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Synthesis of new betaine-type amphoteric surfactants from tall oil fatty acid

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Abstract Two new betaine-type amphoteric surfactants – betaine *N,N*-dihydroxyethyl-*N*-ethyl fatty acid ester and ammonium *N*-(fatty acid ester) ethyl-*N,N*-bis (2-hydroxyethyl)-3-(2-hydroxypropyl) sulfonate – were synthesized using tall oil fatty acids as the raw materials. Processing conditions suitable for synthesizing the intermediates and final products were probed. In addition, the chemical structures of the intermediates and the final products were identified by infrared spectroscopy, hydrogen nuclear magnetic resonance spectroscopy, and elemental analysis.

Key words Tall oil fatty acid · Amphoteric surfactant · Betaine type

Introduction

An amphoteric surfactant is one in which hydrophilic cationic and anionic groups coexist in the same molecule.¹ It has many excellent characteristics, such as being only mildly toxic to humans, causing little irritation to skin and eyes, and being resistant to hard water. It is also a highly concentrated electrolyte, has good biodegradability, and has excellent properties of softening and being antistatic to fiber, and other properties. It has also good compatibility with other typical surfactants (which have a positive synergistic effect), can be absorbed on a surface with positive and negative charges, does not form a hydrophobic layer, and has good

moistening and foaming abilities. It can be widely used in many fields, such as the chemical, textile, dye, pigment, food, pharmaceutical, machining, metallurgy, washing, and petroleum industries. It has been used as a detergent, moistening and foaming agent, corrosion inhibitor, dispersion agent, germicide (bactericide), emulsifying agent, antistatic and softening agent of fibers, a dye, a chelating agent, and a cleaning agent.^{2–7}

A betaine-type surfactant usually means that quaternary ammonium cationic groups and anionic groups such as $-\text{COO}^-$, $-\text{SO}_3^-$, $-\text{OSO}_3^-$, and $-\text{PO}_4^-$ coexist in the same molecule. It has excellent solubility over a wide range of pH values. Its solubility does not obviously decrease even in an isoelectric zone. In addition, unlike the external quaternary ammonium salt, the betaine-type surfactant is compatible with ionic surfactants. Among the betaine-type surfactants, the most important contain sulfonic and carboxylic groups because they have important commercial value and a wide application field. The fatty acid material for producing surfactants comes mainly from castor oil, coconut oil, palm oil, soybean oil, rapeseed oil, and cotton seed oil. However, much of the soybean oil and rapeseed oil is used in the food industry, and the other materials (e.g., coconut oil and palm oil) are not available in China.

The shortage of materials is one of the main factors restricting the development of the Chinese surfactant industry.^{8,9} Therefore, it is necessary to utilize tall oil fatty acid to synthesize surfactants in the future. There are few reports about the synthesis of betaine-type surfactants using tall oil fatty acid in China.

In this study, two new betaine-type amphoteric surfactants – betaine *N,N*-dihydroxyethyl-*N*-ethyl fatty acid ester and ammonium *N*-(fatty acid ester) ethyl-*N,N*-bis(2-hydroxyethyl)-3-(2-hydroxypropyl) sulfonate – were synthesized using tall oil fatty acid as the raw material with new methods, and suitable synthetic conditions of the intermediates and the final products were studied. The chemical structures of the intermediates and the final products were also identified by means of infrared (IR) spectroscopy, hydrogen nuclear magnetic resonance (¹H-NMR) spectroscopy, and elemental analysis.

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Table 1. Composition of tall oil fatty acid^a

Compound	Tall oil fatty acid content (%)
5,9,12-Octadecatrienoic acid	1.6
Oleic acid	85.1
Stearic acid	5.1
9,11-Octadecadienoic acid	3.4
8,11-Octadecadienoic acid	4.8

^aTall oil fatty acid was analyzed by gas chromatography after esterifying with diazomethane

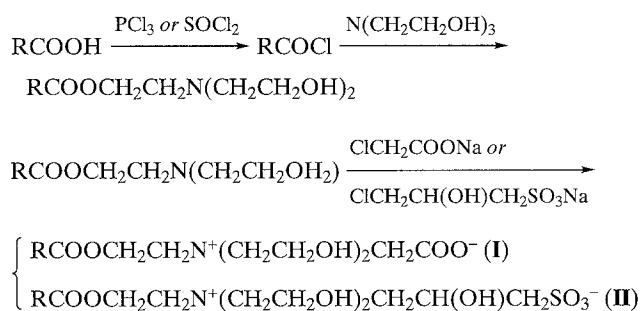
Materials and methods

Materials

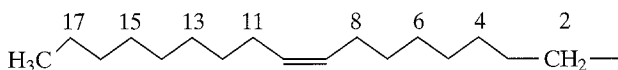
A sample of tall oil fatty acid obtained from the Saxian Forest Chemical Engineering Factory (China) was fractionally distilled, and a fraction containing oleic acid with a purity of 85.1% was produced.¹⁰ The composition of the distilled tall oil fatty acid is shown in Table 1. The average molecular weight of the distilled tall oil fatty acid RCOOH was 281.9 (in R, the average numbers of C and H were 17.0 and 32.9, respectively). Triethanolamine, sulfinyl chloride (dichlorosulfoxide), phosphorus trichloride, epichlorohydrin, sodium hydrogen sulfite, sodium hydroxide, chloroacetic acid, and other reagents were all of analytical grade.

Synthetic course

The synthetic courses of the amphoteric surfactants were as follows.



The structure of R was mainly:



Experiments

Preparation of sodium chloroacetate

Chloroacetic acid was dissolved in anhydrous alcohol and cooled to below 20°C. The saturated solution of sodium hydroxide was dropped slowly into the alcohol solution of chloroacetic acid. The reacted solution was then cooled in an ice-water bath. The crystal obtained by filtering was

washed with anhydrous alcohol and then dried to synthesize compound (I).^{11,12}

Preparation of sodium

3-chloro-2-hydroxypropanesulfonate

3-Chloro-2-hydroxypropanesulfonate was prepared in a 250-ml round-bottomed four-necked flask equipped with an agitator, a thermometer, and a reflux condenser. The reaction temperature was controlled in a waterbath. The flask was charged with 64.7 g (0.62 mol) sodium hydrogen sulfite, 25.0 g (0.20 mol) sodium sulfite, and 130 ml deionized water. The temperature of the solution was adjusted to room temperature after sodium hydrogen sulfite and sodium sulfite were dissolved. Then 50.0 g (0.54 mol) epichlorohydrin was slowly added, with the reaction temperature kept at around 25°–30°C. The reaction was continued at 25°–30°C for another 2 h after adding the epichlorohydrin. The resultant mixture was transferred to a beaker to crystallize in an ice-water bath. The crystal obtained after filtering, washing with deionized water, and drying under vacuum was used for synthesizing compound (II).^{13,14}

Synthesis of fatty acyl chloride

The synthesis of fatty acyl chloride was carried out in a round-bottomed flask with three necks. Tall oil fatty acid 28.2 g (0.1 mol) and benzene 100 ml were added to the flask, and 5.5 g (0.04 mol) phosphorus trichloride was dropped into the fatty acid mixture; the reaction temperature was kept in the range of 50°–55°C. The reaction was continued for another 6 h after adding phosphorus trichloride at 60°C. The reacted liquid was transferred to a separating funnel to remove the phosphorous acid completely. The liquid was first distilled at atmospheric pressure to remove the solvent and then was further fractionally distilled at a pressure of 0.4 kPa to collect the fraction between 175°C and 180°C as the intermediate of synthesizing amphoteric surfactants.¹⁵

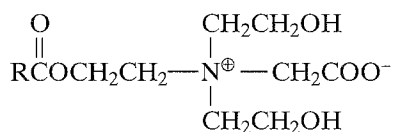
Synthesis of monoester of triethanolamine fatty acid

A three-necked flask was charged with 100 ml benzene and 74.5 g (0.5 mol) triethanolamine. It was then cooled with an ice-water bath to around 13°C. The fatty acyl chloride 30.0 g was dropped slowly into the mixture to react with triethanolamine. The reaction temperature was kept at around 15°C, and the reaction was continued for another 4 h after adding the fatty acyl chloride. The reacted liquid was washed with a saturated solution of sodium chloride until the pH value reached neutrality (a bit of alcohol was added to prevent it from emulsifying). The monoester of fatty acid triethanolamine was obtained after the treated reacted liquid was dried with anhydrous sodium sulfate and distilled to recover benzene.

Synthesis of betaine-type amphoteric surfactants

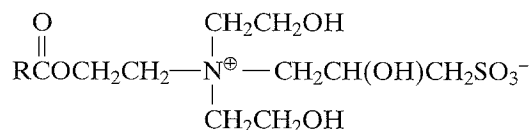
Betaine N,N-dihydroxyethyl-N-ethyl fatty acid ester. Synthesis of compound (I) was carried out in a 250-ml

three-necked flask equipped with an agitator, a thermometer, and a reflux condenser. Aliquots of 100 ml 95% ethanol, 20.60 g (0.05 mol) monoester of fatty acid triethanolamine, and 5.83 g sodium chloroacetate (made into a saturated aqueous solution) were charged and reacted for 8 h at 80°–85°C. The resultant mixture was distilled to remove water and ethanol. The residue was dissolved in 100 ml 95% anhydrous ethanol to remove the inorganic salt by filtering. The filtrate was then distilled to remove ethanol, and the residue was further crystallized with a mixed solvent of ethanol–propanone (3:1 v/v) to obtain compound (I). Its structure is as follows:



Compound (I)

Ammonium N-(fatty acid ester) ethyl-N,N-bis (2-hydroxyethyl)-3-(2-hydroxypropyl) sulfonate. Together, 20.6 g monoester of fatty acid triethanolamine, 9.8 g sodium 3-chloro-2-hydroxy-propane sulfonate, and 100 ml 82% ethanol were charged into a 250-ml three-necked flask. The mixture was heated and refluxed for 6 h. After the reactant was cooled to 50°C and the pH was adjusted to 8–9 with a bit of sodium carbonate, the reactant was continuously refluxed for another 6 h. The unreacted monoester was removed from the reactant by extraction with 100 ml petroleum ether (b.p. 60°–90°C). The ethanol and water contained in the reactant were distilled out, the residue was dissolved in 100 ml anhydrous ethanol, and it was hot-filtered to remove the inorganic salt. The filtrate was condensed to the half volume and cooled. Compound (II) was obtained by crystallization. Its structure is as follows.



Compound (II)

Measurement of alkali and hydroxyl values of monoester of fatty acid triethanolamine

Free alkali test of monoester of fatty acid triethanolamine

The alkali value was expressed as milligrams of KOH in a 1-g sample.¹⁶ The measurement was as follows: A tapered flask was charged with 10 g of sample (exact to 0.004 g). The sample was dissolved in 10 ml neutral ethanol, and 10 drops of phenolphthalein indicator were added; the mixture then was titrated with HCl 0.1 mol/l. The alkali value can be calculated according to the following formula.

$$X = V \times T \times 56.1/m$$

where X is the alkali value; V is the volume of consumed standard hydrochloric acid (ml); T is the concentration of the standard hydrochloric acid (mol/l); m is the amount of sample (g); and 56.1 is the molar mass of KOH, (g).

Measurement of hydroxyl value

The hydroxyl value $I(\text{OH})$ is the amount of KOH needed to neutralize the acetic acid that was consumed when esterifying all of the hydroxyl groups contained in 1 g of sample.¹⁷ The experimental principle was that the acetic anhydride-pyridine solution was used to esterify the hydroxyl groups, and potassium hydroxide was used to neutralize the acetic acid produced while esterifying and hydrolyzing the acetic anhydride. Phenolphthalein was used as an indicator. The hydroxyl value can be calculated according to the following formula.

$$I(\text{OH}) = (V_0 - V_1) \times C \times 56.1/m + X$$

where V_0 is the amount of standard KOH consumed while titrating a blank assay (ml); V_1 is the amount of standard KOH consumed while titrating the sample (ml); C is the concentration of standard KOH (mol/l); X is the positive acid value or negative alkali value of the sample; and $I(\text{OH})$ is the hydroxyl value of the sample (mg KOH/g).

Structural determination of synthesized intermediates and final products

The structure of the synthesized intermediates and final products were determined by means of IR, ¹H-NMR, and elemental analysis.

Results and discussion

Factors influencing the synthesis of sodium 3-chloro-2-hydroxypropane sulfonate

During the course of the reaction between sodium hydrogen sulfite and epichlorohydrin, the pH value of the reaction medium and reaction temperature have an important influence on the reaction results. The suitable reaction conditions were probed to increase the purity of 3-chloro-2-hydroxypropanesulfonate.

Effect of the pH value of sodium hydrosulfite solution on product structure

There are two kinds of reaction that occurred in the reaction process between sodium hydrogen sulfite and epichlorohydrin under different pH values. One is a cycle-broken reaction of the epoxy group under acidic conditions, when sodium 3-chloro-2-hydroxypropanesulfonate is obtained. Another is a substitution reaction of chlorine in the side chain under alkaline conditions, when sodium chloride is produced. The influence of the pH of the sodium hydrogen

Table 2. Relation between pH value of sodium hydrogen sulfite solution and the Cl⁻ content in the reaction liquid

pH of reaction medium	Free Cl ⁻ content ^a (%)
4.01	0.03
4.93	3.92
6.02	4.73
7.02	29.30
8.03	39.15
11.05	47.40
13.01	56.47

^aFree Cl⁻ content (%) = (Cl⁻ tested value, mol)/(epichlorohydrin, mol)

Table 3. Effect of reaction temperature on reaction time in the reaction of sodium hydrogen sulfite and epichlorohydrin

Reaction temperature (°C)	Reaction time (min)
20	150
30	120
40	40
50	21
60	11
70	6
80	4

sulfite solution on the product structure is shown in Table 2. The experimental conditions were as follows: sodium hydrogen sulfite 20.0g (0.20mol) was dissolved in 100ml deionized water, and the pH of the solution was adjusted to 4–13. Epichlorohydrin 16ml (0.20mol) was then dropped into the solution. The reaction temperature was 40°C and the reaction time 2.0h. A 10-ml filtrate sample was removed to analyze the Cl⁻ content. Table 2 shows that the free Cl⁻ content decreased as the pH of sodium hydrogen sulfite became lower. Most of the epichlorohydrin converted to sodium 3-chloro-2-hydroxypropanesulfonate because of the low free Cl⁻ content when the pH was ≤4. Therefore, the suitable pH value was not >4.

Effect of reaction temperature on the reaction time during the sodium hydrogen sulfite and epichlorohydrin reaction process

The relation between the reaction temperature and reaction time is shown in Table 3. Because epichlorohydrin is insoluble in water, the final point of the reaction can be determined by observing the transparency of the reaction liquid. The experimental conditions were as follows: sodium hydrogen sulfite 20.0g (0.20mol) was dissolved in 100ml deionized water, and the pH of the solution was adjusted to 4; epichlorohydrin 16ml (0.20mol) was then dropped into the solution. Experimental results showed that the reaction time decreased as the reaction temperature increased. When the reaction temperature was higher than 50°C, the reaction was completed within several minutes. However, epichlorohydrin could also self-polymerize easily under acidic conditions at high temperature. Hence, the suitable temperature was preferably no more than 50°C.

Table 4. Effect of the triethanolamine/acylchloride molar ratio on the hydroxyl value of reaction products

Triethanolamine/acylchloride ratio (mol/mol)	Hydroxyl value of products (KOH, mg/g)
1	189.3
2	200.4
4	231.7
6	253.7
8	265.6
10	268.6
12	270.1
14	271.5

Main factors influencing the synthesis of monoester of fatty acid triethanolamine

Effect of the fatty acyl chloride/triethanolamine molar ratio on reaction results

Because there are three hydroxyl groups in triethanolamine, the products obtained during the reaction process of triethanolamine with fatty acyl chloride contain not only monoester but also diester and triester. The triethanolamine/fatty acyl chloride molar ratio is the main factor influencing the product composition. The effect of the triethanolamine/acyl chloride molar ratio on reaction results is shown in Table 4. The experimental conditions were as follows: tall oil fatty acyl chloride 30.0g (0.1 mol), benzene used as a solvent at a dose of 100ml, reaction temperature 15°C, and reaction time 6h. Tall oil fatty acyl chloride was added by dropping it under violent agitation. Table 4 shows that the hydroxyl value of products rose along with the increasing triethanolamine/fatty acyl chloride molar ratio, indicating that the monoester content increases correspondingly. When the triethanolamine/acyl chloride molar ratio was increased to 12, the hydroxyl value reached 270.1mg KOH/g. It was found that the product consisted mainly of monoester. When the molar ratio increased to 14, the hydroxyl value of the product reached 271.5mg KOH/g, and it was almost the same as that of the pure monoester (the theoretical hydroxyl value of monoester is 271.7mg KOH/g), showing that the product rarely contained diester and triester. Hence, the triethanolamine/acyl chloride molar ratio should be ≥14 to obtain the almost pure monoester.

Effect of solvents on the reaction results of fatty acyl chloride and triethanolamine

The effect of various solvents on the reaction products is shown in Table 5. The experimental conditions were as follows: triethanolamine 208.6g (1.4mole), fatty acyl chloride 30.0g (0.1 mole), reaction temperature 15°C, reaction time 6h, and solvent dose 100ml. The experimental results show that the various solvents did not heavily influence the hydroxyl value of the reaction products. From the viewpoint of purifying reaction products, however, benzene

is better than other solvents (e.g., dichloromethane, 1,2-dichloroethane, toluene) because of its lower specific gravity and lower boiling point.

The effect of the benzene dose on the hydroxyl value of the products of triethanolamine fatty monoester is shown in Table 6. The experimental conditions were as follows: triethanolamine 208.6g (1.4 mole), fatty acyl chloride 30.0g (0.1 mole), reaction temperature 15°C, reaction time 6h. The various solvent doses had a slight influence on the hydroxyl value of products. The hydroxyl value of products

slightly increased as the solvent dose increased. This might be due to the fact that the colliding probability between monoester and fatty acid decreased with the concentration of monoester being reduced. So, the by-products of diester and triester would be reduced. However, when the solvent dose increased over 120ml, the hydroxyl value of the products did not increase further. On the other hand, the large solvent dose would add the charge of recycling solvent. Hence, the suitable solvent dose was about 90–120ml.

Table 5. Effect of various solvents on the hydroxyl value of reaction products of triethanolamine fatty monoester

Solvent	Hydroxyl value of products (KOH, mg/g)
<i>n</i> -Hexane	271.6
Benzene	271.5
Toluene	271.3
1,2-Dichloroethane	271.2
Dichloromethane	207.8

Table 6. Effect of benzene dose on hydroxyl value of reaction products of triethanolamine fatty monoester

Benzene dose (ml)	Hydroxyl value of products (KOH, mg/g)
0	268.9
30	269.1
60	269.6
90	271.4
120	271.5
150	271.5

Table 7. Structural analyses of betaine-type amphoteric surfactants and their intermediates

Monoester of fatty acid triethanolamine {RCOOCH₂CH₂N(CH₂CH₂OH)₂}

Elemental analysis (%)	C	H	N
Calculated value	81.36	11.38	3.39
Tested value	81.62	11.10	3.32
IR spectra (cm ⁻¹)	3382 (ν _{O-H}), 1076 (R-OH ν _{C-O}), 1420, 1376 (frequency band produced by resonating of primary alcohol δ _{O-H} and ρ _{C-H}), 1735 (ester ν _{C=O}), 1241 (ester ν _{as C-C(=O)-C}), 1168 (ester ν _{as C-O-C}), 910 (ester ν _{s C-O-C}), 875 (ester δ _{s C-O})		

Betaine *N,N*-dihydroxyethyl-*N*-ethyl fatty acid ester{RCOOCH₂CH₂N⁺(CH₂CH₂OH)₂CH₂COO⁻}

Elemental analysis (%)	C	H	N
Calculated value	66.21	10.41	2.94
Tested value	66.38	10.26	2.98
IR spectra (cm ⁻¹)	3450 (ν _{O-H}), 1040 (primary alcohol ν _{C-O}), 1427 (the first frequency band produced by resonating of δ _{O-H} and ρ _{C-H}), 1323 (the second frequency band produced by resonating of δ _{O-H} and ρ _{C-H}), 620–600 (δ _{C-O-H})		
Ester bond —COO ⁻	1740 (ν _{C=O}), 1241 (ν _{as C-C(=O)-C}), 1168 (ν _{as C-O-C}), 910 (ν _{s C-O-C}), 875 (δ _{O-C})		
Alkyl group	1600 (ν _{as COO⁻}), 1400 (ν _{s COO⁻})		
¹ H-NMR (ppm)	3006 (ν _{C-H}), 2921 (ν _{as CH₂}), 2850 (ν _{s CH₂}), 1465 (δ _{CH₂}), 1384 (δ _{s CH₃}), 725 (ρ _{CH₂})		
	0.9 (—CH ₃ , t, 3H), 1.3 (—CH ₂ , s, 20H), 1.6 [—CH ₂ —C—C(=O)—O, t, 2H], 1.8 (O—H, s, 1H), 2.0 (—CH ₂ C=CCH ₂ —, m, 4H), 2.1 [—CH ₂ —C(=O)—O, t, 2H], 3.4 [—C(=O)—O—C—CH ₂ —N ⁺ , t, 2H], 3.6–3.8 (N ⁺ —CH ₂ —C—O, N ⁺ —C—CH ₂ —O, m, 8H), 3.9 (N ⁺ —CH ₂ —COO ⁻ , s, 2H), 5.3 [—CH=CH—, —C(=O)—O—CH ₂ —C—N ⁺ , m, 4H], 6.1 (—O—H, inner molecular hydrogen bond, s, 1H)		

Ammonium *N*-(fatty acid ester) ethyl-*N,N*-bis(2-hydroxyethyl)-3-(2-hydroxypropyl) sulfonate {RCOOCH₂CH₂N⁺(CH₂CH₂OH)₂CH₂CH(OH)CH₂SO₃⁻}

Elemental analysis (%)	C	H	N
Calculated value	58.81	9.62	2.53
Tested value	58.63	9.71	2.62
IR spectra (cm ⁻¹)	3600–3360 (ν _{O-H}), 1030 (primary alcohol ν _{C-O}), 1100 (secondary alcohol ν _{C-O}), 1420 (the first frequency band produced by resonating of δ _{O-H} and ρ _{C-H}), 1330 (the second frequency band produced by resonating of δ _{O-H} and ρ _{C-H}), 620–600 (δ _{C-O-H})		
Ester bond	1740 (ν _{C=O}), 3460 (the multiple frequency peak of ν _{C=O}), 1241 (ν _{as C-C(=O)-C}), 1168 (ν _{as C-O-C}), 910 (ν _{s C-O-C}), 875 (δ _{O-C})		
-SO ₃ ⁻	1220 (ν _{s S-O}), 1200–1180 (ν _{as SO₃⁻}), 1150 and 1050 (ν _{s SO₃⁻}), 730 (δ _{s SO₃⁻})		
Alkyl group	3008 (ν _{C-H}), 2921 (ν _{as CH₂}), 2850 (ν _{s CH₂}), 1465 (δ _{CH₂}), 1384 (δ _{s CH₃}), 725 (ρ _{CH₂})		
¹ H-NMR (ppm)	0.9 (—CH ₃ , t, 3H), 1.3 (—CH ₂ , s, 20H), 1.6 [—CH ₂ —C—C(=O)—O, t, 2H], 1.8 (O—H, s, 2H), 2.0 (—CH ₂ C=CCH ₂ —, m, 4H), 2.1 [—CH ₂ —C(=O)—O, t, 2H], 2.8 (—CH ₂ —SO ₃ ⁻ , t, 2H), 3.4 [—C(=O)—O—C—CH ₂ —N ⁺ , t, 2H], 3.6–3.9 [N ⁺ —CH ₂ —C—O, C—CH(OH)—C—SO ₃ ⁻ , N ⁺ —CH ₂ —C—C—SO ₃ ⁻ , m, 11H], 5.3 [—CH=CH—, C(=O)—O—CH ₂ —C—N ⁺ , m, 4H], 6.1 (—O—H, inner molecular hydrogen bond, s, 1H)		

Structural analyses of the synthesized intermediate and final products

The structures of the synthesized betaine-type amphoteric surfactants and their intermediates have been identified by means of IR, $^1\text{H-NMR}$, and elemental analysis.^{18,19} The analytical results are shown in Table 7. For compound (I), in the IR spectra the strong, wide peak at 3450cm^{-1} was assignable to the absorption of primary alcohol $\nu_{\text{O-H}}$; the weak peak at 3006cm^{-1} was the absorption peak of $\nu_{\text{C-H}}$ in alkyl group R, and 2921 and 2850cm^{-1} were the absorption peaks of ν_{asCH_2} and ν_{sCH_2} , respectively; 1740 and 1241cm^{-1} were explicable as the absorption peaks of $\nu_{\text{C=O}}$ and $\nu_{\text{as C-C(=O)-C}}$ of the ester bond; 1600 and 1400cm^{-1} were caused by ν_{asCOO^-} and ν_{sCOO^-} . In the proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra, the chemical shifts at δ 0.9–2.1 were assignable to alkyl protons [δ 0.9 (3H, t, CH_3 -18), δ 1.3 (20H, s, CH_2 -4–7 and 12–17), δ 1.6 (2H, t, CH_2 -3), δ 2.0 (4H, m, CH_2 -8 and CH_2 -11), δ 2.1 (2H, t, CH_2 -2)]. The characteristic signals for N^{\oplus} were shown at δ 3.9 (2H, s, $\text{N}^{\oplus}\text{-CH}_2\text{COO}^-$), δ 3.4 (2H, t, $\text{COOCCH}_2\text{N}^{\oplus}$), δ 3.6–3.8 (8H, m, $\text{N}^{\oplus}\text{-CH}_2\text{CH}_2\text{OH}$), and δ 5.3 (4H, m, $\text{CH}=\text{CH}$, $\text{COOCH}_2\text{CN}^{\oplus}$). For compound (II), in the IR spectra the strong peaks at 1200 and $1200\text{--}1180\text{cm}^{-1}$ were assignable to the absorption peaks of $\nu_{\text{s-O}}$ and $\nu_{\text{as SO}_3^-}$ of functional group SO_3^- . The data for other functional groups, such as the ester bond, hydroxyl group, and alkyl group, were similar to those in compound (I). In the $^1\text{H-NMR}$ spectra, the characteristic signals of compound (II) were shown at δ 2.8 (2H, t, CH_2SO_3^-), δ 3.4 (2H, t, $\text{COOCCH}_2\text{N}^{\oplus}$), δ 3.6–3.9 (11H, m, $\text{N}^{\oplus}\text{-CH}_2\text{CH}_2\text{OH}$, $\text{N}^{\oplus}\text{-CCH(OH)CSO}_3^-$, $\text{N}^{\oplus}\text{-CH}_2\text{C(OH)CSO}_3^-$), and δ 5.3 (4H, m, $\text{CH}=\text{CH}$, $\text{COOCH}_2\text{CN}^{\oplus}$). It can be seen from the analytical results that the chemical structures of the amphoteric surfactants obtained conformed to the originally designed molecular structures.

Conclusions

The new betaine-type amphoteric surfactants – betaine *N,N*-dihydroxyethyl-*N*-ethyl fatty acid ester and ammonium *N*-(fatty acid ester) ethyl-*N,N*-bis(2-hydroxyethyl)-3-(2-hydroxypropyl) sulfonate – were synthesized using tall oil fatty acid as the main raw material. The reaction temperature and the pH value of the reaction medium for synthesizing sodium 3-chloro-2-hydroxypropanesulfonate were discussed. The test results showed that both the reaction temperature and the pH of the reaction medium had a significant influence on the reaction between sodium hydrogen sulfite and epichlorohydrin. The suitable reaction temperature was $\leq 50^\circ\text{C}$, and the suitable pH was ≤ 4 .

Suitable conditions for synthesizing monoester of fatty acid triethanolamine were probed. The test results showed

that the fatty acyl chloride/triethanolamine molar ratio and the dosage of solvent significantly influenced the product composition. The solvent did not have an obvious influence on the product composition, but there was some influence on the later processing of the reaction products. The analysis results of IR, $^1\text{H-NMR}$, and elemental analysis showed that the chemical structures of the products corresponded to the originally designed molecular structures.

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