Preparation of Tertiary Amine Derivatives From Commercially Available Alcohols and Their Properties as Surfactants

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Abstract

Higher tertiary amines were prepared by transalkylation of triethylamine with commercially available alcohols such as Tergitol 15-S-3 and tridecyl alcohol. This reaction carried out at 250–300 C and 20 kg/cm^2 initial hydrogen pressure, using Cu-Cr-Mn-O catalyst, gave about 80% yield of higher alkyl tertiary amines. Tertiary amine hydrochlorides, quaternary ammonium bromides and amine oxides were prepared from these tertiary amines. Specific surface tension, wetting power, foaming power and foam stability were measured. The characteristic properties with respect to tertiary amine derivatives containing ether linkages were observed. These products have excellent wetting power, reduced surface tension, low foaming power and unstable foam.

Introduction

Higher alkyl tertiary amine derivatives have been widely used in the field of surface active agents. In 1952 Schneider et al. (1) reported the transalkylation reaction of triethylamine with dodecyl alcohol. This reaction is described by the equation:

$$C_{12}H_{25}OH + Et_3N \xrightarrow[H_2\ \text{pressure}]{250\ \text{C, Cu-Cr-Ba-O}} C_{12}H_{25}NEt_2 + EtOH$$

In previous studies it became apparent that copper metal powder could be used as a fairly good catalyst (2) and that various types of tertiary amines are obtainable by the reaction of various alcohols with triethylamine (3,4). Saturated and unsaturated fatty esters also gave corresponding tertiary amines by a one-step process under hydrogenation condition (5,6). Also, a continuous process could be used at atmospheric pressure (7), and various metals such as ruthenium, cobalt and nickel could catalyze the reaction without hydrogen pressure; ruthenium gave especially good yield and selectivity (8).

TABLE I

Hydroxy Compounds Studied

Name and structure of hydroxy compound		Hydroxyl value found
Tergitol 15-S-3[a]		179.0
Tridecyl alcohol[b]		279.1
Nonionic surfactants[c]		
C_9H_{19}–⌬–$(OC_2H_4)_nOH$	n = 2.0	180.8
	n = 5.7	119.0
	n = 10.0	84.6
	n = 14.5	65.3
	n = 21.6	47.9
$C_{12}H_{25}$–⌬–$(OC_2H_4)_nOH$	n = 2.0	160.1
	n = 6.9	99.0
	n = 11.4	73.4

[a] Derived from addition of 3 moles ethylene oxide to linear C_{11}-C_{15} alcohols. Tergitol 15-S-3 from Union Carbide.

[b] Oxo-alcohol of propylene tetramer. Tridecyl alcohol from Esso.

[c] Noigen EA series of Dai-ichi Kogyo Seiyaku.

The purpose of this paper is to report the transalkylation of triethylamine with commercially available alcohols such as Tergitol 15-S-3 and tridecyl alcohol, and the practical application of surface active agents derived from the resulting tertiary amines.

Experimental Procedure

Materials

Analytical data of commercially available hydroxy compounds used are listed in Table I.

Triethylamine was dried with calcium hydride and distilled under atmospheric pressure (bp 89.5 C). Cu-Cr-Mn-O (Nikki Kagaku, N-203) was used as catalyst.

TABLE II

Reaction Products of Triethylamine With Commercial Hydroxy Compounds

		Reaction condition							
Hydroxy compound	Gram	Temperature C	Time, hr	Amine value	Tertiary amine value	Hydroxyl value	Unreacted alcohol, %	Yield, g	Mixed tertiary amine yield, %
Tergitol 15-S-3	100	250	5	128.9	127.1	32.0	16.9	115.2	82.3
Tergitol 15-S-3	100	270	3	129.1	129.0	24.7	13.7	114.9	83.3
Tridecyl alcohol	100	250	5	191.3	188.7	45.3	16.2	114.6	77.5
Tridecyl alcohol	100	300	3	194.0	191.8	42.2	14.5	117.3	80.6
Tridecyl alcohol	100	325	3	200.4	194.3	30.2	10.9	119.6	83.3
Tridecyl alcohol	100	350	3	199.8	183.3	31.0	11.1	113.2	74.3
Nonionic surfactant									
C_9H_{19}–⌬–$(OC_2H_4)_nOH$									
n = 2.0	100	270	3	137.3	135.3	23.5	13.0	114.4	85.6
n = 5.7	200	270	3	98.7	98.2	15.7	13.3	211.0	87.4
n = 10.0	300	270	3	73.3	72.2	9.1	10.7	314.0	89.3
n = 14.5	300	270	3	55.6	55.0	6.9	10.6	310.0	87.3
n = 21.6	300	270	3	42.4	41.9	4.5	9.4	305.5	89.2
$C_{12}H_{25}$–⌬–$(OC_2H_4)_nOH$									
n = 2.0	100	270	3	117.8	116.9	20.1	12.6	110.8	81.4
n = 6.9	200	270	3	76.8	76.0	11.4	11.6	209.9	80.8
n = 11.4	300	270	3	60.9	60.0	7.6	10.4	311.0	85.0

TABLE III

Surface Tension of Surfactants Derived From 15-S-3N and Tridecyl Alcohol

Surfactant	Temperature, C	Surface tension, dyne/cm
Tergitol derivative		
$R-(OC_2H_4)_3NEt_2 \cdot HCl$	25	35.65
	45	29.84
$R-(OC_2H_4)_3\overset{+}{N}Et_3 \cdot Br^-$	25	32.47
	45	30.62
$R-(OC_2H_4)_3\underset{\overset{\downarrow}{O}}{N}Et_2$	25	30.27
	45	27.58
	45	18.46[a]
Tridecyl derivative		
$R-NEt_2 \cdot HCl$	45	48.12
$R-\overset{+}{N}Et_3 \cdot Br^-$	45	37.23
$R-\underset{\overset{\downarrow}{O}}{N}Et_2$	45	29.92
	45	21.15[a]
Reference		
$C_{12}H_{25}\overset{+}{N}Me_3 \cdot Cl^-$	25	51.99
	45	52.85
$C_{12}H_{25}\underset{\overset{\downarrow}{O}}{N}Me_2$	25	29.78
	45	27.71
	45	19.43[a]

Concentration 0.15%; [a]0.15% in 2% HCl aqueous solution.

Analytical Methods

Hydroxy value (OH.V.) was determined by titrating with 0.1 N aqueous KOH to the phenolphthalein end point, after acetylation by acetic anhydride in pyridine (9).

Total amine value (Am.V.) was determined by titrating with 0.1 N $HClO_4$ acetic acid solution in glacial acetic acid using crystal violet as indicator.

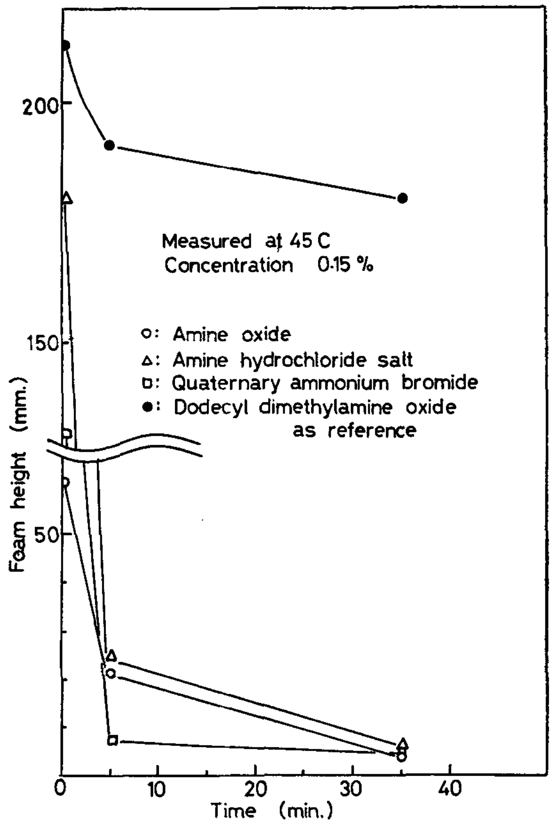

FIG. 2. Foaming power and foam stability of surfactant derived from 15-S-3N (Ross-Miles method).

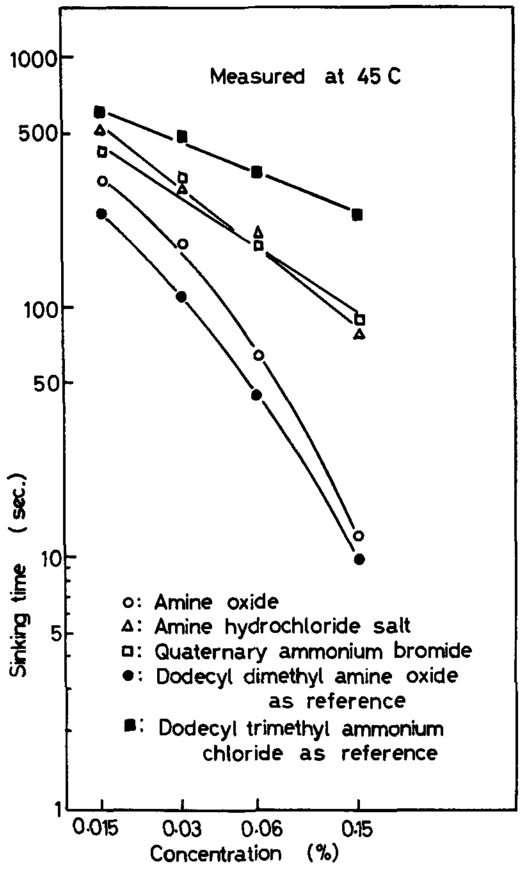

FIG. 1. Wetting power of surfactant derived from 15-S-3N (canvas disk method).

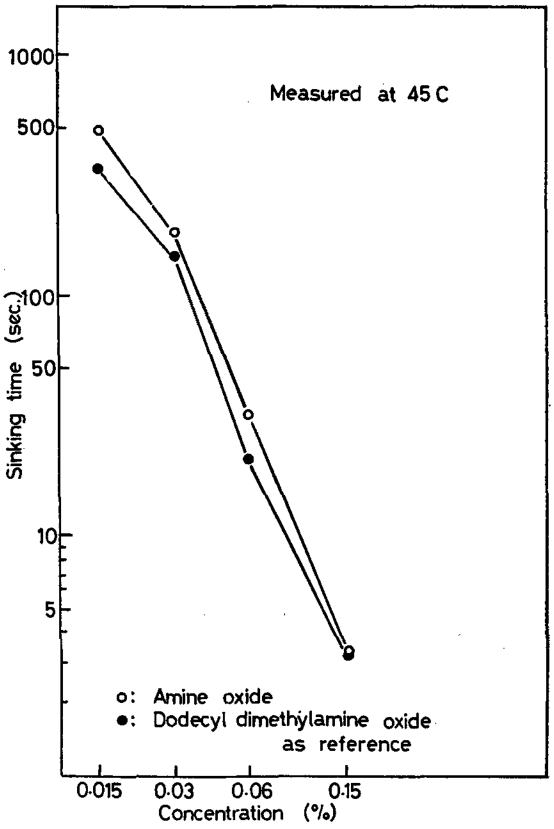

FIG. 3. Wetting power of amine oxide derived from 15-S-3N in 2% HCl aqueous solution (canvas disk method).

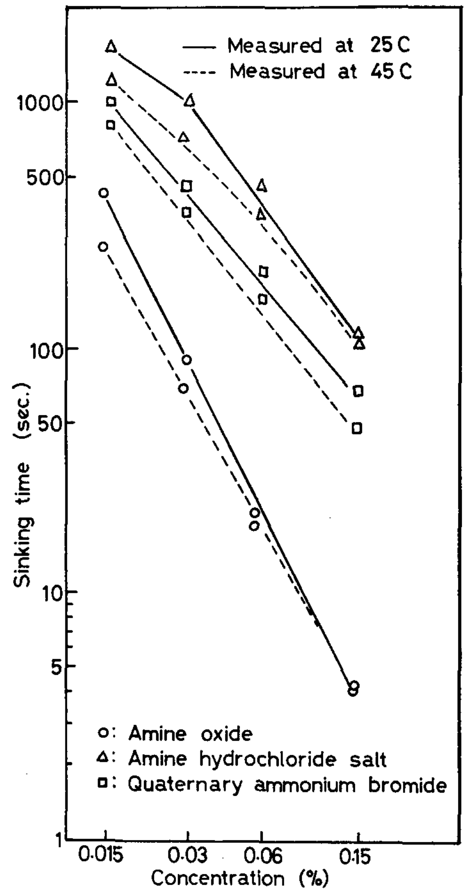

FIG. 4. Wetting power of surfactant derived from tridecyl alcohol.

Tertiary amine value (t-Am.V.) was determined by titrating as mentioned above, after primary and secondary amines in a sample were reacted with acetic anhydride on a boiling water bath for 30 min.

Yields of unreacted alcohol were calculated by dividing OH.V. of the product by OH.V. of the starting alcohol. Yields of tertiary amines were calculated from the equation,

$$\text{Tertiary amine yield} = \frac{\text{Product yield (g)}}{\text{Theoretical yield (g)}} \times \frac{\text{Found t-Am.V.}}{\text{Calculated Am.V.}} \times 100$$

General Procedure for Preparation of Tertiary Amines

Hydroxy compound (100 g), triethylamine (five times the molar quantity of the hydroxy compound) and 10 g of catalyst were placed in a 1000 ml magnetically stirred stainless steel autoclave. Hydrogen was then introduced to 20 kg/cm^2 as initial pressure. The reaction was carried out at 250–300 C for 2–5 hr.

After the reaction, the resulting mixture was dissolved in ethyl ether and the catalyst was removed by filtration. The low boiling materials such as ether, ethanol and triethylamine were removed by evaporation under reduced pressure. OH.V., Am.V. and t-Am.V. of the resulting product were measured without further purification.

These products were allowed to react with 10% aqueous hydrochloric acid and the resulting aqueous solution was extracted four times with ethyl ether to remove unreacted alcohol, and made alkaline with sodium hydroxide to liberate the free tertiary amine. The resulting free tertiary amines were converted to the corresponding hydrochloride, quaternary ammonium bromide and amine oxide by the usual method (11,12).

Measurement of Properties of the Surfactant

The surface activities of the resulting surfactants, such as specific surface tension (Traube Method) (13), wetting power (canvas disk method) (14) and foaming power and foam stability (Ross-Miles Method) (15), were measured at 25 C and 45 C in aqueous solution or 2% hydrochloric acid.

Results and Discussion

Transalkylation Reaction

The analytical data of products from the transalkylation reaction of commercially available hydroxy compounds with triethylamine are shown in Table II. The products consisted of mixed tertiary amine containing one to three higher alkyl groups per nitrogen atom. This reaction can be visualized by the following equation,

$$R'_3N \underset{R'OH}{\overset{ROH}{\rightleftharpoons}} RNR'_2 \underset{R'OH}{\overset{ROH}{\rightleftharpoons}}$$

$$R_2NR' \underset{R'OH}{\overset{ROH}{\rightleftharpoons}} R_3N$$

Since the yield of tertiary amine was calculated under the assumption that only mono higher alkyl tertiary amine was produced, the sum of tertiary amine yield and unreacted alcohol yield does not become 100%. It can be presumed that the tertiary amine produced contained not more than 20% of di- and tri- higher alkyl tertiary amines.

Since transalkylation of the hydroxy compounds having an ethoxy chain gave degradation products of ethoxy chain above 270 C (4), the reaction was carried out at 270 C for 3 hr. Good yields were obtained as was to be expected from the previous results, but the transalkylation reaction of the tri-

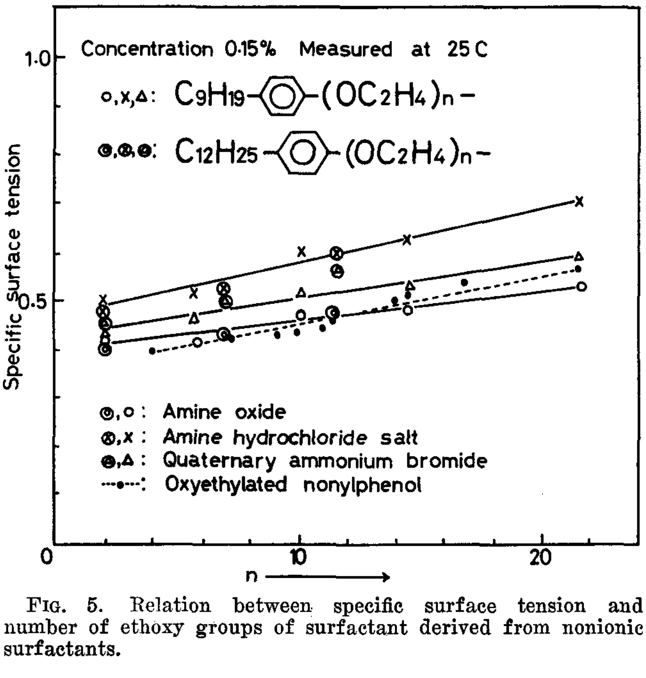

FIG. 5. Relation between specific surface tension and number of ethoxy groups of surfactant derived from nonionic surfactants.

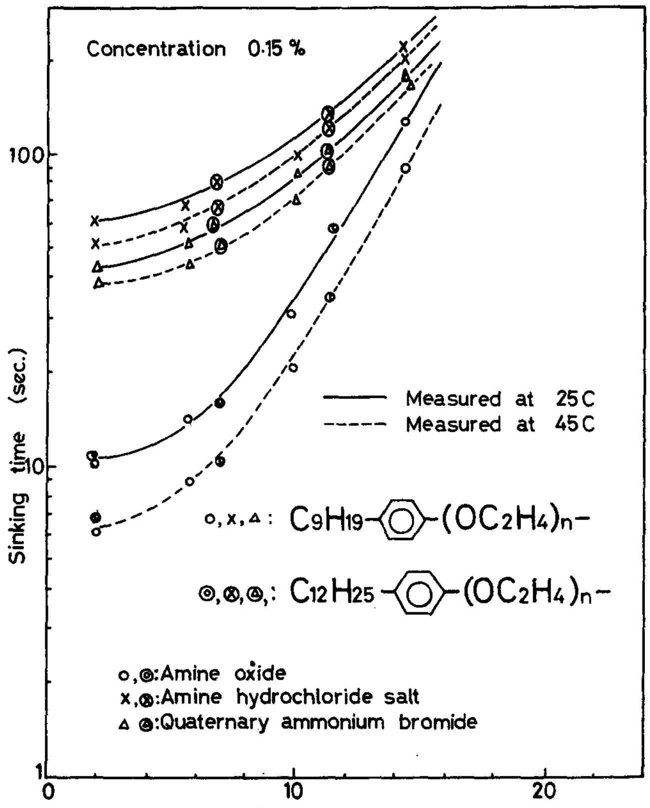

FIG. 6. Relation between wetting power and number of ethoxy groups of surfactant derived from nonionic surfactant.

decyl alcohol (oxo-alcohol) with triethylamine did not give a good result under the same reaction conditions. A higher yield of transalkylated tertiary amine from tridecyl alcohol can be obtained by reaction at 325 C for 3 hr. It is considered that this effect is caused by steric hindrance of the side chain.

Furthermore, the higher the reaction temperature, the more the tertiary amine which the products first formed degrade by hydrogenolysis, giving the higher alkyl primary and secondary amines.

Properties of the Surfactants Derived From the Transalkylated Tertiary Amines

The tertiary amine derived from Tergitol 15-S-3 (15-S-3N) was converted to amine hydrochloride, quaternary ammonium bromide and amine oxide. The surface tension, the wetting power and the foaming power of these surfactants were measured and shown in Table III and Figure 1 and 3. The surface tension of three surfactants derived from 15-S-3 N are superior to commercial dodecyl trimethyl ammonium chloride (Table I), whereas the foaming power and foam stability are very poor (Fig. 2). In addition, it should be noted that the wetting power of these surfactants is excellent for a cationic surfactant (Fig. 1). The properties of the amine oxide are remarkable, especially in 2% hydrochloric acid (Table III and Fig. 3).

Surfactants derived from the tertiary amine produced from tridecyl alcohol also had excellent characteristic properties as shown in Table III and Figure 4, especially with respect to wetting power.

The properties of the amine hydrochlorides, quaternary ammonium bromides and amine oxides of the higher alkyl tertiary amines derived from the nonionic surfactants were also studied. Surface tension of 0.15% aqueous solutions of these surfactants vs. number of ethoxy groups is shown in Figure 5. The surface tensions of these surfactants are inferior to those of the nonionic surfactants, but the amine oxides exhibit comparable properties. The wetting power of 0.15% aqueous solutions of these surfactants is shown in Fig. 6.

The higher alkyl tertiary amines obtained by this process are mixtures containing about 10–17% of di- and tri- higher alkyl tertiary amines. They are colorless and odorless and can be produced easily from alcohols or fatty esters by a one-step process.

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