Analysis of Cationic and Amphoteric Surfactants: III[1]. Structural Analysis of Imidazolinium Cationic Surfactants

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ABSTRACT

Determination of the homologous distribution of imidazolinium cationic surfactants and their structural analysis have been investigated. These surfactants were hydrolyzed under aqueous alkaline media, followed by acid hydrolysis to afford fatty acids and polyamines. The resulting fatty acids were esterified with methanol, and then analyzed by gas chromatography (GC) in order to determine their homologous distribution. The obtained distribution agrees well with that of original fatty acid. Therefore, this method should be applicable to the determination of the homologous distribution of imidazolinium surfactants. The resulting polyamines were acetylated with acetic anhydride in the presence of pyridine. These acetates were analyzed by GC and isolated by preparative thin layer chromatography on silica gel. The structures of these isolates were identified by means of ^{1}H-NMR and IR spectrometry. These structural analyses demonstrated that quaternization of an imidazoline ring selectively occurred at the nitrogen at the 3-position of an imidazoline ring, which was the kinetically favored position in terms of the steric hinderence and the stability of product.

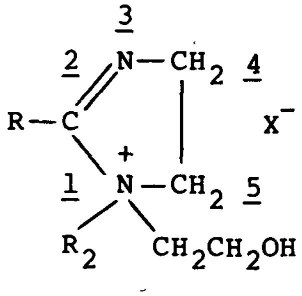
INTRODUCTION

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.

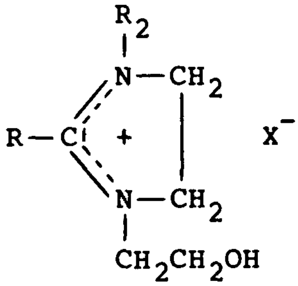
The commercial products are usually mixtures of homologs, and their effectiveness and physical properties depend markedly on the length of the hydrocarbon chain. The analysis of their homologous composition, therefore, is required for the proper use of these products. A number of papers (1) have been published on analysis of cationic surfactants by means of gas chromatography (GC); however, none have presented an entirely convenient method applicable to both cationic and amphoteric surfactants. Previously, one of the authors has investigated the determination of the homologous distribution of cationic and amphoteric surfactants with a quaternary nitrogen atom by way of DMF (N,N-dimethylformamide)-methylate (2) and reaction GC methods (3). However, these methods could not be applicable to the analysis of imidazolinium surfactants because of their complex compositions, as discussed below.

Syntheses of imidazolinium surfactants were first reported by Mannheimer (4) in 1950, in which 1-(2-hydroxyethyl)-2-alkyl-2-imidazoline (HEAI) was allowed to react with sodium monochloroacetate. Subsequent studies on these surfactants made various imidazoline derivatives commercially available. Of these derivatives, the imidazolinium amphoterics have low primary irritation and thus have become important ingredients in the cosmetic field, such as in shampoo. However, imidazolinium derivatives are labile, especially under aqueous alkaline media to afford ring-opening products. Commercially available imidazolinium surfactants, therefore, are usually a complex mixture of these ring-opening products. Recently, some investigations on the structures of these derivatives were reported (5); however, there were a number of unanswered questions.

Mannheimer (4) presented the structure of the products obtained by the reaction of HEAI with sodium monochloroacetate as **I**. However, an imidazoline ring has two tertiary nitrogen atoms, 1 and 3 positions, therefore the isomer as shown in structure **II** may form by the attack of the nitrogen at the 3 position. The studies on these problems were made by some investigators, and Trivedi et al. (6) recently demonstrated by means of ^{1}H- and ^{13}C-NMR spectrometry that the main product obtained by the reaction of 1-methyl-2-benzyl-2-imidazoline with methyl bromide or dimethyl sulfate had a symmetrical structure such as **II**. However, quantitative analysis of these products still remains to be investigated.



I



II

As mentioned above, imidazolinium amphoterics are a complex mixture of hydrolysis products and so it seems difficult to determine their structures completely. On the other hand, cationics having an imidazoline ring are more straightforward to analyze, since imidazoline derivatives are stable under acidic conditions (7). Therefore, the authors initially tried to identify the structure of imidazolinium

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[1] For part II, see reference 3.

TABLE I

Operating Conditions for Gas Chromatography

	A	B
Column	20% DEGS on Chromosorb WAW 60-80 mesh, 2 m × 3 mm id, glass	3% OV-17 on Gas chrom Q 80-100 mesh, 1.5 m × 3 mm id, glass
Oven temp	190 C	230 C
Injection temp	250 C	280 C
Detector temp	250 C	280 C
Detector	FID (H_2 0.6 kg/cm^2, Air 1.0 kg/cm^2)	FID (H_2 0.6 kg/cm^2, Air 1.0 kg/cm^2)
Carrier gas	He 40 mL/min	He 40 mL/min

cationics in order to clarify the structures of imidazolinium surfactants.

This paper deals with both the structural analysis of imidazolinium cationic surfactants and the determination of the homologous distribution of imidazolinium surfactants.

MATERIALS AND METHODS

Apparatus

Gas chromatographic analyses were carried out with a Shimadzu GC-4CM PF. Analyses by gas chromatography-mass spectrometry (GC-MS) were performed on a JEOL JMS-D 300 mass spectrometer equipped with a JEOL JGC-20 KP gas chromatograph and with a JMA-2000 data analyzer system. ^{1}H-nuclear magnetic resonance (NMR) spectra were obtained with a Varian EM 360M NMR spectrometer. (60 MHz) Infrared (IR) spectra were taken on a Hitachi 260-50 IR spectrometer.

Hydrolysis Procedures for Imidazolinium Surfactants

A sample, 0.2-1.0 g, was placed in a 200 mL flask fitted with a reflux condenser, and aqueous 1N potassium hydroxide and dioxane (50 mL each) were added. After refluxing for 2 hr, 55 mL of conc hydrochloric acid was added, and then refluxed for an additional 4 hr.

Determination of Homologous Distributions—Determination of Fatty Methyl Esters

The resulting solution was transferred into a separatory funnel, and extracted with three 70 mL portions of ether. The ethereal layer was combined, and washed with 10% aqueous sodium chloride solution until the aqueous layer became neutral. After drying over sodium sulfate, ether was evaporated. The residue was esterified with methanol in the presence of a few drops of conc sulfuric acid, and then analyzed by GC under the conditions as shown in Table I, column A.

Analysis of Polyamines

Aqueous layer extracted with ether as mentioned above was concentrated to dryness under reduced pressure. A mixture of acetic anhydride and pyridine (5 mL each) was added to the residue, and the resulting suspension was magnetically stirred at room temperature overnight. After evaporating acetic anhydride and pyridine under reduced pressure, the residue was dissolved in ethanol and neutralized with ammonium carbonate. Insoluble matter was filtered off, and then the filtrate was concentrated under reduced pressure to give acetate derivatives of polyamines. Analysis by GC was performed under the conditions as shown in Table I, column B.

Synthesis of Imidazolinium Surfactants

A typical example of quaternization of imidazoline derivatives (4) is described below.

In a 200-mL flask equipped with a reflux condenser and a dropping funnel, there were placed 30 g (0.112 mol) of HEAI (R = $C_{11}H_{23}$) and 10 mL of isopropanol, and the reaction mixture was kept at 80 C with magnetically stirring. Diethyl sulfate (34.5 g, 0.224 mol) was dropped during 15 min to the solution, which was stirred for 4 h at 80 C. Then, 20 mL of water was added to the solution, which was stirred for an additional hour at 80 C. After cooling, the resulting solution was adjusted to pH 4-5 with 0.5N potassium hydroxide, and concentrated under reduced pressure. The residue was dissolved in isopropanol and filtered. The filtrate was concentrated to afford 49.9 g of the quaternized product.

Structural Analysis of the Product Obtained by the Reaction of AAAI with Diethyl Sulfate

The product obtained by the reaction of 1-(2-alkanoylaminoethyl)-2-alkyl-2-imidazoline (AAAI) with diethyl sulfate (2.0 g) was treated as mentioned above to afford 0.5 g of acetylated polyamines. Preparative TLC of the acetylated polyamines on silica gel gave 190 mg of triacetate of N-aminoethyl-N′-ethylethylenediamine (**V**) and 60 mg of diethylenetriamine triacetate.

Triacetate of **V**: IR (neat, cm^{-1}) 3300, 1630, 1550; ^{1}H-NMR (ppm; solvent, CD_3OD) 1.18 (3H, t, J = 6Hz; $CH_2\underline{CH_3}$), 1.88 (3H, s; $\underline{Ac}$NH), 2.05 (3H, s; AcN=), 2.12 (3H, s; AcN=), 3.20-3.55 (10H, br. s; NCH_2); MS m/e 257 (M^+; Found 257.1712, Calcd. for $C_{12}H_{23}N_3O_3$ 257.1738).

Diethylenetriamine triacetate: IR (neat, cm^{-1}) 3300, 1640, 1550; ^{1}H-NMR (ppm; solvent, CD_3OD) 1.93 (6H, s; $\underline{Ac}$NH), 2.10 (3H,s;AcN=), 3.25-3.50 (8H, br. s; NCH_2); MS m/e 229 (M^+; Found 229.1457, Calcd. for $C_{10}H_{19}N_3O_3$ 229.1427).

Structural Analysis of the Product Obtained by the Reaction of HEAI with Diethyl Sulfate

The product obtained by the reaction of HEAI with diethyl sulfate (2.0 g) was treated as the same way as above to give 260 mg of triacetate of N-ethyl-N′-hydroxyethylethylenediamine (**VIII**).

TABLE II

Recovery of Lauric Acid from HEAI ($R = C_{11}H_{23}$) under Various Hydrolysis Conditions

Reaction time (hr)	Recovery of lauric acid (%)		
	1N HCl	2N HCl	4N HCl
1	54.2	79.2	85.3
2	81.9	84.2	89.0
3	84.4	88.8	94.9
4	83.8	91.5	96.3

IR (neat, cm^{-1}) 3450, 1740, 1630, 1230, 1040; ^1H-NMR (ppm; solvent, CD_3OD) 1.09 (3H, t, J = 6Hz; $CH_2\underline{CH_3}$), 1.90-2.15 (9H; Ac), 3.30-3.70 (8H; NCH_2), 4.00-4.25 (2H, m; $\underline{CH_2}OAc$); MS m/e 258 (M^+; Found 258.1589, Calcd. for $C_{12}H_{22}N_2O_4$ 258.1579).

RESULTS AND DISCUSSION

Optimization of Hydrolysis Conditions

It is well known that imidazolinium derivatives are labile under aqueous alkaline conditions to give ring-opening products, amides (7). On treatment of HEAI ($R = C_{11}H_{23}$) with a solution of aqueous 1N potassium hydroxide and dioxane (50 mL each) under reflux condition for 2 hr, the UV absorption band of an imidazoline ring at 230 nm disappeared, which indicated the completion of the ring-opening reaction. In these experiments, dioxane was added in order to suppress foaming and to solubilize the amides formed.

In order to determine acidic hydrolysis conditions for amides, HEAI was hydrolyzed under the conditions mentioned above, and then conc hydrochloric acid was added to obtain the corresponding acidity. The resulting solution was refluxed for 1-4 hr. The recoveries of lauric acid under various conditions were determined by a potentiometric titration method after extraction with ether, and the results are shown in Table II. Since hydrolysis with 4N hydrochloric acid for 4 hr gave satisfactory recovery of lauric acid, hydrolysis conditions of imidazolinium surfactants were determined as mentioned in the Materials and Methods section.

Determination of Homologous Distribution

Cationic and amphoteric surfactants having a known homologous distribution were synthesized. Table III shows a comparison of the homologous distribution of the original fatty acids with that of the corresponding imidazolinium surfactants. The agreement between both distributions was satisfactory, and the standard deviation in the determination was within 3%. Therefore, the present method should be applicable to the determination of the homologous distribution of various imidazolinium surfactants.

TABLE IV

Determination of the Homologous Distributions of Commercial Imidazolinium Surfactants

Homolog	Peak area percent (%)		
		Amphoterics	
	Cationics	Sample 1	Sample 2
C_8	–	4.1	0.1
C_{10}	trace	6.1	0.2
C_{12}	trace	50.2	0.5
C_{14}	1.9	20.4	2.8
$C_{14}F_1$	0.2	–	0.4
C_{16}	31.0	10.1	4.3
$C_{16}F_1$	2.4	0.1	7.1
C_{18}	63.0	3.1	1.0
$C_{18}F_1$	0.5	5.0	74.9
$C_{18}F_2$	0.9	1.0	0.4
$C_{20}F_1$	–	–	1.3
$C_{20}F_2$	–	–	0.2

Table IV shows the examples of the determination of the homologous distribution of commercial imidazolinium surfactants. The obtained homologous distributions of cationics and sample 1 of amphoterics agree closely with those of hydrogenated tallow oil and coconut oil, respectively.

Structural Analysis of the Products Obtained by the Reaction of AAAI with Diethyl Sulfate

In the case of the reaction of AAAI with diethyl sulfate, it may attack two teritary nitrogen atoms, in the 1 and 3-positions of an imidazoline ring. Mannheimer (4) estimated that the attacking position was 1-nitrogen. However, Trivedi et al. (6) demonstrated by means of ^1H- and ^{13}C-NMR spectrometry that quaternization mainly occurred at the nitrogen of 3 position. The authors tried to analyze the reaction products quantitatively.

In the case of the structural analysis, it seems advantageous to analyze polyamines formed by hydrolysis of the

TABLE III

Comparison of the Homologous Distributions of Fatty Acid Methyl Esters and the Corresponding Quaternary Imidazolinium Surfactants

Homolog	Peak area percent (%)			
	Cationics		Amphoterics	
	Original	Found	Original	Found
C_{10}	0.8	0.8	1.0	0.8
C_{12}	95.6	95.5	50.1	50.0
C_{14}	3.5	3.6	24.7	24.0
C_{16}	0.1	0.1	12.6	12.5
$C_{16}F_1$			0.2	0.2
C_{18}			3.5	3.7
$C_{18}F_1$			7.3	7.6
$C_{18}F_2$			1.4	1.2

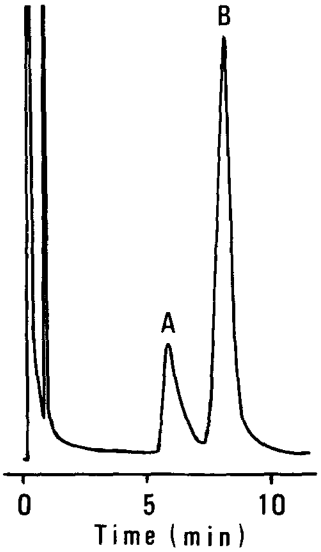


FIG. 1. Gas chromatogram of acetate derivatives of polyamines, which were derived from the product obtained by the reaction of AAAI with diethyl sulfate. (A) Diethylenetriamine triacetate; (B) triacetate of V.

reaction product. If quaternization occurs at 1-nitrogen, hydrolysis of the reaction product will afford polyamine **IV**. If not so, polyamine **V** should be obtained by hydrolysis. Derivation of these polyamines to acetate makes possible to distinguish two polyamines by IR and ^{1}H-NMR spectrometry; i.e., **IV** affords diacetate (two monosubstituted amide groups) whereas **V** gives triacetate (one monosubstituted and two disubstituted amide groups).

$$NH_2CH_2CH_2\overset{\overset{\textstyle Et}{|}}{N}CH_2CH_2NH_2$$

IV

$$NH_2CH_2CH_2NHCH_2CH_2NHEt$$

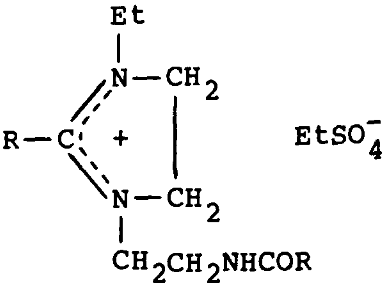
V

The products obtained by the reaction of AAAI with one equivalent mol of diethyl sulfate was treated as described in Materials and Methods section, and the resulting acetylated polyamines were analyzed by GC. As shown in Figure 1, two peaks were observed, and peak area percentages of A and B were 23.5% and 76.5%, respectively.

After isolation of each compound by preparative TLC on silica gel, IR and ^{1}H-NMR spectra were observed. It was found from these spectra that compound A had three amide groups (two monosubstituted and one disubstituted amide groups), however that it had no ethyl group. Thus, this compound could be assigned to diethylenetriamine triacetate, which was derived from unreacted AAAI.

^{1}H-NMR spectrum of compound B showed the presence of three acetyl and one ethyl groups. (Triplet at 1.2 ppm coupled with the signal at 3.3 ppm.) Furthermore, it was found that one monosubstituted and two disubstituted amide groups were present in compound B on the basis of the ratio of 1630 and 1550 cm^{-1} absorption bands of its IR spectrum. Therefore, the structure of compound B is established as triacetate of triamine V.

Thus, it is demonstrated that the reaction product comprises 23.5% of unreacted AAAI and 76.5% of **VI**, which indicates the selective quaternization of 3-nitrogen of an imidazoline ring with diethyl sulfate.

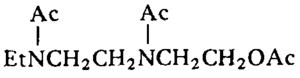


VI

Structural Analysis of the Product Obtained by the Reaction of HEAI with Diethyl Sulfate

In the case of the reaction of HEAI with diethyl sulfate, etherification of hydroxyethyl group of HEAI may occur in addition to quaternization. Therefore, structural analysis of the product obtained by the reaction of HEAI with two equivalent mol of diethyl sulfate was carried out as follows.

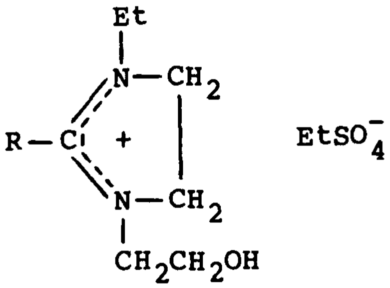
The reaction product was treated as described in the experimental section to give acetylated polyamines. It was found by GC analysis that this acetate comprised 4.4% of hydroxyethylethylenediamine and 95.5% of unknown compound. After isolation of this unknown compound by preparative TLC on silica gel, ^{1}H-NMR and IR spectra were measured. ^{1}H-NMR spectra revealed a triplet at 1.2 ppm (coupled with the broad singlet at 3.30-3.70 ppm) assigned to terminal methyl group, which suggested the presence of $\rangle$N−Et group. Also, the presence of three acetyl groups were assumed from the broad singlet at 2.3 ppm. IR spectrum showed the presence of −OAc group from the strong absorption band at 1740, 1230 and 1040 cm^{-1}. This compound has disubstituted amide group, but had not monosubstituted amide group because of the absence of absorption band near 1550 cm^{-1} From these results, the structure of this compound was established as **VIII**.



$$Et\overset{\overset{\textstyle Ac}{|}}{N}CH_2CH_2\overset{\overset{\textstyle Ac}{|}}{N}CH_2CH_2OAc$$

VIII

Therefore, it has been found that the reaction product of HEAI with diethyl sulfate comprises 4.4% of unreacted HEAI and 95.5% of quaternized product **IX**.



IX

Consequently, structural analysis of the products obtained by the reaction of imidazoline derivatives with diethyl sulfate demonstrated that quaternization of an imidazoline ring selectively occurred at the nitrogen at the 3-position, which was kinetically favored position in terms of the steric hinderence and the stability of the product by delocalization of a positive charge.

ACKNOWLEDGMENT

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