelles because of its hydrophobic character. The concentration in bulk and surface concentration have been reduced. Therefore, the interaction between the combined surfactants is strengthened [28–32].

3. Conclusion

The novel branch fluorinated cationic surfactant N,N,N-trimethyl-2-[[4-[[3,4,4,4-tetrafluoro-2-[1,2,2,2-tetrafluoroo-1-(trifluoromethyl)ethyl]-1,3-bis(tri-fluoromethyl)-1-buten-1-yl]oxy]-benzoyl]amino]-iodide (FQAS) was synthesized successfully. The structure was characterized by FTIR, ¹H-NMR, ¹⁹F-NMR, and MS. The surface activities of FQAS, the effect of temperature, electrolyte, and combination with hydrocarbon surfactant were investigated. The results showed that FQAS exhibited excellent surface activity and combined properties.
4. Experimental

4.1. Materials and Instruments.

4-Perfluoro-1, 3-dimethyl-2-isopropyl)-but-1-enyloxy)-benzoic acid was purchased from Juhua Group Corporation, Quzhou, China. Sulphoxide chloride, N, N-dimethyl ethylenediamine, and iodomethane, which were analytical grade, were purchased from Shuanglin Chemical Reagent Company, Hangzhou, China. Melting points were determined using an X-4 apparatus and uncorrected. FTIR were recorded of Nicolet Avata 370 Fourier transform infrared spectrometer from KBr pellets. NMR (CDCl₃) as solvent. Mass spectra were measured on a Bruker AV500 instrument using TMS as an internal standard and CDCl₃ as solvent. Mass spectra were prepared on a Thermo Finnigan LC Advantage LC/mass detector instrument. The characterization of the surface tension was carried out on DCA-315 equipped with a Wilhelmy plate made of platinum.

4.2. Synthesis of FQAS

4.2.1. 4-((3,4,4,4-Tetrafluoro-2-1,2,2,2-tetrafluoro-1-(trifluoro-methyl)-1-buten-1-yl)oxy)-benzoyl chloride (2). To a solution of 4-([3,3,3,4,4,4-tetrafluoro-2-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-1,3-bis(trifluoro-methyl)-1-buten-1-yl]oxy)-benzoic acid (1) (28.4 gm, 0.05 mol) in CCl₄ (50 mL) and sulphoxide chloride (II.90 gm, 0.10 mol) was added stepwise slowly at room temperature (33–35). After refluxing for 3 h, the solvent and excess of sulphoxide chloride were evaporated to give the viscous liquid.

4.2.2. N-(2-Dimethylamino-ethyl)-4-((3,4,4,4-tetrafluoro-2-1,2,2,2-tetrafluoro-1-trifluoromethyl-ethyl)-1,3-bis-trifluoromethyl-buten-1-enyloxy) benzamide (3). To a solution of compound (2) (2.93 gm, 0.005 mol) and K₂CO₃ (0.69 gm, 0.005 mol) in CH₃CN (40 mL), N,N-dimethyl ethylenediamine (0.58 gm, 0.006 mol) was added dropwise at room temperature [36–38]. After refluxing for 5 h, it was quenched with water (50 mL). Then the resultant solution was extracted by ethyl acetate (3 × 50 mL). The combined organic phase was dried by Na₂SO₄. The solvent was evaporated to give a white residue, which was recrystallized in ethyl acetate and petroleum ether to afford a light yellow solid (3) (2.71 gm, 85%). IR (cm⁻¹): ν(N–H) 3255, ν(C=O) 1655, ν(C=C) 1601,1502, ν(C–F) 1185,1134; ¹H-NMR (CDCl₃) δ = 7.81 (d, J = 9.80 Hz, 2H, ArH), 6.95 (d, J = 8.75, 2H, ArH), 3.56–3.58 (m, 2H, CH₂), 2.50–2.51 (m, 2H, CH₂), 2.30 (s, 6H, CH₃); and MS (EI) m/z 638.09 (M-I).

4.2.3. N,N,N-Trimethyl-2-((3,4,4,4-tetrafluoro-2-1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl)-1,3-bis(trifluoromethyl)-1-buten-1-yl)oxy)(benzoyl)amino)-iodide (4). Compound (3) (3.19 gm, 0.005 mol) and iodomethane (1.42 gm, 0.01 mol) were refluxed in MeCN (50 mL) for 5 h under the atmosphere of N₂, and then the resultant mixture was cooled to room temperature. After the solution was evaporated under reduced pressure, the resulting residue was recrystallized in acetic ether and petroleum ether. The resulting white solid (4) (3.52 gm, 90%) was dried under reduced pressure. IR (cm⁻¹): ν(N–H) 3446, ν(C=O) 1626,1590,1491, ν(C–O) 1242, ν(S=O) 1014, ν(C–F) 1240,979,742. ¹H-NMR (CDCl₃) δ = 8.15 (d, J = 8.55 Hz, 2H, ArH), 6.95 (d, J = 8.70 Hz, 2H, ArH), 3.87–3.85 (m, 2H, CH₂), 3.63–3.65 (m, 2H, CH₂), 2.67 (s, 9H, CH₃); ¹⁹F-NMR (CDCl₃): −188.5 ppm (1F, F), −186.5 (1F, F), −91.3 (6F, CF₃), −90.2 (6F, CF₃), −75.0 (3F, CF₃); MS (EI) m/z 654.1 (M-I).

4.3. Measurements.

The static surface tension was measured using Thermo Cahn surface tension requirements (DCA-315) with platinum plate. The measurement were performed under 293 K after equilibration for 8 h. The solution preparation of FQAS used distilled water.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References


