Analysis of Cationic and Amphoteric Surfactants I. Determination of Their Homolog Distributions by Gas Chromatography on the Basis of the Hofmann Degradation.

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ABSTRACT AND SUMMARY

A method (DMF-Methylate method) has been described for the homolog analysis of cationic and amphoteric surfactants having a quaternary ammonium group. The homolog distribution of cationic and amphoteric surfactants obtained by the DMF-Methylate method closely agrees with that of the original alkyldimethylamines used. Therefore, the DMF-Methylate method should be applicable to the homolog analysis of these surfactants. This method also offers qualitative information for the identification of these surfactants, since the ratio of the α-olefin to the alkyldimethylamine varies with each surfactant. On the basis of the analysis of the elimination products, it was confirmed that the main degradation process was the elimination of a β-hydrogen atom. This mechanism is different from that of the pyrolysis gas chromatography, which will be discussed elsewhere (S. Takano, M. Kuzukawa, and M. Yamanaka, in preparation).

INTRODUCTION

It is well known that cationic and amphoteric surfactants offer a variety of applications in the industrial and household fields such as germicides, textile softeners, and so on. Interest in their applications has increased steadily in recent years because of their unique properties.

The commercial products are usually mixtures of homologs, and their effectiveness and physical properties depend markedly on the chain length of the hydrocarbon groups attached to the quaternary nitrogen. Therefore, analysis of their homolog composition is required for the proper use of these products. A number of papers have been published on analysis of cationic surfactants by means of gas chromatography; however none have presented an entirely convenient method applicable to both cationic and amphoteric surfactants.

Metcalfe (1) attempted to pyrolyze cationic surfactants on an alkaline treated gas chromatographic column. However, no peak had a retention time that corresponded to any of the higher α-olefins, which would result from the Hofmann degradation, however the corresponding tertiary amines were formed. Uno et al. (2) also obtained the same results as Metcalfe with pyrolysis gas chromatography, when a non alkaline treated column was used. However, Laycock (3) and Barry et al. (4) reported that a mixture of α-olefin and tertiary amine was formed under similar conditions. Thus, a mechanism for the pyrolysis of the quaternary ammonium salts has not been established.

On the other hand, Warrington (5) analyzed alkylbenzyldimethylammonium chlorides by way of the tertiary amines formed by the catalytic hydrogenation with palladium-carbon. Also, Kojima et al. (6) reported a similar reductive method with lithium aluminum hydride and sodium borohydride. Jennings et al. (7) reported a modified Hofmann degradation, which was carried out with 4N-potassium hydroxide in a sealed glass tube, for the analysis of alkylbenzyldimethylammonium chlorides.

However, no paper has been reported on the homolog analysis of amphoteric surfactants, so we tried to apply the Hofmann degradation to it. Usually, the Hofmann degradation is conducted by treating the sample with silver oxide and heating under reduced pressure. However, these procedures seemed to be too tedious for an analytical routine work. Therefore, in this study, the degradation method, which was used in the synthesis of aldosterone by Wolff et al. (8), was investigated and improved.

By this method, not only cationic but also amphoteric surfactants can be readily degraded to give chiefly α-olefins and alkyldimethylamines. Their homolog distributions could be determined by the peak areas of the alkyldimethylamines formed by gas chromatography.

EXPERIMENTAL PROCEDURES

Apparatus

Gas chromatography-mass spectrometry (GC-MS) measurements were carried out with a JEOL JMS-D 100 mass spectrometer equipped with a JEOL JGC-20 KP gas chromatograph. Proton nuclear magnetic resonance (NMR) spectra were obtained with a JEOL JNM PS-100 nuclear magnetic resonance spectrometer (100 MHz). Infrared (IR) spectra were obtained with a Hitachi EPI-G2 infrared spectrometer.

Materials

Sodium methoxide (powder) was obtained from Wako Chemicals Co. (Osaka, Japan). Alkylamines, alkyldimethylamines, and dialkylmethylamines were prepared in our laboratory and distilled before use. Alkyltrimethylammonium chloride and iodide (ATMA) were obtained by the quaternization of alkyldimethylamine with methyl chloride and methyl iodide, respectively. Alkylbenzyldimethylammonium chloride (BDMA) was obtained by the quaternization of alkyldimethylamine with benzyl chloride. Dialkyldimethylammonium chloride and iodide (DDMA) were obtained by the quaternization of dialkylmethylamine with methyl chloride and methyl iodide, respectively. These cationic surfactants were recrystallized from acetone. (Alkyldimethylammonio)-methane carboxylate (DAMC) was obtained by the quaternization of alkyldimethylamine with sodium monochloroacetate and recrystallized from acetone and benzene. 2-(Alkylammonio)-ethane-1-carboxylate (AEC) was obtained by the reaction of alkylamine with

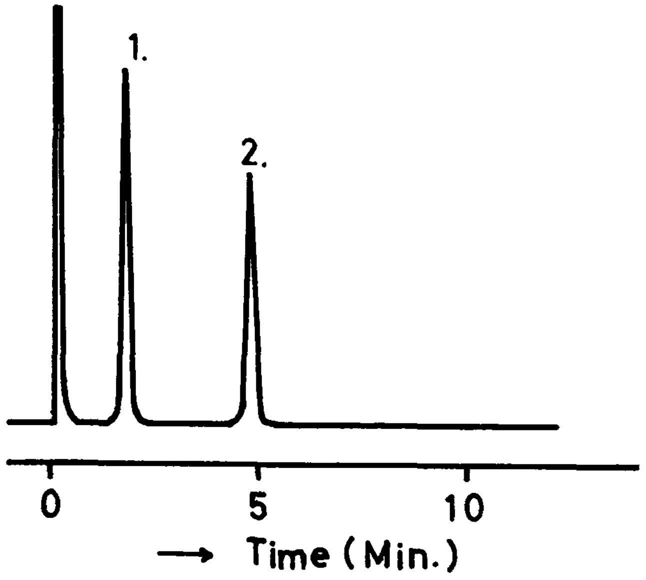

FIG. 1. Gas chromatogram of the degradation products of dodecyltrimethylammonium chloride. 1. 1-dodecene, 2. dimethyldodecylamine.

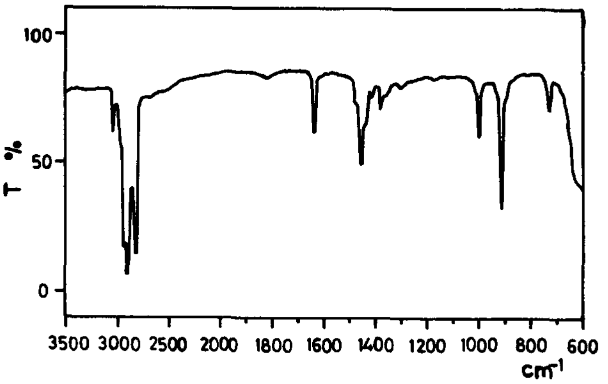

FIG. 2. Infrared spectrum of 1-dodecene isolated from the degradation products of dodecyltrimethylammonium chloride.

β-propiolactone. 2-(Alkyldimethylammonio)-ethane-1-carboxylate (DAEC) was obtained by the quaternization of alkyldimethylamine with β-propiolactone. 4-(Alkyldimethylammonio)-butane-1-sulfonate (DABS) was obtained by the quaternization of alkyldimethylamine with 1,4-butanesultone. These amphoteric surfactants were recrystallized from acetone and ethanol. 2-(Alkyldimethylammonio)-ethane-1-sulfonate (DAES) was obtained by the quaternization of alkyldimethylamine with sodium 2-bromoethanesulfonate. 3-(Alkyldimethylammonio)-propane-1-sulfonate (DAPS) was obtained by the quaternization of alkyldimethylamine with propanesultone. 3-(Alkylammonio)-propane-1-sulfonate (APS) was obtained by the reaction of alkylamine with propanesultone. These were recrystallized from ethanol.

Degradation Procedures

A sample, ca. 0.2 g, was placed in a 100 ml pear-shaped flask fitted with a reflux condenser, and 0.5 g of sodium methoxide and ca. 70 ml of N,N-dimethylformamide (DMF) were added. The solution was refluxed at 180-185 C on an oil bath for an hour, during which DMF slightly decomposed with the evolution of carbon monoxide and dimethylamine. After cooling the flask to room temperature, the reflux condenser was rinsed with ethanol. Then, this solution was transferred to a separatory funnel, and 100 ml of distilled water was added to decompose the excess of sodium methoxide. The aqueous mixture was extracted twice with 60 ml of ether. The ethereal layer was combined, washed with water, dried over anhydrous sodium sulfate, and then evaporated. The obtained product was dissolved in ether and analyzed by gas chromatography.

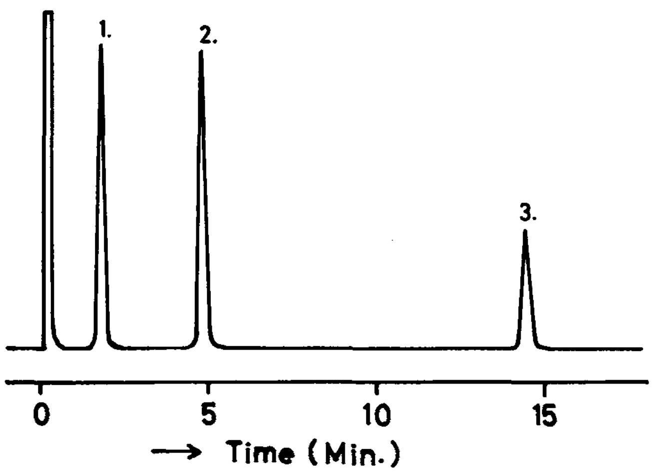

FIG. 3. Gas chromatogram of the degradation products of didodecyldimethylammonium chloride. 1. 1-dodecene, 2. dimethyldodecylamine, 3. didodecylmethylamine.

Gas Chromatographic Conditions

A Hitachi K-53 gas chromatograph equipped with a flame ionization detector was used for all experiments. Pyrex glass columns were used with following packings. The column packings were Chromosorb-W (AW. DMCS. 60-80 mesh) coated with 3% w/w OV-17 for the degradation products of BDMA and Gaschrom Q (80-100 mesh) coated with 3% w/w JXR-Silicone for those of other surfactants. The column temperature was linearly programmed from 100 to 300 C at a rate of 10 C per minute. The injection port and detector temperature were held at 280 C. Helium was used as the carrier gas at a flow rate of 50 ml per minute. All peak areas were determined by a Hitachi Datalyzer-002 (mini computer online system).

RESULTS AND DISCUSSION

Analysis of Degradation Products

Three cationic and seven amphoteric surfactants were degraded under the conditions described above. Each product was identified by GC-MS and IR spectrometry.

Cationic Surfactants

The degradation products of ATMA were α-olefins and alkyldimethylamines; however, in most cases the α-olefins were formed in only 55-60% yield (Fig. 1).

The position of the double bond in the olefin could be identified with IR spectrometry after the isolation from the degradation products of C_{12} ATMA (C_{12} indicates the carbon number of alkyl chain.) with silica gel column chromatography. As shown in Figure 2, the IR spectrum of the isolated olefin showed the characteristic and well-defined absorption bands of α-olefin at 990 and 910 cm^{-1}.

Figure 3 shows the gas chromatogram of the degradation products of C_{12} DDMA. In this case, α-olefins, alkyldimethylamines and dialkylmethylamines were obtained as the degradation products in yields of 38-41, 38-41, and 15-19%, respectively.

On the other hand, the degradation products of C_{16} BDMA gave five peaks on the gas chromatogram, and peaks 1 to 4 were identified as shown in Figure 4. However, peak 5 seemed to contain two components, and both the components indicated the same molecular ion peak of m/e = 359 by GC-MS measurement, which suggested the loss of only one hydrogen atom from the original molecule. Therefore, it is reasonable to consider that these products were formed by rearrangement of methyl or benzyl group [namely, the Stevenson rearrangement (9) or the Sommelet-Hauser rearrangement (9)], but further identification was not made.

In the degradation of BDMA, the yield of each product was 50-60% for alkyldimethylamines, 20-30% for α-olefins, and 10-20% for both alkylbenzylmethylamines and the rearrangement products. In this case, OV-17 was used as a gas chromatographic column for the separation of alkyldimethylamines from alkylbenzylmethylamines.

Amphoteric Surfactants

On the degradation of the amphoteric surfactants, the corresponding α-olefins and alkyldimethylamines were formed, and the ratio of the α-olefin to the alkyldimethylamine varied with each surfactant (Table II). By this ratio, the amphoteric surfactants were classified into two groups. The first group was DAEC, DAES, and DAPS, which were degraded to give alkyldimethylamines predominantly and to give α-olefins in 0-6% yield. The second was DAMC and DABS, which were degraded to give α-olefins in ca. 70% and ca. 40% yields respectively.

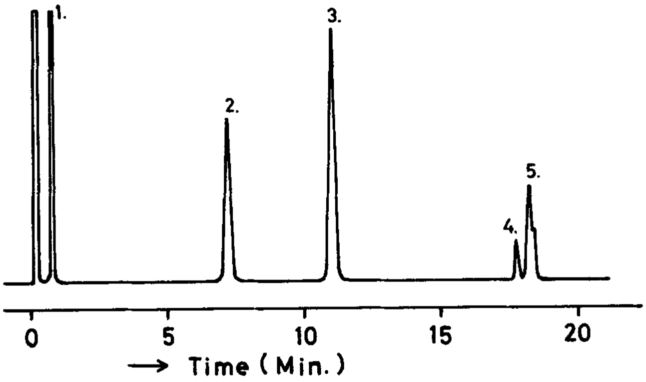

FIG. 4. Gas chromatogram of the degradation products of benzyldimethylhexadecylammonium chloride. 1. benzyldimethylamine, 2. 1-hexadecene, 3. dimethylhexadecylamine, 4. benzylhexadecylmethylamine, 5. rearrangement products.

TABLE I

Effect of Reaction Conditions on the Degradation of $C_{16}H_{33}N^+(CH_3)_2CH_2CH_2CH_2CH_2SO_3^-$

Oil bath temperature (°C)	Reaction time (hr)	Sodium methoxide added (g)	α-Olefin (%)	Alkyldimethylamine (%)
170	1	1.0	11	18
170	1	1.5	33	49
170	3	0.5	1	5
170	5	0.5	2	8
185	1	0.5	44	54

TABLE II

Degradation of Amphoteric Surfactants

Amphoteric surfactant	α-Olefin (%)	Alkyldimethylamine (%)
$C_{12}H_{25}N^+(CH_3)_2CH_2COO^-$	76	25
$C_{16}H_{33}N^+(CH_3)_2CH_2CH_2COO^-$	3	96
$C_{12}H_{25}N^+(CH_3)_2CH_2CH_2SO_3^-$	–	103
$C_{16}H_{33}N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$	6	96
$C_{16}H_{33}N^+(CH_3)_2CH_2CH_2CH_2CH_2SO_3^-$	44	54

On the other hand, AEC and APS could not be degraded under the proposed conditions, so N-methylation was carried out under the reflux condition of methanol with an excess of methyl iodide in the presence of sodium carbonate for an hour. After being cooled to room temperature, sodium carbonate was removed by filtration, then the filtrate was evaporated under reduced pressure. Because the N-methylation was carried out in the presence of a large excess of methyl iodide, it was considered that the N,N-dimethylated quaternary products were chiefly obtained. In fact, under the proposed conditions the N,N-dimethylated AEC and APS were readily degraded to give the same products as DAEC and DAPS, respectively.

Optimum Conditions for the Degradation

Table I shows the effect of reaction conditions on the degradation of DABS, which was more difficult to degrade than any other surfactants. The yield of each product was determined by gas chromatography with tetradecyldimethylamine as an internal standard.

Because of the low solubility of sodium methoxide in DMF, the reaction system was heterogeneous. However, as shown in Table I, the increases in yield resulted from the further addition of sodium methoxide and by raising the temperature of oil bath.

On the other hand, the isomerization of the α-olefins occurred on the addition of more than 1.0 g of sodium methoxide. Since 1-dodecene also isomerized under the same conditions, it was considered that the isomerization occurred after the formation of the α-olefins.

Consequently, the optimum conditions for the degradation were determined as described in the experimental section. Table II shows the results of the degradation of various amphoteric surfactants under these conditions. It is obvious that all surfactants are almost quantitatively degraded.

Reaction Mechanism

Quaternary ammonium hydroxides which have a β-hydrogen atom undergo the Hofmann elimination reaction and give α-olefins as main product. In this reaction, the β-hydrogen atom is removed first by the hydroxide ion. However, an important side reaction, in which attack at the α-carbon atom by hydroxide ion forms alcohols and tertiary amines (10), competes with this elimination. When the counter ion is carbonate, iodide, chloride and so on, this side reaction occurs predominantly. As a result, the yield of α-olefins is reduced to 10-20% (10,11). On the other hand, α-olefins are predominantly formed when the counter ion is methoxide or ethoxide (10,12). In fact, the degradation products obtained by the proposed method closely agreed with those obtained by the ordinary Hof-

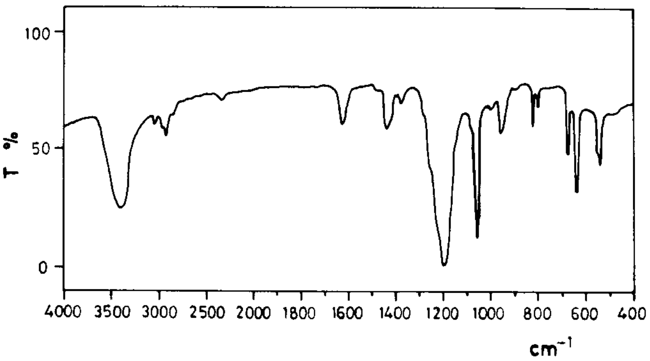

FIG. 5. Infrared spectrum of sodium allyl sulfonate isolated from the degradation products of $RN^{+}(Ch_3)_2CH_2CH_2CH_2SO_3^{-}$.

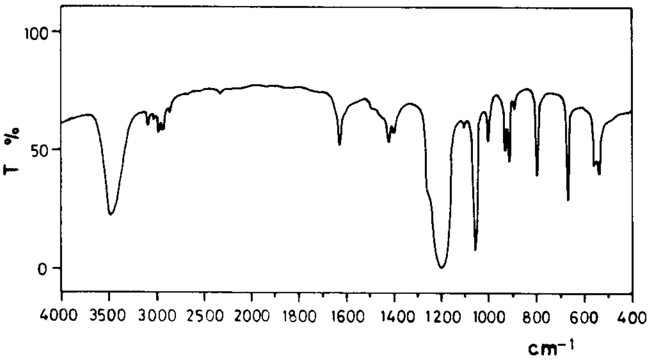

FIG. 6. Infrared spectrum of authentic sodium allyl sulfonate.

mann degradation. However, the proposed method has a great advantage for the degradation of those amphoteric surfactants having a sulfonate group, which could not be degraded by the ordinary Hofmann degradation.

However, most of amphoteric surfactants gave α-olefins in low yield. Furthermore, as shown in Table II, the yield of α-olefin depends on the number of the methylene groups in the polar substituent.

To examine the reason for these interesting facts and to elucidate the elimination mechanism of the polar substituent group, the elimination products of DAPS were identified as follows. Initially, DAPS was degraded under the proposed conditions, and the resulting α-olefins and alkyldimethylamines were removed by the extraction with ether. Then, the elimination product was purified by the use of an anion exchange resin. Figure 5 shows the IR spectrum of the purified product. However, its IR spectrum, in the low wave number region, did not agree with that of sodium allyl sulfonate (Fig. 6) which should be formed by the elimination of the β-hydrogen atom of DAPS. In Figure 5 the absorption bands are near 960 cm^{-1} and 620 cm^{-1}, which suggest the formation of *trans* and *cis* disubstituted ethylene groups, whereas those near 1000 cm^{-1} and 920 cm^{-1}, indicating the presence of a monosubstituted ethylene group, almost disappear. Therefore, it was presumed that partial isomerization of sodium allyl sulfonate occurred during the degradation.

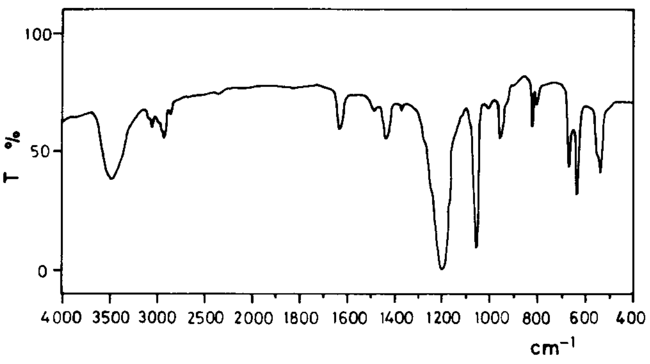

FIG. 7. Infrared spectrum of authentic sodium allyl sulfonate treated by the same procedures as $RN^{+}(CH_3)_2CH_2CH_2CH_2SO_3^{-}$.

Figure 7 shows the IR spectrum of an authentic sample of sodium allyl sulfonate treated by the same procedures as DAPS. This IR spectrum entirely agreed with that of the elimination product of DAPS, which also supports the assumption mentioned above.

Further evidence was obtained by NMR spectrometry. Both sulfonates whose IR spectra are shown in Figure 5 and 7 exhibited doublet peaks at 1.8 ppm and 3.6 ppm (δ), which were assigned with confidence to the methyl protons of $\underline{CH_3}CH{=}CHSO_3Na$ (I) and to the methylene protons of $CH_2{=}CH\underline{CH_2}SO_3Na$ (II), respectively. Therefore, it was confirmed that the purified degradation product was a mixture of I and II and that the extent of the isomerization was about 60% on the basis of these peak areas.

TABLE III

Comparison of the Homolog Analysis of Alkyldimethylamines and the Corresponding Quaternary Ammonium Compounds

Surfactant		Homolog distribution (peak area %)				
		C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
$RN^{+}(CH_3)_3\ Cl^{-}$	Original	0.1	1.8	1.0	17.7	79.5
	Found	–	1.1	1.0	18.0	79.9
$R(R')N^{+}(CH_3)_2\ Cl^{-}$	Original	–	1.0	64.7	34.2	0.1
	Found	–	1.2	64.0	34.7	0.1
$RN^{+}(CH_3)_2CH_2C_6H_5\ Cl^{-}$	Original	0.3	3.5	62.3	32.6	1.2
	Found	–	3.3	60.8	32.9	3.0
$RN^{+}(CH_3)_2CH_2COO^{-}$	Original	0.1	3.8	63.5	31.4	1.2
	Found	–	5.2	60.5	33.0	1.4
$RN^{+}(CH_3)_2CH_2CH_2COO^{-}$	Original	0.3	57.2	34.4	7.7	0.4
	Found	0.3	55.7	35.2	8.1	0.7
$RN^{+}(CH_3)_2CH_2CH_2SO_3^{-}$	Original	0.2	57.4	34.2	7.8	0.6
	Found	–	54.6	35.8	9.1	0.5
$RN^{+}(CH_3)_2CH_2CH_2CH_2SO_3^{-}$	Original	0.2	57.8	33.8	7.6	0.6
	Found	0.4	58.7	32.9	7.2	0.8
$RN^{+}(CH_3)_2CH_2CH_2CH_2CH_2SO_3^{-}$	Original	0.1	3.8	63.5	31.4	1.2
	Found	–	3.7	63.1	32.1	1.1

Thus, it is obvious that degradation of the amphoteric surfactants also occurs by elimination of the β-hydrogen atom, which is the typical Hofmann elimination mechanism. In this respect, the dependence of the yield of α-olefins on the number of the methylene groups in the polar substituent can account for the differences in the activity of the β-hydrogen atom. However, in the case of DAMC, α-olefin is predominantly formed because of the absence of the β-hydrogen atoms at the polar substituent.

In addition, the substituent groups were arranged in order of the ease with which they were eliminated under the proposed conditions. This order appreciably differs from that obtained by the pyrolysis gas chromatography (2).

$$-CH_2CH_2X^- > -(CH_2)_3X^- > (CH_2)_4X^- \simeq -CH_2C_6H_5 > -R \simeq$$
$$-(CH_2)_nX^- \ (n \geqslant 5) > ---> -CH_2X^- > --> -CH_3 \ (X = COO \text{ or } SO_3)$$

Determination of Homolog Distributions

Cationic and amphoteric surfactants having the homolog distribution were synthesized from arbitary mixtures of alkyldimethylamines as described in the experimental section. Table III shows the comparisons of the homolog analysis of the original alkyldimethylamines with that of corresponding quaternary ammonium compounds. The peak areas of alkyldimethylamines can be used directly to calculate wt. percent (5).

As shown in Table III, the agreement between both distributions was satisfactory, and the standard deviations of the determinations were 3-6%. Good agreement was also obtained in the homolog determinations of ATMA and DAMC, though these surfactants gave α-olefins as the main product. Therefore, the proposed method should be applicable to the determination of the homolog distributions of various cationic and amphoteric surfactants having a quaternary ammonium group.

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