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PREPARATION OF AMPHOTERIC SURFACE ACTIVE AGENTS

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9 Claims

ABSTRACT OF THE DISCLOSURE

A method for preparing betaine type amphoteric surface active agents by reacting a tertiary amine containing polyoxyethylene radicals and an alkali metal salt or an ammonium salt of monochloroacetic acid in either

(a) a solvent having the formula



wherein:

R is hydrogen or an alkyl having 1 to 4 carbon atoms, and

n is the integer 1 or 2, or

(b) a mixture of said solvent and an additional solvent selected from the group consisting of methanol, ethanol, propanol or dioxane, with the amount of said additional solvent not exceeding 80% by weight of the total weight of the solvent used.

This application is a continuation of application Ser. No. 593,688 filed Nov. 14, 1966, and now abandoned.

The present invention relates to an improvement in methods for synthesizing betaine type amphoteric surface active agents by a reaction between a tertiary amine and a monochloroacetate, and more particularly to a method for synthesizing betaine type amphoteric surfactants by means of a reaction between a tertiary amine having polyoxyethylene radicals and an alkali metal salt or an ammonium salt of monochloroacetic acid in (a) a solvent of the following Formula 1 or (b) in a water-soluble organic solvent containing at least 20% by weight of a solvent of said Formula 1, namely,



wherein:

R represents an alkyl radical having 1 to 4 carbon atoms, or hydrogen.

n represents an integer 1 or 2.

In the amphoteric surface active agent industry, it has been the general practice that the preparation of betaine type amphoteric surface active agents by amphoterizing amines has utilized a reaction between an amine and an aqueous solution of monochloroacetate. More specifically, the prior methods of synthesizing such amphoteric surface active agents comprise the steps of first dissolving or emulsifying an amine in water, subsequently adding thereto an aqueous solution of sodium monochloroacetate, and heating the mixture at a temperature in the range from 90° C. to 100° C. in the presence of sodium hydroxide to a reaction therebetween. Sodium hydroxide serves to seize the chlorine which is isolated during the course of reaction. The prior methods are satisfactory effecting amphoterization of alkylimidazoline and a satisfactory amphoteric surface active agent is obtained. However, such prior method works very poorly in the amphoterization of polyoxyethylene alkylamine. The fact that the amphoterizing reaction does not proceed satisfactorily, in spite of the intensive solubility of the sodium monochloroacetate in water, may be attributed to the poor solubility of the

polyoxyethylene alkylamine in a strong, alkaline aqueous solution and also to the fact that in said aqueous solution the product accruing from the reaction between the polyoxyethylene alkylamine and the salt of monochloroacetic acid decomposes into an amine and a salt of glycol acid. In fact, it has been observed by the inventors that in such an instance the reaction product shows a tendency to decompose in said aqueous solution to produce an amine. For this reason, the prior amphoterizing processes are not suitable when amines having polyoxyethylene radicals are used as the starting materials. Moreover, the prior amphoterizing processes perform reactions in an aqueous solution as has been described, and as an inevitable consequence, the amphoteric surface active agents which are the final products thus obtained always contained water. For this reason, the separation of the amphoteric surface active agents from the water was accompanied by severe formation of bubbles which, in turn, constituted a serious cause for the difficulty in the separation of effecting water from the surface active agent.

The present invention contemplates providing an improved method for the amphoterization of a tertiary amine having polyoxyethylene radicals, which in practice has been quite difficult using the prior methods. The improved method makes it possible to achieve a smooth progress of the amphoterizing reaction and also easy separation of the solvent from the reaction product as a result of the use of a specific solvent in the reaction.

The amphoterizing reaction performed on tertiary amines, in the present invention, is conducted basically by placing a tertiary amine having polyoxyethylene radicals in contact with an alkaline salt of monochloroacetic acid in a solvent, as will be described hereinafter, and also in the presence of alkali which is intended to seize the chlorine formed during the reaction. According to the present invention there is no particular restriction on the order of the feeding of the materials, such as the amine or amine solution, the monochloroacetate slurry and the alkaline solution. In practice, however, it is preferred to appropriately select the feeding order depending on the nature (chiefly the melting point) of the amine used, in order to obtain a desirable result. Such order of feeding will be made clear in the examples which will be given later.

The solvent which is used in the method of the present invention for the synthesis of amphoteric surface active agents is as indicated by the aforescribed Formula 1. This group of solvents includes ethylene glycol, diethylene glycol, an ethylene glycol monoalkyl ether such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether and ethylene glycol monobutyl ether, and also includes a diethylene glycol monoalkyl ether such as diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monopropyl ether and diethylene glycol monobutyl ether.

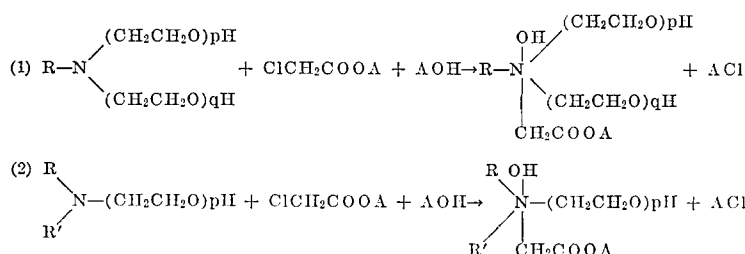
One or more water-soluble organic solvents selected from the group consisting of methanol, ethanol, propanol or dioxane may be used in combination with the aforesaid solvent indicated by the Formula 1, but the amount of such additional organic solvents must not exceed 80% by weight of the total weight of the organic solvent used.

The term "alkaline salt of monochloroacetic acid" as used herein, refers to and includes the sodium, potassium, lithium or ammonium salts respectively, of monochloroacetic acid. These alkaline salts of monochloroacetic acid are prepared by first dissolving monochloroacetic acid in said solvent and then adding an aqueous solution of sodium hydroxide, an aqueous solution of potassium hydroxide, an aqueous solution of lithium hydroxide or ammonia water, while holding said solution at a temperature of 50° C. or less. If an excess of alkali is used during the step of preparing said alkaline salt of

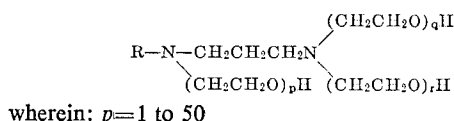
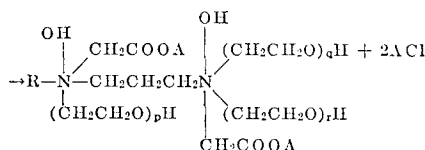
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monochloroacetic acid, there is no need of adding alkali for the purpose of seizing the chlorine produced in the amphoterizing reaction. Because the alkaline salts of monochloroacetic acid are of a poor solubility, it is customary that these salts are obtained in slurry form, but this state of the salts does not in any way adversely affect the amphoterizing reaction. While amphoterizing reactions are performed, in general, at a temperature in the range of from 50° C. to 200° C. for a length of time ranging from 0.5 to 5 hours, it is desirable from the viewpoint of performing an efficient reaction to make an appropriate selection of the conditions of the reaction so as to suit the type of the amines used. It is known that the velocity of amphoterizing reactions increases with an increase in the concentration of the reacting solution. However, the preferred degree of concentration of such reacting solution is usually 50% by weight.

The amines which can be used in the present invention as the starting materials include all of the tertiary amines having a polyoxyethylene radical. However, these tertiary amines may be divided into three types. The amphoterizing reactions for each type of amine are as follows:



wherein: $p+q=2$ to 50



wherein: $p+q+r=3$ to 50

Notes:

R represents an alkyl radical with 6 to 22 carbon atoms.

R' represents an alkyl radical with 6 to 22 carbon atoms.

A represents an alkali metal or NH_4^+ .

Where an excessive amount of a salt of monochloroacetic acid is used, there may occur a reaction between the hydroxyl radical located in the terminal of the polyoxyethylene radical and the salt of monochloroacetic acid, resulting in the polyoxyethylene radical being converted to one of the group of $(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_2\text{COOA}$. However, it is to be noted that the present invention includes such phenomenon.

While it is one of the noteworthy features of the present invention to use a solvent as is indicated in the aforesaid Formula 1 as the solvent for the amphoterizing reaction, this solvent is presumed to have a specific ability as far as amphoteric reactions are concerned. For example, when a water-soluble methanol, ethanol, propanol or dioxane is used as the only reaction solvent in the same manner as described for the use of the solvent of the present invention, there is obtained no satisfactory progress in the amphoterizing reaction. This is considered to be due to the fact that the solubility of the salt of the monochloroacetic acid in the water-soluble solvent indi-

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cated by the Formula 1 is markedly greater than it is in other water-soluble solvents.

According to the present invention, not only the amphoterization of polyoxyethylene alkylamines by a salt of monochloroacetic acid can be carried out with a satisfactory efficiency and in a relatively short period of time, but also the reaction products are easily separated from the solvent. When a considerable amount of water is present in the solvent used in the reaction, the water is boiled together with the co-present ethylene glycol monoalkyl ether, diethylene glycol monoalkyl ether or the like, and as a consequence, it can be easily removed almost without developing any bubbling.

EXAMPLE 1

To 104 gr. of monochloroacetic acid packed in a reaction vessel were added 426 gr. of a mixed solvent of ethylene glycol monomethyl ether and methanol (the ratio by weight being 4:6), thereby dissolving the former in said solvent. The resulting solution was neutralized by the addition thereto of 88 gr. of aqueous solution of a 50% sodium hydroxide, while holding the solution at a

temperature of 50° C. or less. Into this mixture were introduced 88 gr. of aqueous solution of a 50% sodium hydroxide and also 362 gr. of polyoxyethylene laurylamine (the mean additional mol number of ethylene oxide being 4), then allowing the mixture to react at a temperature between 85° C. and 90° C. for 2 hours while being stirred.

After filtering the reacted solution and after removing the by-product thereon, the precipitate was washed with isopropanol. The filtered sodium chloride liquid and the washing liquid were mixed together. After removing the solvent by distillation under a reduced pressure, the residue was mixed with benzene to dissolve the residue therein. The resulting solution was filtered to completely remove the sodium chloride, a by-product. The filtered liquid was distilled under a reduced pressure to remove benzene therefrom, and thus 459 gr. of reaction product were obtained.

The rate of reaction was determined on the reaction product by measuring the total base content (the sum of nitrogen and sodium) of the reaction product by the potentiometric titration using hydrochloric acid, and by measuring the nitrogen content by Kjeldahl method, as follow:

Total base content— 4.33×10^{-3} eqv./gr.
 Nitrogen content—2.96%
 Reaction ratio—105.2%
 Yield—99.8%

EXAMPLE 2

To a tertiary amine containing polyoxyethylene radicals packed in a reaction vessel was added an organic solvent, thereby dissolving the amine in the solvent. Separately therefrom, monochloroacetic acid was dissolved in an organic solvent, and while holding the resulting solution at a temperature of 50° C. or less, said solution was neutralized by the use of a 50% aqueous solution of caustic alkali. The neutralized solution was added to said amine solution. This was added to a 50% aqueous solution of caustic alkali and the mixture was heated to cause a reaction.

By treating the reacted solution in the same manner as in Example 1, a reaction product was obtained. The rate of the reaction was determined by the same analytical procedure.

The type and the amount of the amine, the organic solvent and the caustic alkali used are shown in Table 1, while the reaction conditions and the analysis of the reaction product and the yield are shown in Table 2.

tralize this solution while holding the latter at a temperature of 50° C. or less. Into this solution was introduced a solution of a tertiary amine containing polyoxyethylene radical in an organic solvent and also a 50% aqueous solution of caustic alkali, and the mixture was heated to effect a reaction while being stirred. The reacted solution was then treated in the same manner as in Example 1 and a reaction product was obtained. The

TABLE 1

Number	Amine solution				Alkaline salt of monochloroacetic acid			
	Type	R	p+q+r	Grams	Solvent, grams	Mono-chloro-acetic acid, grams	Solvent, grams	Caustic alkali 50% aqueous solution, grams
1.....	I	C ₁₈ H ₃₇	2	400	Ethyleneglycolmono-methylether, 209	116	Ethyleneglycolmono-methylether, 263	NaOH 98
2.....	I	C ₁₈ H ₃₇	50	618	Ethyleneglycolmono-butylether, 585	26	Ethyleneglycolmono-butylether, 59	NaOH 22
3.....	I	C ₁₈ H ₃₅	10	708	{Ethyleneglycolmono-methylether, 215 Methyl alcohol, 322	104	{Ethyleneglycolmono-methylether, 94 methyl Alcohol, 141	NaOH 88
4.....	II	C ₁₈ H ₃₇	15	296	{Ethyleneglycolmono-ethylether, 74 Isopropyl alcohol, 173	26	{Ethyleneglycolmono-ethylether, 20 Isopropyl Alcohol, 45	KOH 31
5.....	II	C ₁₈ H ₃₇	30	553	Diethyleneglycolmono-ethylether, 483	42	Diethyleneglycolmono-ethylether, 96	NaOH 36
6.....	III	C ₁₈ H ₃₇	15	987	Methyl alcohol, 670	209	Ethyleneglycolmono-butylether, 446	NaOH 176
7.....	III	C ₁₈ H ₃₇	30	412	{Diethyleneglycolmono-methylether, 48 Isopropyl alcohol, 266	52	Diethyleneglycolmono-methylether, 130	KOH 62

TABLE 2

No.	Reaction		Product		Reaction ratio, percent	Yield	
	Tempera-ture (° C.)	Time, hours	Total base content X10 ⁻³ eq. v./g.	N content percent		grams	percent
1.....	85-90	2	4.39	3.05	101.4	503	98.7
2.....	95-100	3	0.770	0.541	99.5	631	98.2
3.....	81	2	2.45	1.72	99.2	797	98.9
4.....	85-86	5	1.51	1.07	97.6	312	96.1
5.....	100-105	5	1.02	0.715	100.0	563	96.7
6.....	80-81	3	3.38	2.37	100.0	1,160	98.1
7.....	85-87	4	2.08	1.47	98.1	450	95.9

EXAMPLE 3

Into the monochloro acetic acid packed in a reaction vessel was introduced an organic solvent, thereby dissolving the said acid. The resulting solution was mixed with a 50% aqueous solution of caustic alkali to neu-

rate of the reaction was determined by the same analytical procedure as used in Example 1.

The type and the amount of the amine, the organic solvent and the caustic alkali are shown in Table 3, while the reaction conditions, the analysis of the reaction product and the yield are shown in Table 4.

TABLE 3

Number	Amine solution				Alkaline salt of monochloroacetic acid			
	Type	R	p+q+r	grams	Solvent, grams	Mono-chloro-acetic acid, grams	Solvent, grams	Caustic alkali 50% aqueous solution, grams
8.....	I	C ₁₂ H ₂₅	10	397	{Ethyleneglycol-82 Monoethylether, 82	66	{Ethyleneglycol-50 monoethylether, 50	KOH, 79
9.....	I	C ₁₈ H ₃₇	4	446	{Methyl alcohol, 191 Ethyleneglycol-monobutylether, 255	104	{Methyl alcohol, 115 Isopropyl alcohol 255	NaOH, 88
10.....	I	C ₁₈ H ₃₇	30	398	Diethyleneglycol-monomethylether, 355	26	Diethyleneglycol-monomethylether, 59	NaOH, 22
11.....	I	C ₁₈ H ₃₅	2	356	1,4-dioxane, 185	104	{Ethyleneglycol-monoehtylether, 84 1,4-dioxane, 151	NaOH, 88
12.....	II	C ₁₂ H ₂₅	10	397	Ethyl alcohol, 301	52	Diethyleneglycol-monoehtylether, 125	NaOH, 44
13.....	II	C ₁₈ H ₃₅	20	175	{Ethyleneglycol, 8 Isopropyl alcohol, 145	13	Ethyleneglycol, 29	NaOH, 11

TABLE 4

No.	Reaction		Product		Reaction ratio, percent	Yield	
	Tempera-ture, ° C.	Time, hour	Total base content X10 ⁻³ eq.v./g.	N content percent		Grams	Percent
8.....	80	2	2.65	1.87	99.2	451	96.1
9.....	90-92	5	3.67	2.58	99.5	533	98.0
10.....	100-110	1	1.18	0.825	100.3	411	97.3
11.....	93-94	3	4.43	3.05	103.2	433	95.4
12.....	79-80	4	2.20	1.56	98.2	425	95.3
13.....	85-86	5	1.34	0.936	100.6	181	96.6

7 EXAMPLE 4

Into the monochloroacetic acid packed in a reaction vessel was introduced an organic solvent, thereby dissolving the former. While holding the resulting solution at a temperature of 50° C. or less, the solution was neutralized by the addition of a 50% aqueous solution of caustic alkali. The resulting mixture was mixed with a tertiary amine containing polyoxyethylene radicals and also with a 50% aqueous solution of 50% caustic alkali, and the mixture was heated to effect a reaction while being stirred.

By treating the reacted solution in the same manner as in Example 1, a reaction product was obtained. The rate of the reaction was determined by the same analytical procedure as used in Example 1.

The type and the amount of the amine, the organic solvent and the caustic alkali used in the reaction are shown in Table 5, while the conditions of the reaction, the analysis of the product and the yield are shown in Table 6.

TABLE 5

Amine					Alkaline salt of monochloroacetic acid				
Number	Type	R	p+q+r	Grams	Mono-chloro-acetic acid, grams	Solvent, grams		Caustic alkali 50% aqueous solution, grams	Caustic alkali 50% aqueous solution, grams
14.....	I	C ₁₂ H ₂₅	2	274	104	{ Ethyleneglycol-monomethyl-ether, 101 Isopropyl alcohol, 237 }		NaOH, 88	NaOH, 88
15.....	I	C ₁₈ H ₃₇	10	355	52	{ Ethyleneglycol-monoethylether, 387 }		NaOH, 44	NaOH, 44
16.....	i	Tallow	8	201	35	{ Ethyleneglycol-monomethyl-ether, 223 }		NaOH, 30	NaOH, 30
17.....	III	C ₁₂ H ₂₅	3	375	198	{ Ethyleneglycol-monomethyl-ether, 100 1,4-dioxane, 397 }		NaOH, 168	NaOH, 168
18.....	III	C ₁₂ H ₂₅	15	452	104	{ Ethyleneglycol, 516 }		KOH 123	KOH 123

TABLE 6

No.	Reaction		Product		Reaction ratio, percent	Yield	
	Temperature, ° C.	Time, hours	Total base content, ×10 ⁻³ eqv./g.	N content, percent		Grams	Percent
14.....	80-85	3	5.28	3.61	104.7	368	98.7
15.....	95-100	1	2.39	1.65	102.5	400	99.0
16.....	105-110	1	2.79	1.91	105.1	233	99.7
17.....	92-94	3	6.95	4.99	95.2	555	97.2
18.....	95-100	3	3.52	2.49	97.8	549	97.0

EXAMPLE 5

To 208 gr. (2.2 mols) of monochloroacetic acid packed in a reaction vessel were added 755 gr. of a mixed solvent of ethylene glycol monomethyl ether and 1,4-dioxane (the ratio by weight being 1:1), thereby dissolving the former in said solvent. The resulting solution was neutralized by the addition thereto of 246 gr. (2.2 mols) of aqueous solution of a 50% potassium hydroxide, while holding the solution at a temperature of 50° C. or less. Into this mixture were introduced 626 gr. (1.0 mol) of polyoxyethylene laurylamine (the mean additional mol number of the ethylene oxide being 10) and also 246 gr. of aqueous solution of a 50% potassium hydroxide, then the mixture was allowed to react at a temperature between 95° C. and 100° C. for 4 hours.

The reacted solution was then treated in the same manner as Example 1, and 811 gr. of reaction product were obtained. In the same analytical procedure, the rate of reaction was determined, with the following result:

Total base content—3.44×10⁻³ eqv./—gr.
Nitrogen content—1.63%
Yield—97.0%

From this result of analysis, it is noted that the reaction product is a result of reaction between 1 mol of polyoxy-

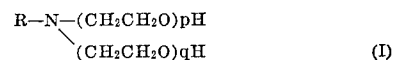
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ethylene laurylamine and about 2 mols of potassium monochloro acetate.

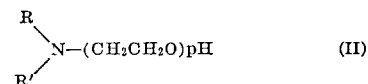
The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for preparing betaine type amphoteric surface active agents, which comprises reacting:

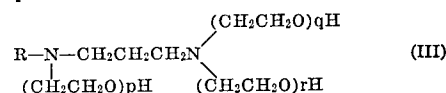
(A) a tertiary amine selected from the group consisting of compounds represented by the following Formulas I through III, namely,



wherein: $p+q=2$ to 50



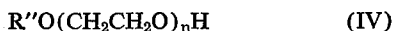
wherein: $p=1$ to 50



wherein: $p+q+r=3$ to 50
wherein:

- R is an alkyl radical having 6 to 22 carbon atoms,
- R' is an alkyl radical having 6 to 22 carbon atoms, with
- (B) an alkaline salt selected from the group consisting of the sodium, potassium, lithium and ammonium salts of monochloroacetic acid,
- (C) in the presence of alkali, the amount of said alkali being approximately equivalent, on a molar basis, to the amount of said alkaline salt, and
- (D) in a solution containing a minor amount of water and the balance of the solution being a solvent selected from the group consisting of (a) solvents represented by the following Formula IV and (b) mixtures containing at least 20 percent by weight of the solvent represented by said Formula IV and the balance of said mixture being a water-soluble organic solvent selected from the group consisting

of methanol, ethanol, propanol, dioxane and mixtures thereof,



wherein:

R'' is selected from the group consisting of alkyl radicals having 1 to 4 carbon atoms and hydrogen,

n is the integer 1 or 2.

2. A method for preparing betaine type amphoteric surface active agents according to claim 1, wherein the solvent used in the reaction is selected from the group consisting of ethylene glycol and ethylene glycol monoalkyl ether in which the alkyl radical has 1 to 4 carbon atoms.

3. A method for preparing betaine type amphoteric surface active agents according to claim 1, wherein the solvent used in the reaction is selected from the group consisting of diethylene glycol and diethylene glycol monoalkyl ether in which the alkyl radical has 1 to 4 carbon atoms.

4. A method for preparing betaine type amphoteric surface active agents according to claim 1, wherein the solvent used in the reaction consists of a mixture containing 20 percent or more by weight of a member selected from the group consisting of ethylene glycol and ethylene glycol monoalkyl ether in which the alkyl radical has 1 to 4 carbon atoms, and the balance consisting of one or more members selected from the group consisting of methanol, ethanol, propanol and dioxane.

5. A method for preparing betaine type amphoteric surface active agents according to claim 1, wherein the solvent used in the reaction consists of a mixture containing 20 percent or more by weight of a member selected from the group consisting of diethylene glycol and diethylene glycol monoalkyl ether in which the alkyl radical has 1 to 4 carbon atoms and the balance consisting of one or

more members selected from the group consisting of methanol, ethanol, propanol and dioxane.

6. A method for preparing betaine type amphoteric surface active agents according to claim 2, wherein the alkali is selected from the group consisting of aqueous solutions of sodium hydroxide, potassium hydroxide, lithium hydroxide and ammonia.

7. A method for preparing betaine type amphoteric surface active agents according to claim 3, wherein the alkali is selected from the group consisting of aqueous solutions of sodium hydroxide, potassium hydroxide, lithium hydroxide and ammonia.

8. A method for preparing betaine type amphoteric surface active agents according to claim 4, wherein the alkali is selected from the group consisting of aqueous solutions of sodium hydroxide, potassium hydroxide, lithium hydroxide and ammonia.

9. A method for preparing betaine type amphoteric surface active agents according to claim 5, wherein the alkali is selected from the group consisting of aqueous solutions of sodium hydroxide, potassium hydroxide, lithium hydroxide and ammonia.

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