



Synthesis and interface activity of a series of carboxylic quaternary ammonium surfactants

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ABSTRACT

Quaternary ammonium salt cationic surfactants are inevitably involved in many industrial applications because of their distinguishingly chemical performances, but the effect of anions on different performances of quaternary ammonium salt cationic surfactants is also scarcely discussed. In this study, four carboxylic quaternary ammonium surfactants, cetyl-trimethyl ammonium acetate (CTAAC), cetyl-trimethyl ammonium butyrate (CTABU), cetyl-trimethyl ammonium hexanoate (CTAHE) and cetyl-trimethyl ammonium caprylate (CTACA) were prepared to study the effect of carboxylate groups on the performances of four surfactants. Surface properties including critical micelle concentration (CMC), the surface tension at the CMC (γ_{CMC}), maximum surface excess (r_{max}), minimum surface area (A_{min}) were investigated. The results showed that the surface activity of CTAAC was the highest compared with other members in the prepared surfactants. Foamability and foam stability of four surfactants were evaluated with the standard Ross-Miles method. The results indicated that foamability and foam stability followed the order of CTAAC > CTABU > CTAHE > CTACA under the same condition. In addition, the emulsion stability measurements of surfactants showed their low emulsifying tendency towards crude oil at 60°C.

Keywords: Quaternary ammonium surfactant; Surface tension; Foam properties; Emulsion stability

1. Introduction

Surfactants have enjoyed great interest and have been extensively studied over the years because their wide application in commonly used products such as fabric softeners, cosmetics, electron coatings [1–4], antimicrobial agents as well as in mining and paper manufacturing [5] but also for their mildness to eyes, skin, and clothes and their biodegradability. Researchers have introduced many kinds and uses of surfactants in industrial and biological areas [6]. The cationic

surfactants are one of the most widely studied surfactants in recent years. Since the cationic surfactants have commendable applications in laundry detergents for their ability to improve the packing of anionic surfactant molecules at the stain-water interface which is attributed to the fact that cationic surfactants could effectively reduce the surface tension of soil-water interface [7,8]. According to the functional group [9–11], the most investigated and commercially-available cationic surfactants are amphiphiles based on quaternary ammonium salts [12–14]. Structurally, they possess a

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pH-independent positive charge since nitrogen is covalently linked to four different alkyl or aryl groups. Therefore, the positive charge on quaternary ammonium salt cationic surfactants make them adsorbed onto oppositely charged surfaces due to ion exchange, which leads to their extensive applications, such as biocides, asphalt additives, corrosion inhibitors, cosmetics, fabric softeners, textile auxiliaries, petroleum recovery, wastewater treatment, dispersants after oil spill, etc [15–18].

Generally, there are one hydrophilic head group and one hydrophobic tail group in a molecule of quaternary ammonium salt cationic surfactant. In these general surfactants, there are limited to the improvement of their performances [19]. Hence, in order to further improve performances of quaternary ammonium salt cationic surfactants, one of the traditional methods is an introduction of new functional groups into the hydrophilic part. The presence of the positively charged nitrogen atom in cationic may be ensured by the introduction of alkyl, hydroxyalkyl, and other functional groups enabling them to obtain surfactants of outstanding performances. However, the method of obtaining new surfactants by changing anions has received little attention, and the effect of anions on different performances of quaternary ammonium salt cationic surfactants is also scarcely discussed [20,21]. In this paper, carboxylic quaternary ammonium surfactants, cetyl-trimethyl ammonium acetate (CTAAC), cetyl-trimethyl ammonium butyrate (CTABU), cetyl-trimethyl ammonium hexanoate (CTAHE), cetyl-trimethyl ammonium caprylate (CTACA) were designed and prepared. The molecular structures and synthesis process were shown in Fig. 1. Their molecular structures had the same different ions with the same charges even though their hydrophobic and hydrophilic groups were the same. Therefore, the aim of the present work was to discuss the effect of different carboxylic groups on the surface tension, foam properties as well as emulsion stability.

2. Experimental setup

2.1. Materials

The oil was obtained from a low-permeability reservoir in the Changqing Oilfield, China. The viscosity, density, and components analysis of the oil were analyzed and are shown in Table 1. Cetyl-trimethyl ammonium chloride (CTAC), AR, purity was purchased from Tianjin Kemiou Chemical

Table 1
Viscosity, density and component of the Changqing crude oil sample

Parameter	Value
Density (g cm ⁻³)	0.89
Viscosity ^{30°C} (mPa s)	188
Saturated (%)	46.64
Aromatic (%)	28.02
Wax (%)	0.78
Resin (%)	18.16
Asphaltene (%)	6.40

Reagent Co. Ltd., China. Sodium hydroxide, acetate, butyrate, hexanoate, caprylic acid, AR, were supplied from Xian Reagent Ltd., China. Methanol, AR, was obtained from Chengdu Aikeda Chemical Reagent Co. Ltd., China. The distilled water was used in all experiments.

2.2. Synthesis of new surfactants

A mixture of intermediates CTAC (5.0 g, 0.015 mol) and sodium hydroxide CTAC (0.6 g, 0.015 mol) in 1:1 ratio in 100 mL methanol solvent were added into 250 mL round bottom flask at 25°C. The end of the reaction was determined by a certain white powder. Then, the supernatant was reacted with acetate (0.9 g, 0.015 mol), butyrate (1.32 g, 0.015 mol), hexanoate (1.74 g, 0.015 mol) and caprylic acid (2.16 g, 0.015 mol), respectively, the reaction mixture was vigorously stirred for 3 h at the reflux temperature of 85°C. After the reaction finished, the methanol solvent was removed by rotary evaporation, the crude product obtained was subsequently washed twice with 50 mL of ethyl acetate, and purified by recrystallization in fresh acetone at least three times. The precipitates after removal of acetone through vacuum filtration were dried in a vacuum drying oven for 24 h, which was given pure corresponding carboxylic quaternary ammonium surfactants. Their chemical equations are shown in Fig. 1. ¹H-NMR of CTAAC (D6-DMSO, 400 MHz): δ 3.65(s, 9H), 3.20(t, J = 7.6 Hz, 2 H), 2.35(s, 3 H), 1.69(m, 2 H), 1.28–1.31(m, 36 H), 0.96 (t, J = 7.6 Hz, 3 H); ¹H-NMR of CTABU (D6-DMSO, 400 MHz): δ 3.65(s, 9 H), 3.20(t, J = 7.6 Hz, 2 H), 2.30(t, J = 7.6 Hz, 2 H), 1.69(m, 2 H), 1.66(m, 2 H), 1.28–1.31(m, 36 H), 0.97(s, 3 H),

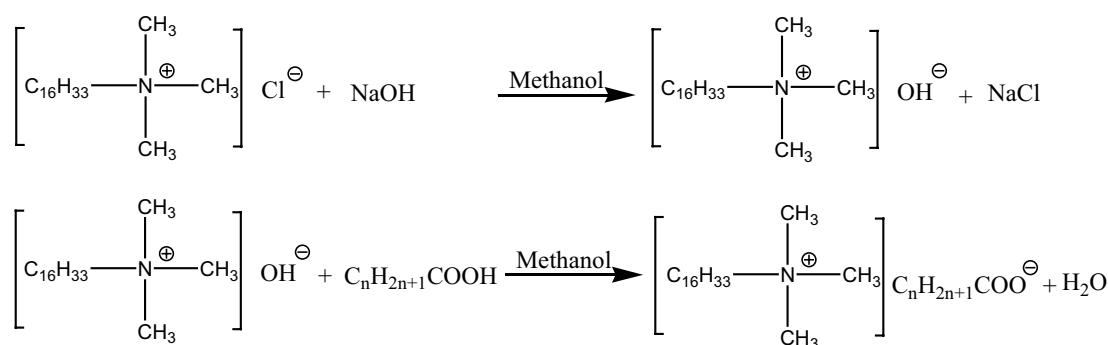


Fig. 1. Synthesis route of carboxylic quaternary ammonium surfactants.

0.96(t, $J = 7.6$ Hz, 3 H); $^1\text{H-NMR}$ of CTAHE (D6-DMSO, 400 MHz): δ 3.65(s, 9 H), 3.20(t, $J = 7.6$ Hz, 2 H), 2.30(t, $J = 7.6$ Hz, 2 H), 1.69(m, 2 H), 1.66(m, 2 H), 1.28–1.32(m, 40 H), 0.96–0.97(m, 6 H); $^1\text{H-NMR}$ of CTACA (D6-DMSO, 400 MHz): δ 3.65(s, 9 H), 3.20(t, $J = 7.6$ Hz, 2 H), 2.30(t, $J = 7.6$ Hz, 2 H), 1.69(m, 2 H), 1.65(m, 2 H), 1.28–1.32(m, 44 H), 0.96–0.97(m, 6 H).

2.3. Surface tension measurement

The surface tension of prepared surfactant aqueous solutions was conducted on a thermostated K-12 processor tensiometer (Krüss, Germany) using the plate method in a single-measurement way [22]. The platinum ring was cleaned several times by distilled water and acetone before each measurement to obtain the standard surface tension value (72.00 ± 0.50 mN m^{-1}) at the temperature of 25°C. The surface solutions were prepared at the least 1 d before the measurement, and the values of surface tension were the average over three measurements until those values were reproducible [23–25].

2.4. Foam properties

There are many methods for generating foam, such as the sparge tube technique or gas flow and whipping [26]. The standard method for evaluating the foam properties is the Ross-Miles method [27]. First, 300 mL surfactant aqueous solutions, with a concentration range of 80–5,000 mg L^{-1} , were prepared at the temperature of 25°C. Among those solutions, 250 mL aqueous solution in the separating funnel was dropped slowly into the bottom of the cylinder with 90 cm height and 2.9 mm inner diameter. After the solution in the separating funnel had run out, the time was recorded immediately. The foam height was immediately recorded at 0 min and 3 min. Foamability was determined by the initial foam height. Foam stability was determined by the ratio of the foam height at 0 and 3 min [24]. All values of foam height were the average over three measurements until those values were reproducible.

2.5. Microstructure of foam

100 mL surfactant solutions were prepared and blended at 7,000 rpm for 3 min. The foam was first generated by using the Waring Blender (7012S, Waring Ltd., America) and then the microstructure of foam was measured by an optical microscope, whose light source was the polarized light [28].

2.6. Emulsion stability

In order to determine the emulsion stability of carboxylic quaternary ammonium cationic surfactants. Those prepared surfactant samples were added into crude oil to prepare emulsions with different concentrations. The experiment procedures as follows: A certain volume of crude oil was measured and placed in a controlled heating apparatus at 60°C at 30 min. Next, some volumes of surfactant solutions were added to the crude oil and mixed in a measuring cylinder (50 mL capacity) for 30 min.

25 mL of the newly prepared emulsions were measured and shaken up and down for 10 times every 1 min and allowed to settle [29,30]. The volume of the oil phase (V) could be observed and measured. The calculation Eq. (1) as follows:

$$\omega = \frac{(25 - V)}{25} \times 100\% \quad (1)$$

3. Results and discussion

3.1. Surface tension properties

The determination of the surface activity of the synthesized carboxylic quaternary ammonium cationic surfactants was based on the surface tension measurements of the surfactants solutions at a range of concentrations in the study. The relation between surface tension and $\log C$ is clearly shown in Fig. 2, it was indicated that the surface tension values firstly decreased continuously with the increase of solution concentrations, the tendency was attributed to the gradually adsorption of surfactant molecules at the air-water interface. The attractive forces between surfactant and water molecules were much lower than those persisting among water molecules, thereby resulting in surfactant orientation with hydrophobic tail protruding into the air and hydrophilic head acting as a surface anchor [31,32]. This trend continues to a critical point where a minimum value of surface tension was obtained. When surfactant concentration exceeded critical micelle concentration (CMC), the surface tension values kept almost a constant, which illustrated the complete surface saturation of surfactant molecules [22].

The CMC values and surface tension at the CMC (γ_{CMC}) were showed in Table 3. For the five surfactants, the γ_{CMC} values followed the order CTAAC < CTABU < CTAHE < CTAC < CTACA, which was indicated that CTAAC had low surface adsorption and the high area occupied by one molecule compared with individual systems. The difference

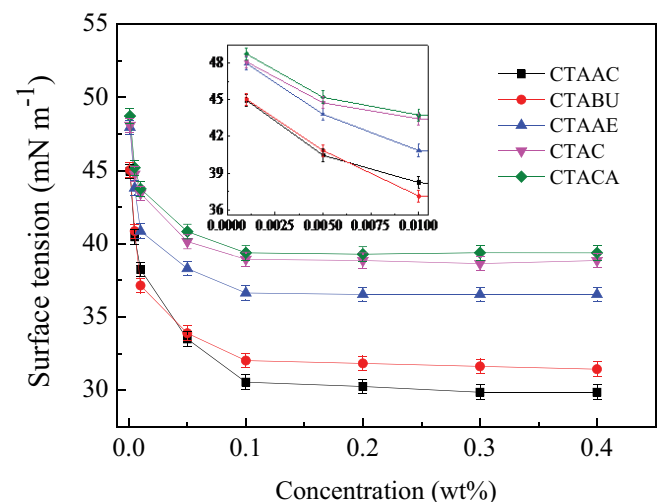


Fig. 2. Surface tensions of five surfactants aqueous solutions at 25°C.

Table 2
Abbreviation of the dicarboxylic cationic surfactants

Number of methylene	Name of different surfactant	Abbreviation
0	Cetyl-trimethyl ammonium acetate	CTAAC
2	Cetyl-trimethyl ammonium butyrate	CTABU
4	Cetyl-trimethyl ammonium hexanoate	CTAHE
6	Cetyl-trimethyl ammonium caprylate	CTACA

Table 3
Surface properties of different surfactants at room temperature

Surfactants	CMC (mmol L ⁻¹)	γ_{CMC} (mN m ⁻¹)	π_{CMC} (mN m ⁻¹)	$10^6 \Gamma_{\text{max}}$ (mol m ⁻²)	A_{min} (nm ²)
CTAAC	0.29	30.65	41.35	1.32	1.26
CTABU	0.27	32.07	39.93	1.28	1.30
CTAHE	0.26	36.73	35.27	1.05	1.58
CTAC	0.31	38.93	33.07	0.94	1.77
CTACA	0.23	39.61	32.39	0.92	1.80

could be attributed to the molecular structures of five surfactants. The series of carboxylic quaternary ammonium cationic surfactants had the same hydrophobic and hydrophilic groups except for carboxylic groups. Therefore, the carboxylic groups should be the principal factor to determine the differences between the aggregation properties [33]. Through the comparison of CTAAC, CTABU, CTAHE, and CTACA, it could be concluded that as the number of methylene segments of carboxylic groups increased (0, 2, 4, 6), the γ_{CMC} values gradually increased. This difference was explained that the methylene segments in carboxylic groups directly affected the distribution of surfactant molecules at the air-water interface. From Table 3, it could be inferred that the arrangement distance between the two hydrophobic tails was gradually increased with the increase of methylene segments, which influenced the adsorption capacity of surfactant molecules at the interface. For the CTAAC molecule with the shortest methylene segment in the carboxylic group, the lowest γ_{CMC} value suggested that the CTAAC molecule could be more tightly packed to each other at the air-water interface. Therefore, the surface tension evaluation was in good agreement with the general tendency that a fewer number of methylene segments of the carboxylic group favored the reduction of the surface tension [20].

To better understand the absorbing capacity of the five surfactants to reduce the surface tension of solutions, π_{CMC} value is referred to the effectiveness of surface tension reduction and calculated according to the following Eq. (2) [34]:

$$\Pi_{\text{CMC}} = \gamma_0 - \gamma_{\text{CMC}} \quad (2)$$

where γ_0 is the surface tension of distilled water with a value of 72.00 mN m⁻¹ at the temperature of 25°C (mN m⁻¹), other symbols are the same as the previous study. The π_{CMC} values indicated the maximum reduction in surface tension caused by the dissolution and those values are listed in Table 3, it is

shown that the π_{CMC} values of five surfactants followed the order CTAAC > CTABU > CTAHE > CTAC > CTACA. The larger values of CTAAC proved that it had superior surface activity than the other surfactants [34].

Γ_{max} and A_{min} are effective measures of the maximum surface excess concentration and packing densities at the air-solution interface, respectively. Their values are obtained according to the Gibbs adsorption isotherm Eq. (3) [35]. The minimum area, A_{min} is a traditional measure of packing densities and calculated according to the Gibbs adsorption isotherm Eq. (4) [36].

$$\Gamma_{\text{max}} = \frac{1}{2.303nRT} \left(\frac{\partial \gamma}{\partial \log C} \right)_T \quad (3)$$

$$A_{\text{min}} = \frac{1}{N_A \Gamma_{\text{max}}} \quad (4)$$

where Γ_{max} is the saturated adsorption amount ($\mu\text{mol m}^{-2}$), n is a constant dependent on the specific circumstances, which is concerning the number of solute species whose adsorption amount at the interface changes along with the surfactant concentration, R is the universal gas constant (8.314 J K⁻¹ mol⁻¹), T is the absolute temperature (K), and $(\partial \gamma / \partial \log C)_T$ is the slope below the CMC in the surface tension plots. A_{min} is the minimum surface area (nm²), N_A is Avogadro's constant (6.022×10^{23} mol⁻¹).

The Γ_{max} and A_{min} values of five surfactants in this study were determined at the temperature of 25°C and summarized in Table 3. From Table 3 it can be observed that the Γ_{max} values decreased with increasing methylene segments of carboxylic groups in the four surfactants (besides CTAC), which indicated that the surface adsorption at the air-water interface was mainly determined by the number of methylene segments of carboxylic groups. For CTACA molecule with long

methylene segments in the carboxylic group, its hydrophobic tails at the air-water interface usually packed loosely to each other which leads to very low surface excess concentrations [37]. When the methylene segments in the carboxylic increased, the value of A_{\min} increased as well, which showed that carboxylic groups with long methylene segments were more inclined to curl and as a result, the A_{\min} values were easily getting larger [22].

3.2. Foam properties

Foam has extensive applications in a wide range of industrial fields such as pharmaceutical, textile, flotation, food industries, water treatment, and enhanced oil recovery due to their lightness and greatly specific surface areas [38,39]. Thus, it is critically necessary to investigate foam properties in this study. In general, the foam properties of a surfactant are measured in terms of its foamability and foam stability [39]. The foam height at 0 min (H_0) is defined as foamability, and the foam height ratio at 0 and 3 min (R_3) is defined as foam stability.

For CTAAC, CTABU, CTAHE, CTAC, and CTACA solutions, the values of H_0 and R_3 of five surfactants in this study were determined and summarized in Table 4 at the temperature of 25°C, it could be observed that the values of H_0 and R_3 exhibited a gradual increase with the increase of surfactant concentration until the surfactant concentrations reached 0.3 wt.%. When the concentration was greater than 0.3 wt.%, the values of H_0 and R_3 had no obvious change and maintained at a relatively stable value. So, 0.3 wt.% was fixed for the optimum concentration of five surfactants for further investigation. Notably, the maximum value of H_0 and R_3 of the CTAC solution was no more than 19.2 cm and 66.7%, which was much lower than that of CTAAC, CTABU, and CTAHE solution tested by the same method. What worse, CTACA solution showed the lower maximum value of H_0

and R_3 than CTAC solution, which was no more than 16.5 cm and 60.2%. These results indicated that CTACA had the worst foamability and foam stability, and the CTAAC showed the best foamability and foam stability compared with other members in the prepared surfactants.

The mechanism of foamability and foam stability of CTAAC, CTABU, CTAHE, CTAC and CTACA solutions could be studied. Foamability is usually affected by many factors such as surface tension, structures, types of surfactants, electrostatic charges, and so on [40]. In terms of this study, CTAAC had the lowest surface tension and the best foamability. It is consistent with the idea that the low surface tension could promote foaming according to Rosen's study [41]. In addition, there are many factors affecting foam stability, including solution concentration of surfactants, surface viscosity, drainage of the liquid film, diffusion of gas between bubbles, and so on [38]. According to this study, the drainage of the liquid film plays a significant role in affecting the foam stability. The five surfactants had same hydrophilic groups and hydrophobic groups, but their anions were different. Hence, the anions of five surfactants ultimately determined the drainage of the liquid film. Analyzing the data represented in Table 3 indicated that the R_3 values gradually increased as the increase methylene segments of carboxylic groups in the four surfactants (besides CTAC), this was attributed to the arrangement of methylene segments of carboxylic groups at the air-water interface. The graph of a schematic representation of surfactants was presented in Fig. 3, where the shorter methylene segments of carboxylic groups lead to the tight distribution of hydrophobic tails, which resulted in strong liquid film strength. Finally, the foam stability obviously improved. Meanwhile, the curl of longer methylene segments of carboxylic groups of CTACA leads to higher surface tension, which was also not conducive to the thermodynamic stability of the foam system.

Table 4
Foamability and foam stability of surfactants with different concentration at 25°C

Surfactant	Foam height and ratio	Concentration (wt.%)									
		0.08	0.2	0.4	0.6	0.8	1.0	2.0	3.0	4.0	5.0
CTAAC	H_0 (cm)	10.5	13.2	17.8	22.8	24.5	27.2	28.0	28.0	27.3	25.5
	H_3 (cm)	7.9	10.3	14.3	19.5	22.6	25.5	27.6	27.6	26.8	24.9
	R_3 (%)	75.5	14.3	80.5	85.7	92.3	93.9	98.6	98.6	98.2	97.9
CTABU	H_0 (cm)	8.5	10.0	14.8	19.2	21.5	23.2	25.0	26.8	25.5	25.2
	H_3 (cm)	6.2	7.8	11.3	16.5	19.2	22.3	23.4	26.1	24.7	23.9
	R_3 (%)	72.5	78.0	79.3	86.2	89.5	96.2	93.7	97.4	96.9	95.0
CTAHE	H_0 (cm)	6.8	8.5	11.5	16.2	20.0	21.8	22.0	23.2	22.0	21.2
	H_3 (cm)	2.7	3.6	5.6	8.5	11.8	13.5	11.8	20.5	19.9	18.9
	R_3 (%)	40.2	42.8	48.9	52.4	59.2	61.9	59.2	88.4	90.5	89.2
CTAC	H_0 (cm)	0.0	4.5	6.9	12.2	15.8	17.2	18.5	19.2	18.9	18.0
	H_3 (cm)	0.0	0.8	1.5	4.8	6.7	9.0	10.2	12.8	11.2	10.5
	R_3 (%)	0.0	19.0	21.7	39.3	43.8	52.3	55.1	66.7	59.3	58.3
CTACA	H_0 (cm)	0.0	0.0	0.0	0.0	7.5	12.5	13.0	16.5	16.0	15.5
	H_3 (cm)	0.0	0.0	0.0	0.0	1.5	4.7	5.9	9.1	9.6	9.2
	R_3 (%)	0.0	0.0	0.0	0.0	20.5	38.2	45.9	55.2	60.2	59.8

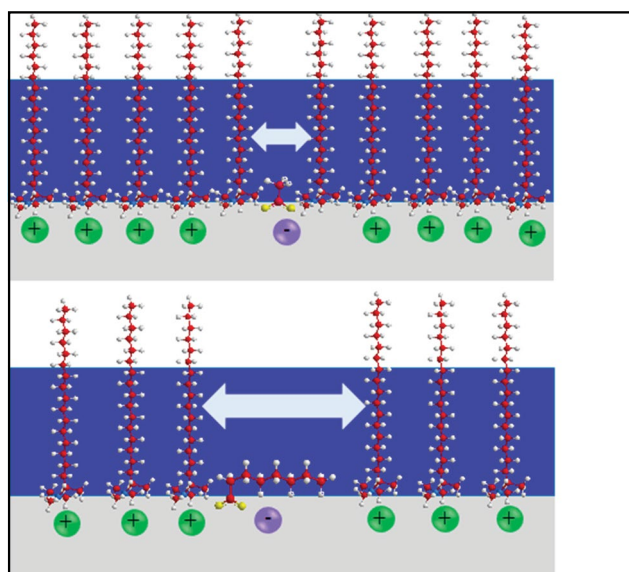


Fig. 3. Structural distribution of carboxylic quaternary ammonium surfactants in aqueous solution.

3.3. Effect of temperature on the foaming abilities

The foam produced from a surfactant aqueous solution can be applied to different fields. But, the sensitivity of foam to temperature varies greatly [39]. Therefore, it is highly necessary for the present study by subjecting five surfactants to a range of temperature environments to observe the effect of temperature change on the foamability and foam stability.

The foam height and the foam height ratio at 0 and 5 min of CTAAC, CTABU, CTAHE, CTAC and CTACA solutions vs. the different temperatures are plotted in Fig. 4. For all the solutions with a fixed concentration of 0.3 wt.%, the change tendency of H_0 values was exceedingly similar at the temperature range 30°C–70°C. That is, the H_0 values of the studied all surfactant solutions began to increase above 30°C and continued to do so with increasing temperature, which showed that the foamability benefited from a rise in temperature. However, the H_3 and R_3 values for five surfactant solutions have no obvious change at 30°C and 40°C. The studied five surfactants obtained their maximum H_3 and R_3 values, possibly owing to their lower gas diffusion rate at these temperatures. When the temperature exceeded 70°C, the H_3 and R_3 values reached the

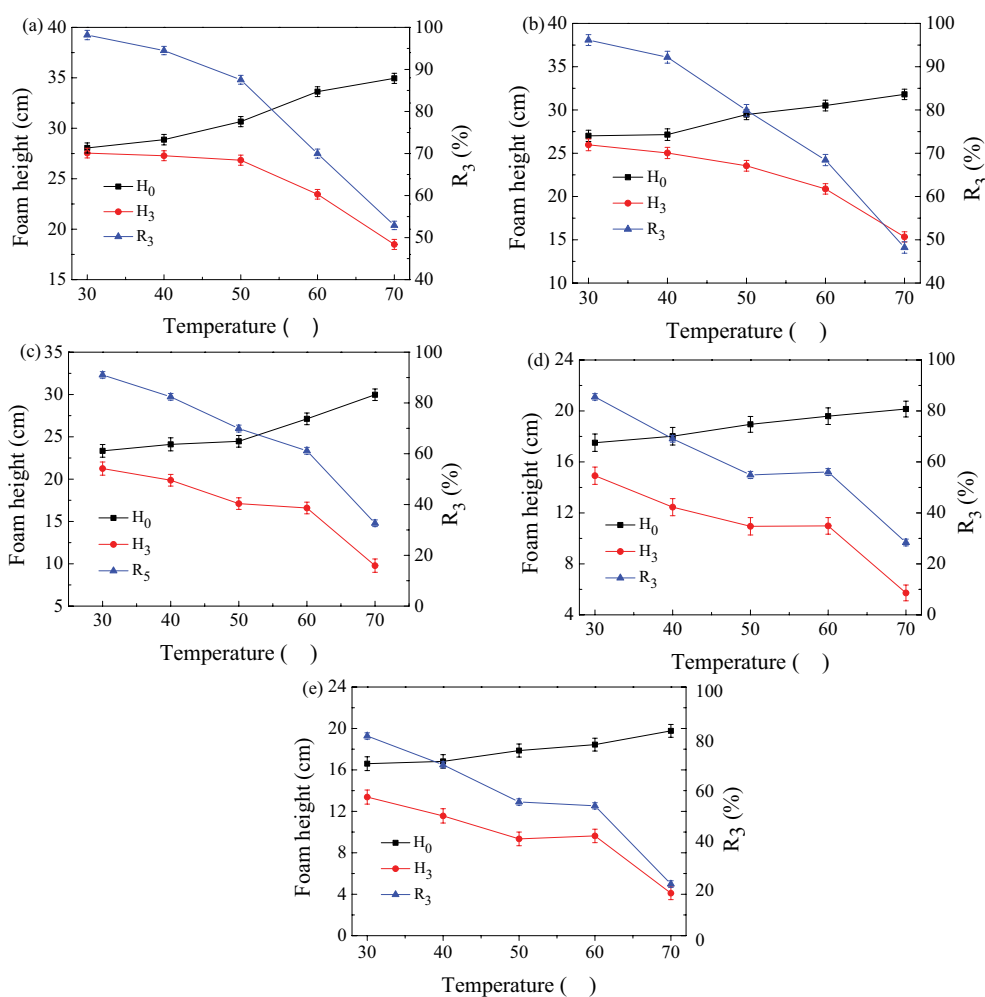


Fig. 4. Foamability and foam stability of five surfactants at the different temperature (a) CTAAC, (b) CTABU, (c) CTAHE, (d) CTAC, and (e) CTACA.

lowest. It was indicated that the higher temperature had an adverse effect on foam stability. The reason was that at higher temperatures, surface viscosity was believed to be the main influence, causing increasingly rapid liquid [39]. Thus, the foam stability was relatively improved at lower temperatures and weakened with rising temperature, this phenomenon was consistent with previous foam stability studies at high temperatures [42–44]. Comparison of foamability and foam stability of five surfactant solution at the temperature from 30°C to 70°C, the results showed that the foamability and foam stability of CTAAC was superior to that of other surfactants. The H_0 and R_3 values of CTAAC had the maximum H_0 and R_3 values at an average of 34.9 cm and 52.9% at 70°C, far larger than that of other surfactants (CTABU: 31.8 cm and 48.2%; CTAHE: 29.8 cm and 32.5%; CTAC: 20.2 cm and 28.4%; CTACA: 19.7 cm and 20.5%). Therefore, CTAAC obtained the best performance on foamability and foam stability at the temperature of 30°C–70°C, its prominent performance could be ascribed to the fact that the thermal motion of surfactant molecules more tension with the temperature increasing, the original distribution and arrangement of molecule at the air-water interface changed, and the strength of interfacial liquid film was reduced, thus, the foam stability was poor [45].

3.4. Microstructure of foam

From the above experimental results, it was established that the CTAAC was selected as a prominent foaming agent in terms of its foamability and foam stability. In order to further investigate the kinetics of drainage and coalescence in bulk foam generating CTAAC aqueous solution with a fixed

concentration of 0.3 wt.%. The microscope with 40-fold magnification was employed to visualize the microstructure as a function of time. It is observed from Fig. 5 that the foam microstructure due to the temperature of 30°C and 40°C hardly presented an obvious change when the time was less 8 min, that is, the foam had good shapes with regular circles or ellipses and gas was in affecting as a dispersed phase. However, the contact between foams was not close, and the size distribution of foam was relatively uniform [46]. It was indicated that CTAAC bubbles had a better uniformity at the low temperature (around 30°C–40°C). At 50°C, the bubbles were observed to keep regular circles in the initial state. No obvious coalescence occurred when the bubbles encountered each other. As time passes, the exceedingly obvious change of foam microstructure was taking place, that is, the shapes of bubbles were regular polygons and the between bubbles occurred to directly contact due to remarkable coalescence. At high temperature (around 60°C–70°C), it was observed that the small bubbles were merged into the big ones and a spontaneous and continuous reduction of foam density is presented in Fig. 5 at 2 min. The bubbles size of CTAAC increased dramatically after 6 min, which was a quite serious coalescence process. Interestingly, the bubbles after 6 min were indicated a highly development of liquid drainage. Meanwhile, a loose distribution and remarkable disproportionation were detected in bubbles, where still remained a certain thickness in liquid films after 8 min. Consequently, at 30°C and 40°C, CTAAC bubbles showed the slowest coalescence in gas bubbles and could develop the thicker liquid films as time goes on, however, the most obvious coalescence is present in CTAAC bubbles at 70°C [47]. Therefore, the high temperature was adverse to foam stability, this owned to

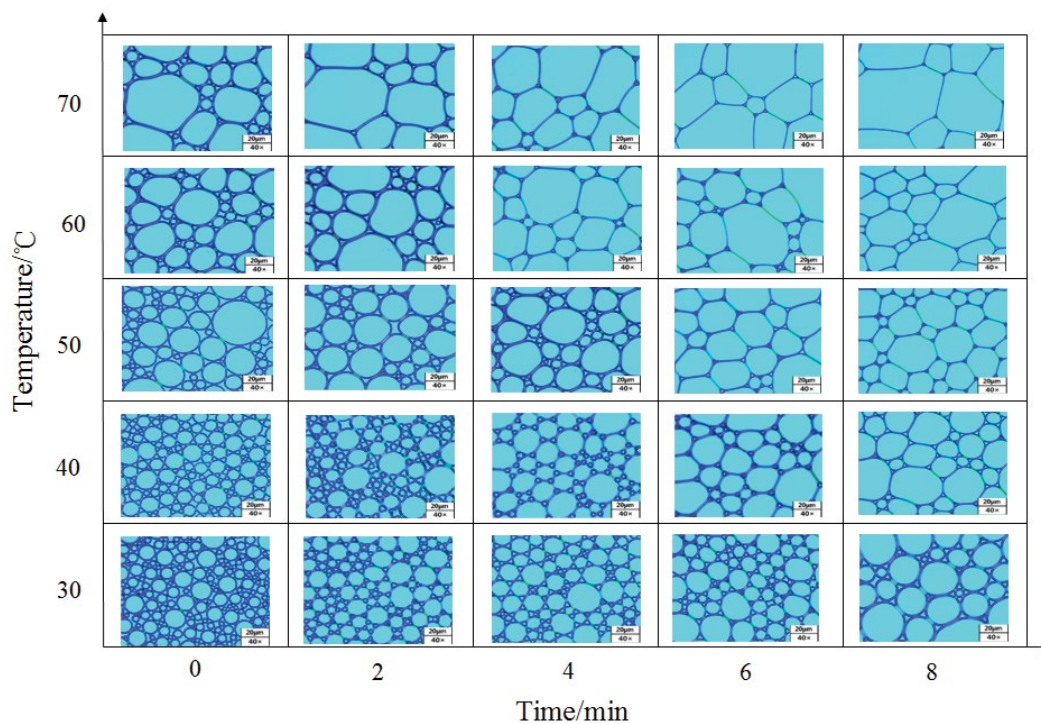


Fig. 5. Microphotographs of foam of CTAAC changes with time.

high-pressure difference and gas diffusion among bubbles, ultimately leading to obvious bubbles coarsening and lamellae breakage [48].

3.5. Emulsion stability

The emulsion is a thermodynamically unstable multiphase dispersion system, and in which one liquid is dispersed in the form of tiny droplets in the other that is incompatible with it [49]. This characteristic is mainly determined by the complex composition of emulsion, with three components: an aqueous phase, an oil phase, and an emulsifier, the surfactant is usually considered to act as emulsifiers, and it can effectively reduce the interfacial tension and form interface film at the oil-water interface, therefore, can accelerate as well as stabilize water-in-oil emulsions. It is observed from Fig. 6 which simply shows the processes of emulsion formation and separation [50]. The first step of separating the emulsion is started owing to relatively weak repulsive forces, as well as if the adhesion energy is sufficiently large, adhesion is sure to be facilitated, which is the so-called flocculation phenomenon [51]. Once the interface film breaks, a significant coalescence process of droplets is immediately taking place.

Usually, the different emulsifiers are provided with different emulsification rates under the same studied conditions, and the emulsification rate is an exceedingly significant consideration restricting the application of emulsifiers in petroleum and gas industries [52,53]. Quaternary ammonium cationic surfactant as a type of emulsifier is applied to many filed since it has a higher emulsification rate and thermal stability than conventional cationic surfactant. Five surfactant solutions with a fixed concentration of 0.3 wt.% were prepared, and then the emulsification rate was measured. What's more, the crude oil to surfactant solution volume ratio was 80:20, and the emulsifying temperature was 60°C. From Fig. 7 it can be seen that the emulsification rate of five surfactant solutions followed the order of CTAAC > CTABU > CTAHE > CTAC > CTACA under the same condition, which showed that CTAAC had the best performance on emulsion stability compared with other members in the

prepared surfactants. This could be attributed to the distribution and arrangement of surfactant molecules at the oil-water interface. The hydrophobic tails of CTAAC could pack loosely to each other which resulted in the highest interfacial film strength among other surfactants. Therefore, the emulsion stability was significantly improved.

As presented in above text that CTAAC as emulsifier had an excellent thermal stability. The effect of surfactant solution concentration on emulsion stability was also studied in our currently study. When the temperature is 60°C, the CTAAC solution concentration is 0.05, 0.10, 0.30, 0.50 and 1.0 wt.%. The plots of the emulsification rate against the aging time varied from 2 to 20 min is shown in Fig. 8, it could be indicated that there were a great differences on emulsion stability at different concentration of surfactant solution when the aging time of CTAAC solution was fixed. For the concentration of 0.05 and 0.10 wt.%, the emulsification rate of CTAAC solution rapidly decreased with the increase of aging time, but for the concentration of 0.5 and 1.0 wt.%, the emulsification

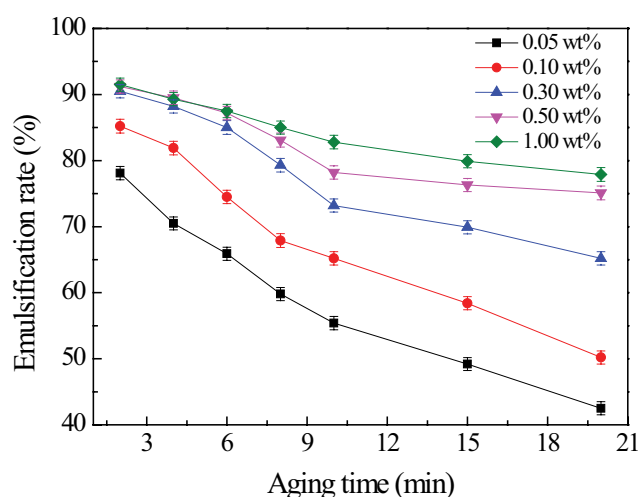


Fig. 7. Emulsification rate of CTAAC solution with different concentrations.

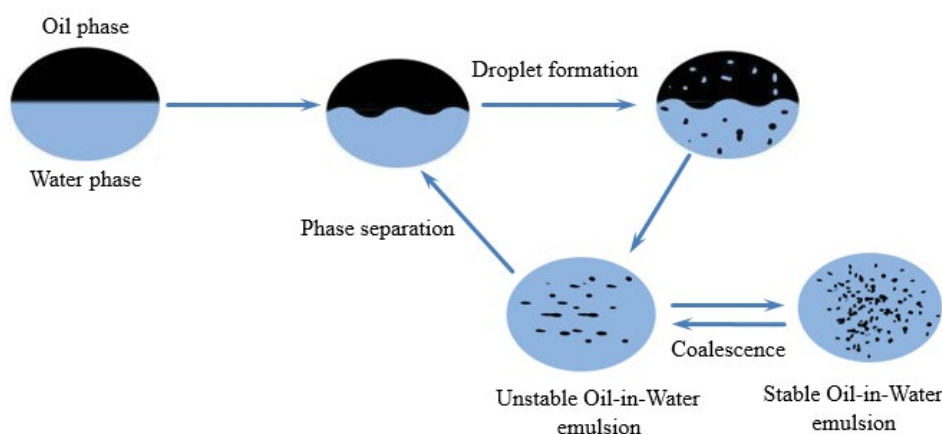


Fig. 6. Steps of emulsion formation and separation [50].

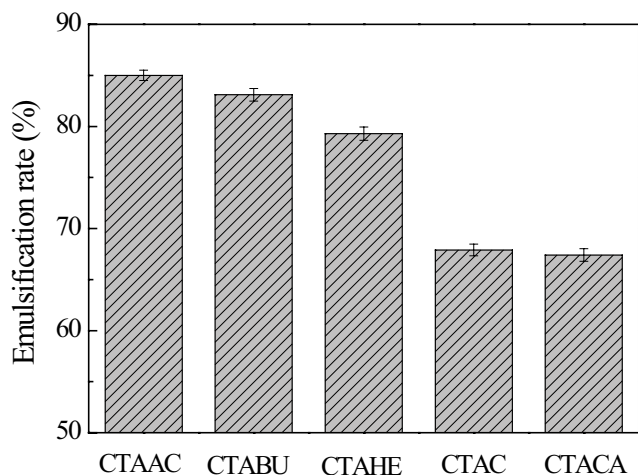


Fig. 8. Emulsification rate of five surfactant solutions with 0.3 wt.% at 8 min.

rate of CTAAC solution decreased in 10 min, and then had no obvious change with the increase of aging time. Hence, CTAAC solution concentration played an important role in affecting emulsions stability. This could be attributed to two aspects as following: on the one hand, owing to the thermodynamically unstable system of the emulsion, the emulsion stability obviously decreased with the increase of aging time at lower surfactant solution concentrations, on the other hand, the interfacial film strength was relatively poor when the emulsion concentration was low, Therefore, the emulsion system was extraordinary sensitive due to the change of external environment. All in all, the above two aspects effect determined the final emulsion stability [54].

4. Conclusion

In this paper, a series of novel carboxylic quaternary ammonium surfactants were designed and prepared to study further the relationship between the structures of surfactants with carboxylic groups and their surface tension, foam properties and emulsion stability were investigated. Five quaternary ammonium surfactants with different carboxylic groups would generate different surface phenomena and micellization behavior could be obtained. When the number of methylene segments in carboxylic groups decreased, the CMC values gradually increased, however, the ability of the surfactant to reduce the surface tension was getting stronger. The experimental results of foam properties showed that the CTAAC exhibited the best performances on foamability and foam stability which measured at different concentrations and temperatures. The emulsification properties of four surfactants as a type of emulsifier were investigated in our currently study. It was found that the emulsion stability followed the order of CTAAC > CTABU > CTAHE > CTACA at the temperature of 60°C.

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