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Shi-Fa Wang · Takeshi Furuno · Zhi Cheng

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

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Abstract Two new amino acid-type amphoteric surfactants – disodium *N*-(2-fatty acyl amino) ethyliminodiacetate and disodium *N*-(2-fatty acyl amino) ethyl-*N*,*N*-bis[3-(2-hydroxy) propylsulfonate] amine – were synthesized using tall oil fatty acids as the raw material. Suitable processing conditions 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 · Amino acid type

Introduction

The amphoteric surfactant is a surfactant 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, among 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 daily chemicals, textiles, dyes, pigments, food, pharmaceuticals, machining, metallurgy, washing, petroleum, and others. It has been used as a detergent, in moistening and foaming agents; as a corrosion inhibitor, a dispersion agent, a germicide (bactericide), an emulsifying agent, an antistatic and softening agent of fibers; in dyes; and as a chelating agent and a cleaning agent.[2–7]

Amino acid-type amphoteric surfactant is one of the early amphoteric surfactants. It has wide utilization fields, and its output is a little higher than that of others. Among the hydrophilic groups, the positive charges are carried by amino groups, and the negative charges are usually carried by $—COO^-$, $—SO_3^-$, $—OSO_3^-$, $—PO_4^-$, and others. The common amino acid-type amphoteric surfactants have two types of aminocarboxylic acid and aminosulfonic acid. The fatty acid materials used to come mainly from castor oil, coconut oil, palm oil, soybean oil, rapeseed oil, and cottonseed oil. Much of the soybean oil and rapeseed oil is consumed in the food industry, however, and other materials such as coconut oil and palm oil are not available in China. The shortage of materials is one of the main factors restricting development of the Chinese surfactant industry.[8,9] Therefore, it is necessary to utilize tall oil fatty acid as a material for synthesizing surfactants in the future. There have been no reports about the synthesis of amphoteric surfactants using tall oil fatty acid in China. In this study, two new amino acid types of amphoteric surfactant – disodium *N*-(2-fatty acyl amino) ethyliminodiacetate and disodium *N*-(2-fatty acyl amino) ethyl-*N*,*N*-bis[3-(2-hydroxy) propylsulfonate] amine – were synthesized using tall oil fatty acid as the raw material with new methods, and suitable synthetic conditions of the intermediates and final products were studied. The chemical structures of the intermediates and final products were also identified by means of infrared (IR) spectroscopy, hydrogen nuclear magnetic resonance (H-NMR) spectroscopy, and elemental analysis.

S.-F. Wang · T. Furuno (✉)
Faculty of Science and Engineering, Shimane University, Matsue 690-8504, Japan
Tel. +81-852-32-6563; Fax +81-852-32-6123
e-mail: t-furuno@riko.shimane-u.ac.jp

S.-F. Wang · Z. Cheng
College of Chemical Engineering of Forest Products, Nanjing Forestry University, Nanjing 210037, China

Materials and methods

Materials

The 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 was 281.9. Ethylenediamine, sulfinyl chloride (dichlorosulfoxide), phosphorus trichloride, epichlorohydrin, sodium hydrosulfite, sodium hydroxide, chloroacetic acid, and other reagents were all of analytical grade.

Synthetic course

The synthetic course of the amphoteric surfactants was as follows.

$$RCOOH \xrightarrow{PCl_3 \text{ or } SOCl_2} RCOCl \xrightarrow{NH_2CH_2CH_2NH_2} RCONHCH_2CH_2NH_2$$

$$RCONHCH_2CH_2NH_2 \xrightarrow[ClCH_2CH(OH)CH_2SO_3Na]{ClCH_2COONa \text{ or}} \begin{cases} RCONHCH_2CH_2N(CH_2COONa)_2 \text{ (I)} \\ RCONHCH_2CH_2N(CH_2CHOHCH_2SO_3Na)_2 \text{ (II)} \end{cases}$$

Experiments

Preparation of sodium chloroacetate

Chloroacetic acid was dissolved in anhydrous alcohol and was 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 with an ice-water bath. The crystal obtained by filtering was washed with anhydrous alcohol and then dried to synthesize the 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 with a waterbath. The flask was charged with 64.7 g sodium hydrosulfite, 25.0 g sodium sulfite, and 130 ml deionized water. The temperature of the solution was adjusted to room temperature after sodium hydrosulfite and sodium sulfite were dissolved. Then 50.0 g epichlorohydrin was slowly added, and the reaction temperature was kept 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 the compound (II).[13,14]

Table 1. Composition of tall oil fatty acid

Compound	Tall oil fatty acid (%)
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

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

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) of 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 the 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° and 180°C as the intermediate of synthesizing amphoteric surfactants.

Synthesis of N-aminoethyl fatty acylamide

A four-necked flask equipped with a stirrer, a reflux condenser, and a thermometer was charged with 100 ml benzene and 91.7 g (1.526 mol) ethylenediamine. The mixture was then cooled to about 6°C. The fatty acyl chloride (30.05 g) was dropped slowly into the mixture to react with ethylenediamine at <10°C for 4 h. Then 50 ml distilled water was added to remove the surplus ethylenediamine. The benzene-containing layer was washed with saturated sodium chloride solution until reaching the neutrality (determined with pH test paper); it was then dried with anhydrous sodium sulfate and distilled to recover the benzene. The distilled residue was dissolved in ethyl acetate, and 7.6 ml 35% hydrochloric acid was added to the ethyl acetate solution. The crystal obtained was washed with 150 ml ethyl acetate three times to remove the bisamide by-product. The ethyl acetate was recovered by distillation, and the residue was the by-product bisamide. The crystal was then dissolved in deionized water, and 22 ml 20% NaOH was added. The water solution was extracted with 50 ml benzene four times. The benzene layer was then washed with an NaCl-saturated solution, and the intermediate *N*-aminoethyl fatty acylamide was obtained after distilling to remove benzene.

Synthesis of amphoteric surfactants

The synthesis of amphoteric surfactants I and II was carried out in a three-necked flask equipped with an agitator, a thermometer, and a reflux condenser. For synthesis of compound I, the flask was charged with 16.2 g (0.05 mol) *N*-aminoethyl fatty acylamide, 100 ml 95% alcohol, and 11.7 g sodium chloroacetate (made into a saturated aqueous solution). Then 20 g 20% sodium hydroxide solution was slowly dropped into the flask, with the pH values of the reaction system maintained at around 8.0–8.5 at 60°C. The reaction was continued at 60°C for another 3 h after adding all the sodium hydroxide. Then the reaction temperature was increased to 90°–95°C to react for another 4 h. The resultant mixture was distilled to remove water and alcohol. The residue was dissolved in 100 ml 95% alcohol and was heated to reflux for 1 h. The solution was then hot-filtered to remove the solid sodium chloride. The filtrate was cooled to obtain the raw crystal. A white solid disodium *N*-(2-fatty acylamino)ethyliminodiacetate was finally obtained by recrystallization with anhydrous alcohol. The yield of compound I was 89.7%.

The synthetic method for compound II, disodium *N*-(2-fatty acylamino) ethyl-*N*,*N*-bis-[3-(2-hydroxy) propylsulfonate] amine, was similar to that described above, except sodium 3-chloro-2-hydroxypropanesulfonate was used instead of sodium chloroacetate. The yield of compound II was 83.9%.

Structural determination of synthesized intermediates and final products

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

Results and discussion

Main factors influencing the synthesis of fatty acyl chloride

During the process of chlorination of fatty acid, the various chlorinating agents, dosage of the chlorinating agent, and the solvent dosage directly influence the qualities of the obtained fatty acyl chloride. Suitable chlorination conditions were examined to reduce the factors influencing the synthesis of amphoteric surfactants.

Effect of chlorinating agents and their dosage on the acyl chlorination of fatty acid

All of the $SOCl_2$, PCl_3, PCl_5, and $POCl_3$ can be used as a chlorinating agent to chlorinate the fatty acid, although the agents usually used are $SOCl_2$ and PCl_3. The effect of the chlorination on tall oil fatty acid is shown in Table 2. The experimental conditions were as follows: tall oil fatty acid 28.2 g (0.1 mol), PCl_3 5.5 g (0.04 mol), or $SOCl_2$ 14.3 g (0.12 mol); reaction temperature 60°C; reaction time 6 h; benzene used as a solvent at a dose of 100 ml.

Table 2. Effects of chlorinating agents on the chlorination reaction of fatty acid

Chlorinating agent	Yield of acyl chloride (%)	Color of acyl chloride
$SOCl_2$	96.0	Deep brown
PCl_3	95.8	Light yellow

Table 3. Effect of phosphorus trichloride on the chloridization reaction of tall oil fatty acid

Dose of phosphorus trichloride (mol)	IR characteristic peaks of reaction products (cm^{-1})
0.020	1708, 1801, 1835, 1750
0.035	1708, 1801, 1835, 1750
0.040	1801, 1835, 1750
0.045	1801
0.050	1801

Point 1708 cm^{-1} is the absorbent peak of carboxyl group $\nu_{C=O}$; 1835 cm^{-1} and 1750 cm^{-1} are the absorbent peaks of fatty acid anhydrides $\nu_{asC=O}$ and $\nu_{sC=O}$; 1801 cm^{-1} is the absorbent peak of acyl chloride $\nu_{C=O}$

It can be seen in Table 2 that the yields of fatty acyl chloride were almost the same in the presence of excess chlorinating agents of sulfinyl chloride and phosphorus trichloride, but the colors of the obtained products were obviously different. The color of fatty acyl chloride obtained using phosphorus trichloride as a chlorinating agent was much lighter than that using sulfinyl chloride. The color of the fatty acyl chloride has an influence on the reaction products that follow. Therefore, phosphorus trichloride was selected as the chlorinating agent for the chlorination of tall oil fatty acid.

The influence of the phosphorus trichloride doses on product composition is shown in Table 3. The experimental conditions were as follows: tall oil fatty acid 28.2 g; reaction temperature 60°C; reaction time 6 h; and benzene dose 56.4 g. The resultant reaction liquors were measured with IR spectra after separating the phosphorous acid contained in them. The characteristic peak of 1708 cm^{-1} was the absorbent peak for carboxyl group $\nu_{C=O}$; 1835 cm^{-1} and 1750 cm^{-1} were the absorbent peaks for fatty acid anhydride $\nu_{asC=O}$ and $\nu_{sC=O}$; and 1801 cm^{-1} was the absorbent peak for acyl chloride $\nu_{C=O}$. By comparing the IR spectra of various samples obtained with different doses of phosphorus trichloride, it was found that characteristic IR peaks for the samples were slightly different; that is, the product compositions were different from each other. When the dose of phosphorus trichloride was <0.035 mol, unreacted fatty acid and the by-product fatty acid anhydride still existed in the reaction product in addition to the goal product fatty acyl chloride. When the phosphorus trichloride dose was increased to 0.04 mol, free fatty acid was not seen, but the fatty acid anhydride still existed in the reacted liquor. When the phosphorus trichloride dose was >0.45 mol, peaks at

1835 cm^{-1} and 1750 cm^{-1} were almost gone from the IR spectra. A possible reason is that the following reactions took place during the process of fatty acid reacting with PCl_3.

$$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3 \quad (1)$$

$$RCOCl + RCOOH \longrightarrow RC(=O)-O-CR(=O) + HCl \quad (2)$$

$$RC(=O)-O-CR(=O) + PCl_3 \longrightarrow 2RCOCl + POCl \quad (3)$$

The test results showed that the phosphorus trichloride dose had to be >35% (0.045 mol) of its theoretical dose, so the fatty acid could be completely converted to acyl chloride. Therefore, the suitable dose of phosphorus trichloride was 0.045 mol.

Effect of solvent dosage on the chlorination of fatty acid

When PCl_3 was used as a chlorinating agent, the main by-product was H_3PO_3 with a small amount of fatty acid polymer. H_3PO_3 was removed mainly owing to gravity settling. The influence of solvent doses on the settling velocity of phosphorous acid is shown in Table 4. The test conditions were as follows: fatty acid 28.2 g and PCl_3 5.5 g; the reaction temperature and time were 60°C and 6 h, respectively; benzene was the solvent. It was known that the various solvent doses had an influence on separation of H_3PO_3 from the reaction mixture. The subsiding time was reduced as the solvent dose increased. A high solvent/fatty acid ratio increases the amount of solvent to be recovered. The most suitable solvent dose was 56.4 g (benzene/fatty acid weight ratio was 2:1).

Table 4. Effects of solvent doses on the separation of phosphorous acid from the product

Solvent dose (g)	Subsiding time (h)	Weight of phosphorous acid obtained (g)
0	2.0	0
	4.0	1.82
	6.0	2.72
28.2	2.0	1.73
	4.0	2.71
56.4	1.0	1.96
	2.0	2.72
112.8	0.5	2.41
	1.0	2.72

Influence of ethylenediamine dose on synthesis of N-aminoethyl fatty acylamide

The reaction between fatty acyl chloride and ethylenediamine was easily carried out. During the reaction process the by-product bisamide was also produced. The amount of bisamide depended on the ethylenediamine/fatty acyl chloride molar ratio. The influence of the various doses of ethylenediamine on the bisamide yield is shown in Table 5. The test conditions were as follows: reaction temperature 6°C; reaction time 5 h; fatty acyl chloride 30.05 g (0.1 mol); benzene 100 ml. The feeding sequence of the materials was as follows: Ethylenediamine was added first, and then fatty acyl chloride was dropped slowly into the reaction flask.

It was known from the test results that the amount of bisamide decreased as the dose of ethylenediamine increased. When the ethylenediamine dose was increased to 1.2 mol, the amount of bisamide was 0.7 mmol (0.4 g); and 98.6% of the fatty acyl chloride had been converted to monoamide. Hence, the suitable ethylenediamine/fatty acyl chloride molar ratio was more than 12:1, and the surplus ethylenediamine could be recovered by vacuum distillation.

Structural analyses of the synthesized intermediate and final products

The structures of the synthesized amino acid-type amphoteric surfactants and their intermediates have been identified by means of IR, H-NMR, and elemental analyses. The analytical results are shown in Table 6. 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 amino acid-type amphoteric surfactants – disodium *N*-(2-fatty acyl amino) ethyliminodiacetate and disodium *N*-(2-fatty acyl amino) ethyl-*N*,*N*-bis-[3-(2-hydroxy) propylsulfonate] amine – were synthesized using tall oil fatty acid as the main raw material. Suitable conditions for

Table 5. Effect of ethylenediamine on the amount of by-product bisamide

Parameter	Result, by ethylenediamine dose (0.1–1.4 mol)								
	0.1	0.2	0.3	0.4	0.6	0.8	1.0	1.2	1.4
Amount of bisamide (mol × 10^2)	1.00	0.80	0.49	0.39	0.29	0.20	0.12	0.07	0.05
Yield of monoamide[a] (%)	80.0	84.0	90.2	92.2	94.2	96.0	97.6	98.6	99.0

[a] The yield of monoamide was moles based on the total moles of fatty acyl chloride

Table 6. Structural analyses of amino acid amphoteric surfactants and their intermediates

Parameter	Value
Acyl chloride of tall fatty acid (RCOCl)	
Elementary analysis (%)	
Calculated value	
C	71.88
H	9.71
Tested value	
C	71.86
H	10.11
IR spectra (cm^{-1})	3008 ($\nu_{=C-H}$), 1650 ($\nu_{C=C}$), 1376 (δ_{sCH3}), 2927 (ν_{asCH2}), 2854 (ν_{sCH2}), 1461(γ_{CH2}), 725 (ρ_{CH2}), 1801 (—COCl$\nu_{C=O}$), 956 (—COCl$\nu_{O=C-Cl}$), 682 (ν_{C-Cl})
N-Aminoethyl fatty amide ($RCONHCH_2CH_2NH_2$)	
Elementary analysis (%)	
Calculated value	
C	74.07
H	12.34
N	8.64
Tested value	
C	74.04
H	12.36
N	8.63
IR spectra (cm^{-1})	3370 (ν_{asNH2}), 3270 (ν_{sNH_2}), 3303 (—CONH—ν_{N-H}), 3093 (frequency band produced by resonating of $\nu_{C=O}$ and δ_{N-H}), 1641 (—CONH—$\nu_{C=O}$), 1560 (—CONH—δ_{N-H}), 1615 (—$NH_2\delta_{N-H}$), 910 ~ 770 (ρ_{NH_2}), 721 (—CONH—ρ_{N-H})
Disodium *N*-(fatty acyl amino) ethylimino diacetate [$RCONHCH_2CH_2N(CH_2COONa)_2$]	
Elementary analysis (%)	
Calculated value	
C	59.49
H	8.68
N	5.78
Tested value	
C	59.51
H	8.66
N	5.76
IR spectra (cm^{-1})	
Acylamide group	3303 (—CONH— ν_{N-H}), 3087 (frequency band produced by resonating of $\nu_{C=O}$ and δ_{N-H}), 1641 (—CONH—$\nu_{C=O}$), 1560 (—CONH— δ_{N-H}), 1263 (frequency band produced by resonating of —CONH— ν_{C-N} and δ_{N-H}), 1240 ($\nu_{asC-N-C}$), 1197 (ν_{sC-N-C}), 721 (—CONH— ρ_{N-H})
Carboxyl group	1386 (ν_{sCOO^-}), 1550 (ν_{asCOO^-})
Amine group	1120 ($\nu_{asC-N-C}$), 1080 (ν_{sC-N-C})
Alkyl group	3006 ($\nu_{=C-H}$), 2921 (ν_{asCH_2}), 2850 (ν_{CH_2}), 1650 ($\nu_{C=C}$), 1465 (δ_{CH_2}), 1384 (δ_{sCH_3})
H-NMR (ppm)	0.9 (—CH_3, t, 3H), 1.3 (—CH_2—, s, 20H), 1.6 (—CH_2—C—C(=O)—N, t, 2H), 2.0 (—CH_2C=CCH_2—, m, 4H), 2.2 (—CH_2—C(=O)—N, t, 2H), 2.8 (—C(=O)—N—C—CH_2—N, t, 2H), 3.4 (—N—CH_2COONa, —C(=O)—N—CH_2—C d, 6H), 5.3 (—CH=CH—, m, 2H), 6.2 (—C(=O)—NH, s, 1H)
Disodium *N*-(fatty acyl amino) ethyl-*N*,*N*-bis-[3-(2-(hydroxy) propylsulfonate)] amine {$RCONHCH_2CH_2N[CH_2CH(OH)CH_2SO_3Na]_2$}	
Elementary analysis (%)	
Calculated value	
C	48.43
H	7.76
N	4.36
Tested value	
C	48.41
H	7.76
N	4.35
IR spectra (cm^{-1})	
Hydroxyl group	3450 (ν_{O-H}), 1100 (ν_{C-O}), 1420 (the first frequency band produced by resonating of δ_{O-H} andρ_{C-H}), 1340 (the second frequency band produced by resonating of δ_{O-H} and ρ_{C-H}), 620 ~ 580 (δ_{C-O-H})
Acylamide group	3303 (ν_{N-H}), 3087 (the frequency band produced by resonating of $\nu_{C=O}$ and δ_{N-H}), 1641 (—CO_NH— $\nu_{C=O}$), 1560 (—CONH— δ_{N-H}), 1263 (the frequency band produced by resonating of $\nu_{C=N}$ and δ_{N-H})
Amine group	1120 (tertiary amine $\nu_{asC-N-C}$), 1072 (tertiary amine ν_{sC-N-C})
Sulfonic group	1197 (ν_{asSO3-}), 1070 ($\nu_{sSO_3^-}$), 690 ($\delta_{sSO_3^-}$)
Alkyl group	3006 ($\nu_{=C-H}$), 2921 (ν_{asCH_2}), 2850 (ν_{sCH_2}), 1650 ($\nu_{C=C}$), 1465 (δ_{CH_2}), 1384 (δ_{sCH_3})
H-NMR (ppm)	0.9(—CH_3, t, 3H), 1.3 (—CH_2—, s, 20H), 1.6 (—CH_2—C—C (=O)—N, t, 2H), 1.8 (O—H, s, 2H), 2.0 (—CH_2C=CCH_2—, m, 4H), 2.2 (—CH_2—C(=O)—N, t, 2H), 2.8 (—C(=O)—N—C—CH_2—N, —N-CH_2—C(OH)—, m, 4H), 3.4 (C—CH(OH)—C, —C(=O)—N—CH_2—C, d, 4H), 5.3 (—CH=CH—, m, 2H), 6.2 (—C(=O)—NH, s, 1H)

the synthesis of fatty acyl chloride were probed. The test results showed that the chlorinating effect of phosphorus trichloride (PCl_3) was better than that of sulfinyl chloride. The suitable dose of PCl_3 was more than 35% of the theoretical dose. Benzene was used as the solvent for acyl chlorination, and the suitable benzene/fatty acid ratio was 2:1 (w/w). The influence of the ethylenediamine/fatty acyl chloride molar ratio on the yield of the by-product bisamide was discussed. When the ethylenediamine/fatty acyl chloride molar ratio was more than 12:1, 98.6% or more of the acyl chloride could be converted to monoamide. The structures of the intermediates and final products synthesized have been identified by IR, H-NMR, and elemental analysis.

References

1. Wang ZM, Xu YP (1990) Brief introduction of amphoteric surfactant (in Chinese). In: Amphoteric surfactant. China Light Industry Publishing, Beijing, pp 1–2
2. Liang ML, An BC (1986) Synthesis and application of the imidazoline-type amphoteric surfactant (in Chinese). J Fine Petroleum Chem Eng 5:14–27
3. Li YR, Li NX (1990) Study on the synthesis and its properties of new-type hydroxy-phosphate ester-containing amphoteric surfactant. J Fine Chem Eng 7(4,5):79–83
4. Ohara S, Kawakubo H (1999) Detergents containing betaine amphoteric surfactants (in Japanse). Jpn Kokai Tokkyo Koho JP 11 50,091

5. Yuuhei S, Haduki O (1999) Oral composition (in Japanese). Jpn Kokai Tokkyo Koho JP 11 49,654
6. Zhang JM, Meng ZG (1998) Studies on the structures and the properties of some amphoteric surfactants (in Chinese). Shanghai Dacue Xuebao Ziran Kexueban 4:703–706
7. He YJ, Zhang ZY (1998) Syntyhesis and properties of new amphoteric surfactant alkylamidophosphobetaines (in Chinese). Huadong Ligong Daxue Xuebao 24:741–745
8. Zhang DY (1989) Development status of Chinese surfactant industry (in Chinese). J Chem Ind Daily Use 3:19
9. Yuan HQ (1995) Present situation of Chinese detergent (in Chinese). J Chem Ind Daily Use 2:20
10. Wang SF, Furuno T, Cheng Z, Katoh S (2000) Composition of acidic components in Chinese raw tall oil. J Wood Sci 46:258–262
11. Wang BR (1985) Hydration of organic acid (in Chinese). In: Organic synthesis reaction. Science Publishing House, Beijing, p 814
12. Chemistry Department of Nanjing University (1967) Prepatation of sodium chloroacetate (in Chinese). In: Organic synthesis (I). Science Publishing House, Beijing, p 323
13. Li SA, Zhang ZY (1990) Synthesis of imidazoline sulfonate amphoteric suftactant (in Chinese). Fine Chem Eng 7(4,5):75–78
14. Bagolino CA, Pacific L, Quaresima ET (1989) *O*-Alkanoyl derivatives of 3-amino-2-hydroxypropanesulfonic acid having anticonvulsant activity and pharmaceutical compositions containing same for the therapeutical treatment of epilepsy. European Patent Application EP 309,421