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Synthesis of 1-hydroxyethyl-2-alkyl-2-imidazoline and its derivative sulfonate amphoteric surfactant from tall oil fatty acid

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Abstract 1-Hydroxyethyl-2-alkyl-2-imidazoline (HEAI) and its derivative sulfonate amphoteric surfactant were synthesized using tall oil fatty acid as the raw material. Suitable experimental conditions for synthesizing the intermediate and final products were probed. Their chemical structures were also investigated by means of infrared spectroscopy and hydrogen nuclear magnetic resonance spectroscopy. Based on the results of these analyses, it has been found that during the reaction process of HEAI with sodium 3-chloro-2-hydroxypropane sulfonate under alkaline condition the imidazoline ring was hydrolyzed to amides, and the obtained amphoteric surfactant was actually a complex mixture of amides. An etherification reaction in the hydroxyethyl group was also observed when the HEAI/sodium 3-chloro-2-hydroxypropane sulfonate molar ratio was more than 1:1.

Key words 1-Hydroxy-2-alkyl-2-imidazoline · Imidazolinium amphoteric surfactant · Tall oil fatty acid

Introduction

2-Alkyl-2-imidazoline obtained by the reaction of fatty acid with monosubstituted ethylenediamine is a useful intermediate that can be widely used to produce a fiber softening agent, emulsifier, antistatic agent, dispersion agent, corrosion inhibitor, antirust agent, and amphoteric surfactant. An imidazolinium amphoteric surfactant is one of the most important amphoteric surfactants. It has been widely used especially in personal care products (e.g., hair shampoos and conditioners, liquid soaps, shower gels, cleansing lotions) because it is biologically degraded rapidly and completely, and has good foaming ability on its own and in combination with a wide range of other surfactants. It also has exceptionally low irritation effects on skin.[1,2] In addition, imidazolinium amphoteric surfactant can also be used in highly acidic and alkaline household cleaning agents.

Fatty acids or fatty esters are usually employed as starting materials for synthesizing 2-alkyl-2-imidazoline, and they may be substantially pure materials or mixtures of various fatty acids or their esters. The other starting material is a monosubstituted ethylenediamine, such as *N*-hydroxyethylethylenediamine (HEEDA) or *N*-aminoethylethylenediamine. The development of the Chinese surfactant industry was heavily restricted because of a shortage of vegetable oil, and there have been few reports about utilizing Chinese tall oil fatty acid. Synthesis of new amino acid-type amphoteric surfactants from tall oil fatty acid was reported in a previous paper.[3] In this study synthesis of 1-hydroxyethyl-2-alkyl-2-imidazoline (HEAI) and its derivative imidazoline sulfonate surfactant was examined to widen the application of Chinese tall oil fatty acid further. Their chemical structures were also identified by means of infrared (IR) spectroscopy and hydrogen nuclear magnetic resonance (^{1}H-NMR) spectroscopy.

Materials and methods

Materials and agents

The tall oil fatty acid used was the same as that in a previous report.[3] The composition of the tall oil fatty acid was 2,9,12-octadecatrienoic acid (1.6%), oleic acid (85.1%), stearic acid (5.1%), 9,11-octadecadienoic acid (3.4%), and 8,11-octadecadienoic acid (4.8%). Its average molecular weight was 281.9. 1-Chloro-2,3-epoxypropane, sodium hydrogen sulfite, sodium hydroxide, HEEDA, and other reagents were all analytical grade.

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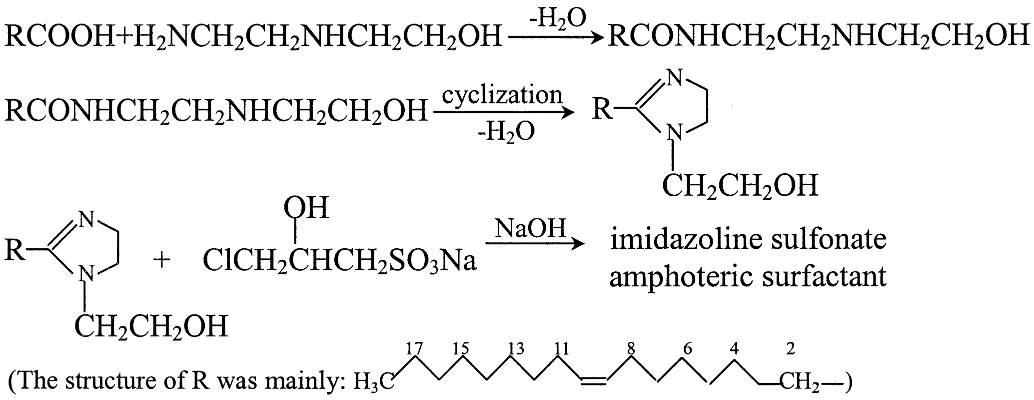


Synthetic course

The synthetic courses of HEAI and its derivative were as follows.

Preparation of HEAI

A four-necked flask equipped with a stirrer, a reflux condenser, a water segregator, and a thermometer was charged with 56.4 g (0.2 mol) of tall oil fatty acid, 0.2 mol of HEEDA, and 100 ml of xylene. The reactant was refluxed at 140°–150°C until no more water came over from the water separator. The water segregator was removed, the pressure of the reaction system was adjusted to 14.66 kPa, and the reaction temperature was raised to 250°C for another 30 min. A semisolid product was obtained.

Synthesis of imidazoline sulfonate amphoteric surfactant

The synthesis of amphoteric surfactant of HEAI sulfonate was carried out in a three-necked flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser. The flask was charged with 20 ml of deionized water, 10.5 g (0.03 mol) of HEAI, and 5.9 g (0.03 mol) of 3-chloro-2-hydroxypropanesulfonate and heated to 80°–90°C. Under stirring, 10% aqueous sodium hydroxide (about 12 ml) was then slowly dropped into the flask. The reaction was not finished until the pH of the reaction mixture went down to 7–8. The resultant mixture was then desiccated under vacuum to remove the water. Following the addition of 50 ml of anhydrous alcohol to dissolve the desiccated product, the undissolved NaCl was removed by filtration. The filtrate was then distilled to recover the alcohol and obtain the light yellow transparent semisolid.

Measurement of HEAI content

Several methods, such as gas-liquid chromatography (GLC), thin-layer chromatography (TLC), high-performance liquid chromatography (HPLC), and spectrophotometry have been used in other studies to measure the content of the imidazoline ring.[4–6] GLC, TLC, and HPLC were not suitable for this study, however, because the fatty acid used was a mixture and the product was not easily quantitatively determined by these methods. Furthermore, GLC was not certain to provide ideal analysis results because the amino-amide could be cyclized further into the imidazoline cycle when the column temperature was higher than 200°C. These shortcomings could be overcome with spectrophotometry. It has been shown by researchers that the position of the maximum absorption peak of HEAI (λ_{max}) is 230 nm, and that of its corresponding salt is 228 nm. Moreover, the length of the alkyl group did not have any effect on the position of the maximum absorption peak or the molar absorption value. Therefore, it is suitable for measuring the molar content of the imidazoline cycle.

The measuring process was as follows: The HEAI sample (0.01–0.03 g) was dissolved in 50 ml of anhydrous alcohol, and the solution was used to measure the HEAI content. The liquid thickness was 0.1 cm, and the scanning range was 190–270 nm. The measured value for the sample was corrected using the value of the blank test. The HEAI content ($X\%$) can be calculated according to the following formula.

$$X\% = \frac{D \times M \times V}{E \times L \times m \times 10}$$

where D is the photodensity; M is the molar weight average (g/mol); V is the solvent volume (ml); E is the molar absorptivity (6550/mol·cm); L is the liquid thickness for light passing through (cm); and m is the sample weight (g).

Structural determination of synthesized intermediates and final products

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

Results and discussion

Main factors influencing the synthesis of HEAI

In the reaction process between tall oil fatty acid and HEEDA, in addition to obtaining the desired product

HEAI, the by-products diacylamide and fatty acid ester were also produced. The existence of diacylamide leads to the formation of particulate matter or causes turbidity during the aging period for imidazoline aqueous solution. Suitable reaction conditions were explored to increase the yield of HEAI and decrease the amount of by-products.

Effect of the HEEDA/tall oil fatty acid molar ratio on HEAI yield

The effect of the HEEDA/tall oil fatty acid molar ratio on HEAI yield is shown in Fig. 1. The experimental conditions were as follows: tall oil fatty acid 26.4g (0.2mol), xylene 100ml (used as a solvent). The reactant was first refluxed and the water removed with a water segregator for 4h at 150°C. The reaction temperature was then raised to 210°C, and the solution was stirred for another 4h. It was known from Fig. 1 that the yield of the product rose along with the increasing HEEDA/fatty acid molar ratio. When the molar ratio was 2.2:1.0 the HEAI yield reached 89.3%. However, the yield did not increase obviously even if the molar ratio was higher than 2.2:1.0.

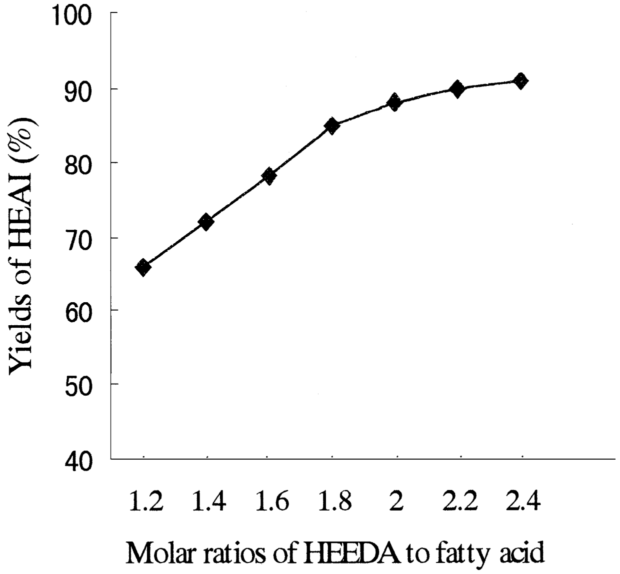


Fig. 1. Relation of molar ratios of raw materials with the yields of 1-hydroxyethyl-2-alkyl-2-imidazoline (*HEAI*)

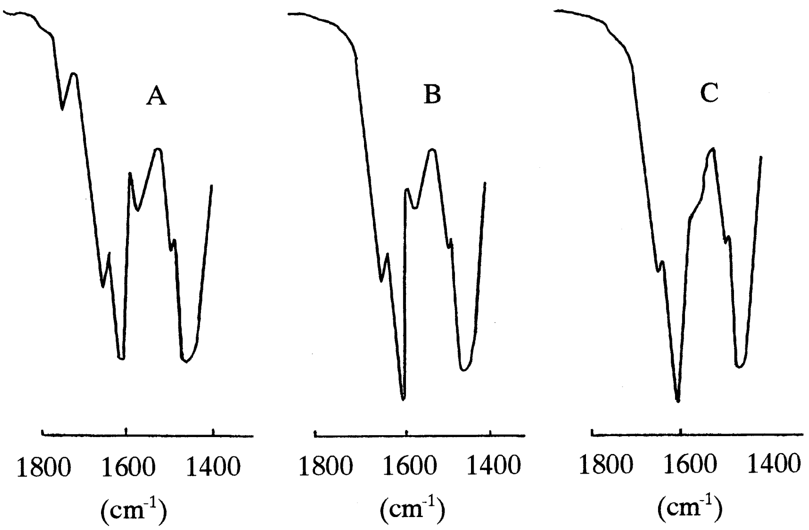
The partial IR spectra of products obtained at various molar ratios are shown in Fig. 2. It was found that the various products had different characteristic absorption peaks. When the molar ratio was 1:1, in addition to a strong peak at $1604\,\text{cm}^{-1}$ (the characteristic peak of the imidazoline cycle), there was a peak at $1735\,\text{cm}^{-1}$ (the absorption peak of ester-bond carbonyl group) and peaks at 1650 and $1550\,\text{cm}^{-1}$ (the absorption peaks of the amide). The peak strength at $1735\,\text{cm}^{-1}$ disappeared when the molar ratio was more than 1.8:1.0. At peaks at 1650 and $1550\,\text{cm}^{-1}$, their strength weakened gradually along with the increasing of molar ratio; but the peak at $1650\,\text{cm}^{-1}$ did not disappear completely even when the molar ratio was higher than 2.2:1.0.

Effect of reaction temperature on HEAI synthesis

The reaction of fatty acid with HEEDA is endothermic. Increasing the temperature is beneficial to the reaction. During the course of synthesizing HEAI, the ideal method was to form the monoamide intermediate secondary amide; the intermediate was then dehydrated and cyclized to form HEAI. However, because the two amino groups exist in the same molecule, the by-product diamide was also probably formed in addition to the main product, secondary monoamide, during the stage of acylation when the reaction temperature was increased. The effect of the acylation temperature on the reaction products explored is shown in Table 1.

The experimental conditions were as follows: acylation time 4h, HEEDA/fatty acid molar ratio 2.2:1.0. Table 1 indicates that the by-product diamide content increased along with the increasing reaction temperature. It was also found in the experimental procedure that the color of the reactant rapidly deepened, and a black brown product was

Fig. 2. Infrared (IR) spectra of HEAI obtained under various *N*-hydroxyethylethylenediamine (HEEDA)/fatty acid molar ratios. The HEEDA/tall oil fatty acid molar ratios in **A**, **B**, and **C** were 1:1, 1.8:1.0, and 2.2:1.0, respectively



finally obtained when the acylation temperature was higher than 170°C. This might be due to the fact that amine was severely oxidized, which led to the deep color. Because of the color of the product, the diamide content, and the fatty acid conversion ratio, the suitable acylation temperature was determined to be 150°–170°C.

The effect of the cyclization temperature of the intermediate on the reaction products is shown in Table 2. The pressure in the reaction system was 14.66 kPa, and the other conditions were the same as mentioned above. It was found from the data in Table 2 that the HEAI yield increased along with the rise in temperature. It reached 91.3% (molar percentage based on fatty acid) when the cyclization temperature was 215°C, but when the temperature rose further the yield decreased. In addition, the color of the resultant HEAI obviously deepened when the cyclization temperature rose to 250°C. Therefore, the suitable cyclization temperature was 215°–235°C.

Effect of reaction time on HEAI synthesis

The effect of acylation time on the reaction products was explored under the conditions of a HEEDA/fatty acid molar ratio of 2.2 : 1.0, an acylation temperature of 150°C, a cyclization temperature of 215°C, and a system pressure at the cyclization stage of 14.66 kPa. During the experimental process, at the acylation stage the amount of water segregated by xylene decreased greatly after refluxing for 4 h. Little water separated out after refluxing for 5.5 h. Hence, the suitable acylation time was 5.5 h.

Table 1. Effect of acylation temperature on reaction products

Acylation temperature (°C)	Bisamide content (%)	Conversion ratio of fatty acid (%)
130	0.6	74.5
150	3.7	95.3
170	4.5	96.1
190	5.8	97.0

Table 2. Effect of cyclization temperature on reaction products

Cyclization temperature (°C)	HEAI yield (%)	Bisamide content (%)
195	84.7	3.9
215	91.3	3.8
235	91.1	3.9
250	90.2	4.1

HEAI, 1-hydroxyethyl-2-alkyl-2-imidazoline

Table 3. Effect of cyclization time on reaction products

Cyclization time (h)	HEAI content (%)	Bisamide content (%)	Color of reaction products
2	81.7	3.7	Light brown
4	91.3	3.8	Light brown
6	91.2	3.9	Brown
8	91.2	4.0	Deep brown

The effect of cyclization time on the reaction products is shown in Table 3. The HEAI yield increased with prolongation of the cyclization time. The contents of both the desired HEAI and the by-product diamide in the reaction products were almost constant after 4 h, but the color of the obtained products gradually deepened. When the cyclization time was more than 8 h, the products were black-brown. The suitable cyclization time was therefore 4–6 h.

Effect of various reaction conditions on the synthesis of imidazolinium amphoteric surfactant

The reaction of HEAI with 3-chloro-2-hydroxypropanesulfonate is a nucleophilic substitution, and the reaction was carried out under alkaline conditions. The pH value of reaction medium and the reaction temperature have some influence on it.

Effect of reaction medium pH on the solubility of imidazoline sulfonate amphoteric surfactant

The effect of reaction medium pH on the solubility of imidazoline sulfonate is shown in Table 4. The experimental conditions for synthesizing imidazoline sulfonate were as follows: HEAI 17.50 g (0.05 mol), sodium 3-chloro-2-hydroxypropanesulfonate 9.83 g (made into a saturated solution with distilled water), 10% aqueous NaOH solution 20 ml, water 50 ml (as the solvent), reaction temperature 80°C, and reaction time 6 h. After ending the reaction, one part of the reaction liquid was removed and dissolved in 100 parts of water to observe the solubility of the reaction products. As can be seen from Table 4, the solubility of the products obtained at different pH values differed greatly. The solubility of the reaction products decreased with the increasing pH of the reaction medium. This was due to the fact that sodium 3-chloro-2-hydroxypropanesulfonate was hydrolyzed to sodium 2,3-dihydroxypropanesulfonate. However, during nucleophilic substitution, —Cl was much more active than —OH as a leaving group, and sodium 2,3-dihydroxypropanesulfonate could not react with HEAI. Therefore, HEAI did not react completely and caused the solution to become turbid. Hence pH 8 was suitable for the reaction medium.

Effect of reaction temperature on the quaternarization of HEAI

During the reaction of HEAI with sodium 3-chloro-2-hydroxypropanesulfonate, the influence of the temperature on the reaction time and the solubility of the reaction liquid

Table 4. Effect of pH on reaction products

pH	Effect[a]
8	Transparent (clear)
10	Slightly muddy after 24 h
13	Muddy (turbid)

[a] Solubility of obtained products

are shown in Table 5. The reaction time refers to the period from the end of adding the NaOH solution until the pH of the reaction medium is stabilized. As can be seen in Table 5, the time needed for the reaction varied at different reaction temperatures. The reaction time decreased along with the rise in the reaction temperature. The solubility of the reaction products obtained at the various reaction temperatures was also slightly different. The products obtained at 40°–80°C had good solubility in water; but when the reaction temperature rose to 100°C the aqueous solution of the resultant products was somewhat turbid. Hence, the suitable reaction temperature was 80°C, and the time required was about 6h.

Structural analyses of the synthesized HEAI and its derivative amphoteric surfactant

The structures of the synthesized HEAI and its derivative sulfonate amphoteric surfactants have been identified by means of IR, ^{13}C-NMR, and ^{1}H-NMR.[7–10] Products I and II were obtained when the HEAI/3-chloro-2-hydroxypropanesulfonic acid molar ratios were 1:1 and 1:2, respectively. In the IR spectrogram of tall oil fatty acid, the strong peak at 1708cm^{-1} was assignable to an absorption of $\nu_{C=O}$. The peaks at 1415 and 1284cm^{-1} were the absorptions of δ_{C-O-H} and ν_{C-O}, respectively, in the carboxyl group. Compared with the IR spectrogram of tall oil fatty acid, the peaks at 1708, 1415, and 1284cm^{-1} completely disappeared in the IR spectrogram of HEAI, and a strong peak occurred at 1604cm^{-1} that belonged to the absorption of $\nu_{C=N}$ of the 2-imidazoline ring. With ^{13}C-NMR, the peaks at 167.7 and 167.2ppm were the carbon chemical shifts of C=N in the imidazoline ring.

Table 5. Effect of reaction temperature on reaction time

Reaction temperature (°C)	Reaction time (h)	Solubility of products
40	25	Clear
60	24	Clear
80	6	Clear
100	2	Slightly turbid

For product **I**, in the IR spectrogram, there were strong absorption peaks at 1650, 1640, and 1560cm^{-1}. It was shown that product **I** contained a tertiary acylamide group (1650cm^{-1}, $\nu_{C=O}$) and a secondary acylamide group [1640cm^{-1} $\nu_{C=O}$, 1560cm^{-1} δ_{N-H} in —C(=O)N—H]. The peaks at 1425 and 850cm^{-1} belonged to ν_{C-N} and δ_{C-N}, respectively, in the acylamide group. The strong peaks at 1220, 1200–1180, and 1050cm^{-1} were assignable to the absorption of ν_{S-O}, $\nu_{as\ SO3}{}^{-}$, and $\nu_{s\ SO3}{}^{-}$, respectively. In the proton nuclear magnetic resonance (^{1}H-NMR) spectra, the chemical shifts at δ 0.9–2.1 were assignable to the alkyl protons: [δ 0.9 (t, CH_3—, C-18), δ 1.3 (s, —CH_2—, C4–7 and C12–17), δ 1.6 (t, CH_2, C-3), δ 2.0 (m, CH_2, C-8 and C-11), δ 2.2 [t, —CH_2—C(=O)N, C-2], δ 2.4 (m, C—CH_2—N—CH_2—C—), δ 2.5–2.7 [—C(=O)NCCH_2—N—], δ 2.8 [t, C—N—CH_2—C(OH)], δ 3.1 (m, —CH_2—SO_3^-), δ 3.3–3.4 [m, —C—CH_2(OH)], δ 3.5–3.8 [m, —C(=O)N—CH_2—,

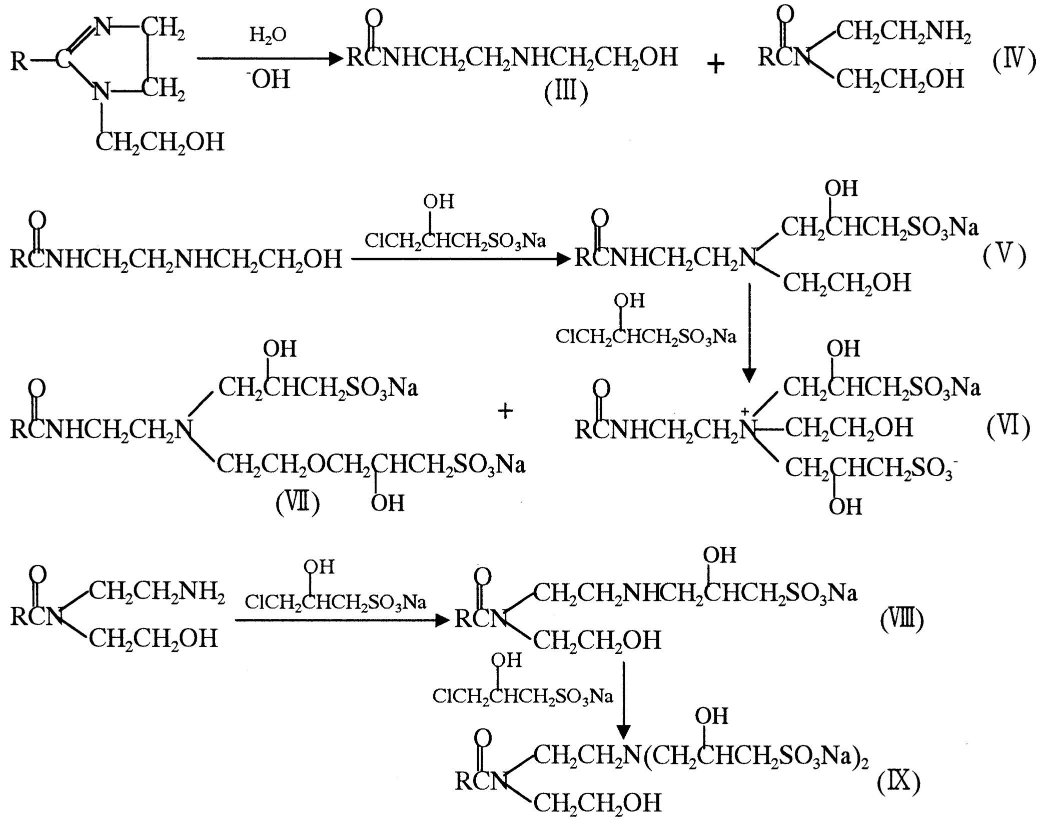


Fig. 3. Reaction pathway and products from the reaction of HEAI with sodium 3-chloro-2-hydroxypropanesulfonate

—C(=O)N—C—CH(OH)—C—], δ 5.3 (t, —CH=CH—, C-9 and C-10), δ 6.1 [—C(=O)NH—], δ 6.6 (s, NC—C—OH), δ 7.5 [C—C(OH)—C—SO_3^-)]. For product **II** in the IR spectrogram, most of the peaks were the same as those of product **I**. In addition, there were two peaks, at 1100 cm^{-1} ($\nu_{C—O—C}$) and 950 cm^{-1} ($\delta_{C—O—C}$), that did not appear in product **I**.

Analytical results showed that in imidazoline sulfonate amphoteric surfactants the characteristic peak of the 2-imidazoline ring at 1604 cm^{-1} clearly disappeared, whereas strong peaks occurred at 1650, 1640, and 1560 cm^{-1}. It was shown that during the reaction process the imidazoline ring of HEAI was completely hydrolyzed to amides, and the secondary amide was predominantly formed. The hydrolyzed products reacted further to sodium 3-chloro-2-hydroxypropanesulfonate. It was demonstrated from the ^{1}H-NMR spectra that product **I** contained both secondary and tertiary amides, but the ether link was not found in either its IR or ^{1}H-NMR spectra. However, the IR absorption peaks of the ether link were observed at 1100 and 950 cm^{-1} in product **II**. Therefore, the probable reaction pathway and reaction products for HEAI reacting with sodium 3-chloro-2-hydroxypropanesulfonate are summarized in Fig. 3. Product **I** probably contained compounds **V** and **VIII**, with compound **V** being the main component. Product **II** probably contained mainly compounds **VI**, **VII**, and **IX**, with compound **IX** being the main component.

Conclusions

HEAI and its derivative sulfonate amphoteric surfactant were synthesized using tall oil fatty acid as the main raw material. The effects of the HEEDA/tall oil fatty acid molar ratio and the reaction temperature and time of the acylation and cyclization reactions on the synthesis of HEAI were discussed. The test results showed that the suitable conditions for synthesizing HEAI were as follows: HEEDA/tall oil fatty acid molar ratio 2.2 : 1.0; xylene as both solvent and water-carrying agent; acylation temperature 150°–170°C; acylation time 5.5 h, cyclization temperature 215°–235°C; and the cyclization time 4–6 h.

Suitable conditions for synthesizing imidazoline sulfonate amphoteric surfactant were explored. The pH of the reaction medium and the reaction temperature and time had major effects on the solubility of amphoteric surfactant. The suitable pH value, reaction temperature, and reaction time were pH 8, 80°C, and 6 h, respectively.

The structures of synthesized HEAI and its derivative sulfonate amphoteric surfactant were analyzed by means of IR spectroscopy and ^{1}H-NMR. Analytical results indicated that the imidazoline ring did not exist in its derivative amphoteric surfactant, as the absorption peak at 1604 cm^{-1} disappeared completely. The obtained amphoteric surfactants were a complex mixture, and the probable structures of the components were explored.

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