

Analysis of Cationic and Amphoteric Surfactants: V.

Structural Analysis of the Amphoteric Surfactants Obtained by the Reaction of 1-(2-Hydroxyethyl)-2-alkyl-2-imidazoline with Sodium Monochloroacetate

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ABSTRACT

Structural analysis of the amphoteric surfactants obtained by the reaction of 1-(2-hydroxyethyl)-2-alkyl-2-imidazoline (HEAI) with sodium monochloroacetate has been carried out. These amphoteric surfactants were hydrolyzed under aqueous alkaline media, followed by acid hydrolysis to afford fatty acid and diamine derivatives. The resulting diamine derivatives were identified by the isolation and their syntheses, and were quantitatively analyzed by gas chromatography. Based upon the results of these analyses, it has been found that the reaction products can be divided into two typical types. The reaction products have simpler compositions than those of ethyl acrylate. However, these amphoteric surfactants are characterized by the presence of appreciable amounts of hydrolysis products of amides, soap and free diamine derivative **XI**.

INTRODUCTION

Imidazolinium amphoteric surfactants have been widely used as important ingredients in the cosmetic field, such as in shampoo, because of their low primary irritation. Syntheses of these amphoteric surfactants were first reported by Mannheimer in 1950 (1), in which 1-(2-hydroxyethyl)-2-alkyl-2-imidazoline (HEAI) was allowed to react with sodium monochloroacetate. The presented structure of the reaction products by Mannheimer was revised by subsequent studies on these derivatives (2, 3); however, there were a number of unanswered questions.

In the previous papers, the authors identified the structures of imidazolinium cationics (4) and the amphoteric surfactants obtained by the reaction of HEAI with ethyl acrylate (5), and demonstrated that quaternization selectively occurred at 3-nitrogen atom of an imidazoline ring. In the case of the reaction of HEAI with ethyl acrylate in the absence of solvent, it has been found that ethyl acrylate adds appreciably to the carbon atoms alpha to an imidazoline ring. Furthermore, these amphoteric surfactants synthesized in the presence of water were a complex mixture of amides, since imidazoline derivatives were labile under aqueous alkaline condition (6, 7).

The reaction of HEAI with monochloroacetate derivatives seems to be interesting in terms of the reactivity to HEAI compared with that of ethyl acrylate. In addition, these amphoteric surfactants are most widely used among various imidazoline derivatives in the cosmetic field. Therefore, the authors investigated the structural analysis of the amphoteric surfactants obtained by the reaction of HEAI with sodium monochloroacetate.

MATERIALS AND METHODS

Apparatus and Reagents

Apparatus and reagents are similar to those previously described (5).

Hydrolysis Procedures and Analysis of Carboxylic Acids

These procedures are similar to those previously described (5).

Analysis of Diamine Derivatives

Aqueous layer extracted with ether was concentrated to dryness under reduced pressure, and 100 mL of *n*-propanol was added to the residue. The resulting solution was saturated with gaseous hydrogen chloride and refluxed for 2 hr. After cooling, *n*-propanol was distilled off under reduced pressure, and acetic anhydride and pyridine (3 mL each) were added to the residue, which was magnetically stirred at room temperature overnight. The solution was concentrated to dryness under reduced pressure, and the residue was dissolved in *n*-propanol and neutralized with ammonium carbonate. After filtration, the filtrate was concentrated under reduced pressure and analyzed by gas chromatography (GC) under the conditions described previously (5).

Synthesis of Diamine IV and VI (Scheme 1 in Figure 1)

Acetic anhydride (5.10 g, 50 mmol) was slowly dropped into the magnetically stirred solution of *N*-hydroxyethyl-ethylenediamine (2.08 g, 20 mmol) in 20 mL of methanol, and the reaction was continued for an additional 3 hr. Concentration of the solution gave 3.66 g of *N,N'*-diacetyl-*N*-hydroxyethylethylenediamine (97.3% yield).

The above diacetate (3.34 g, 17.7 mmol) was dissolved in 10 mL of dioxane, and 0.51 g of sodium hydride (21.3 mmol) was added slowly. Ethyl monochloroacetate (2.6 g, 21.2 mmol) was added and stirred for 5 hr at 70°C. A small amount of ethanol was added to the cooled solution to decompose excess sodium hydride, and chloroform was added to the solution. After filtration, the filtrate was concentrated. Preparative thin layer chromatography (TLC) of the residue on silica gel afforded diacetyl monoethyl ester of **IV** (1.5 g, 30.9% yield) and diacetyl diethyl ester of **VI** (130 mg, 2.0% yield).

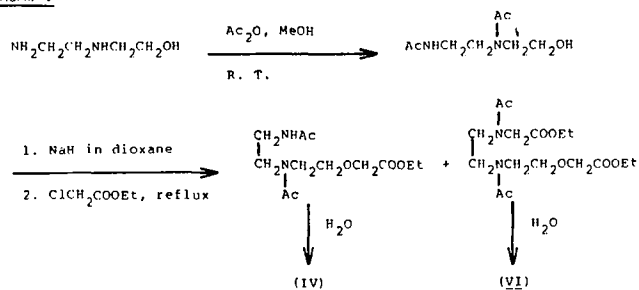
Diacetyl monoethyl ester of IV. IR (neat, cm^{-1}) 3300, 1740, 1630, 1540, 1280, 1210, 1040; $^1\text{H-NMR}$ (ppm; solvent, CD_3OD) 1.24 (3H, t, $J=6\text{Hz}$; CH_2CH_3), 1.90 (3H, d, $J=2\text{Hz}$; Ac), 2.10 (3H, d, $J=2\text{Hz}$; Ac), 3.25–3.75 (8H; NCH_2), 4.08 (2H, s; CH_2COO), 4.20 (2H, q, $J=6\text{Hz}$; COOCH_2); MS m/e 274 (M^+ ; found 274.1499, calcd. for $\text{C}_{12}\text{H}_{22}\text{N}_2\text{O}_5$ 274.1527).

Diacetyl diethyl ester of VI. IR (neat, cm^{-1}) 3400, 1730, 1630, 1200, 1120, 1040; $^1\text{H-NMR}$ (ppm; solvent, CD_3OD) 1.25 (6H, t, $J=7\text{Hz}$; CH_2CH_3), 2.11 (3H, s; Ac), 2.15 (3H, s; Ac), 3.40–3.70 (8H; NCH_2), 4.05 (4H, s; CH_2COO), 4.12 (4H, q, $J=6\text{Hz}$; COOCH_2); MS m/e 360 (M^+ ; found 360.1889, calcd. for $\text{C}_{16}\text{H}_{28}\text{N}_2\text{O}_7$ 360.1894).

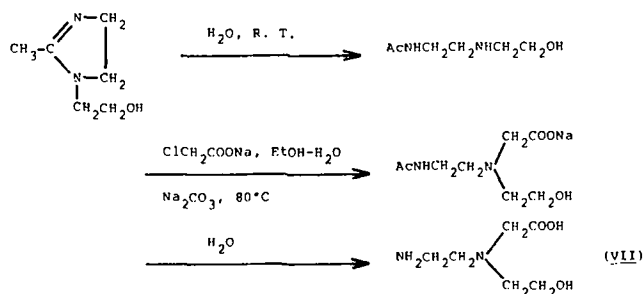
Synthesis of Diamine VII (Scheme 2 in Figure 1)

Sodium monochloroacetate (349.5 mg, 3 mmol) and sodium carbonate (250 mg, 2.4 mmol) were added to the solution of *N*-acetyl-*N'*-hydroxyethylethylenediamine (292

Scheme-1



Scheme-2



Scheme-3

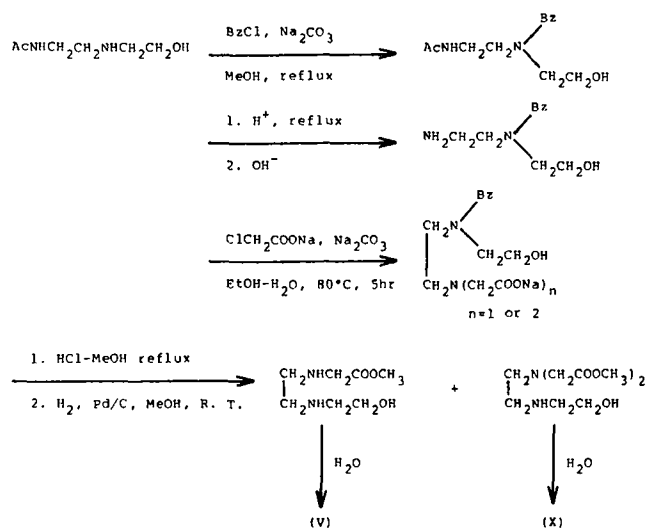


FIG. 1. Estimated products from the reaction of HEAI with monochloroacetate derivatives.

mg, 2 mmol) in 5 mL of ethanol, and water was added until clear solution was obtained. The solution was stirred at 80 C for 5 hr, and then concentrated to dryness under reduced pressure. *n*-Propanol (50 mL) was added to the residue and saturated with gaseous hydrogen chloride. The solution was refluxed for 2 hr, and then filtered, concentrated and dried under reduced pressure. Acetic anhydride and pyridine (1 mL each) was added to the residue, and the solution was stirred at room temperature overnight. The solution was concentrated to dryness under reduced pressure, and then dissolved in *n*-propanol. After filtration, the filtrate was concentrated, and preparative TLC of the residue on silica gel gave 192 mg of diacetyl monopropyl ester of **VII** (35.2% yield).

IR (neat, cm^{-1}) 3320, 1740, 1650, 1560, 1240, 1180, 1040; $^1\text{H-NMR}$ (ppm; solvent, CDCl_3) 0.90 (3H, t, $J=7\text{Hz}$; CH_2CH_3), 1.64 (2H, sextet, $J=7\text{Hz}$; CH_2CH_3), 1.97 (3H, s; Ac), 2.03 (3H, s; Ac), 2.60–2.95 (4H; NCH_2), 3.23 (2H, m; AcNHCCH_2), 3.34 (2H, s; NCH_2COO), 3.85–4.22 (4H; CH_2OAc and COOCH_2); MS m/e 288 (M^+ ; found 288.1663, calcd. for $\text{C}_{13}\text{H}_{24}\text{N}_2\text{O}_5$ 288.1683).

Syntheses of Diamine **V** and **X** (Scheme 3 in Figure 1)

Benzyl chloride (1.21 g, 9.6 mmol) and sodium carbonate (0.2 g) were added to a solution of *N*-acetyl-*N'*-hydroxyethyl-ethylenediamine (584 mg, 4.0 mmol) in 5 mL of methanol, and the solution was stirred at room temperature overnight. After concentration of the solution under reduced pressure, preparative TLC of the residue on silica gel gave 380 mg of *N*-acetyl-*N'*-benzyl-*N'*-hydroxyethyl-ethylenediamine (40.3% yield), which was hydrolyzed with 4N hydrochloric acid under refluxing conditions. The solution was concentrated under reduced pressure, and then neutralized with ethanolic potassium hydroxide. Sodium monochloroacetate (243 mg, 2.09 mmol) and sodium carbonate (0.2 g) were added to a solution of the residue in a mixture of ethanol and water (2 mL each), and refluxed for 5 hr. After cooling, the solution was concentrated to dry-

ness under reduced pressure, and the residue was dissolved in 50 mL of methanol saturated with gaseous hydrogen chloride, followed by refluxing for 2 hr. After filtration, the filtrate was concentrated and dried under reduced pressure. The residue was dissolved in 5 mL of methanol, and 50 mg of 10% Pd/C was added. The reaction mixture was hydrogenated at room temperature and atmospheric pressure overnight to remove the benzyl group. After *n*-propyl esterification followed by acetylation, the mixture was separated by preparative TLC on silica gel to afford 80 mg of triacetyl monopropyl ester of **V** (15.7% yield), 30 mg of **Xa** and 160 mg of **Xb**, lactamization products of **X** (6.8 and 36.5% yields).

Triacetyl monopropyl ester of V. IR (neat, cm^{-1}) 3470, 1740, 1640, 1230, 1040; $^1\text{H-NMR}$ (ppm; solvent, CDCl_3) 0.90 (3H, t, $J=7\text{Hz}$; CH_2CH_3), 1.63 (2H, sextet, $J=7\text{Hz}$; CH_2CH_3), 1.98 (3H, d, $J=2\text{Hz}$; Ac), 2.03 (3H, s; Ac), 2.12 (3H, d, $J=2\text{Hz}$; Ac), 3.40–3.70 (6H; NCH_2), 3.85–4.30 (6H; $\text{CH}_2\text{COOCH}_2$ and CH_2OAc); MS m/e 330 (M^+ ; found 330.1788, calcd. for $\text{C}_{15}\text{H}_{26}\text{N}_2\text{O}_6$ 330.1790).

Lactam Xa. IR (neat, cm^{-1}) 3400, 1740, 1640, 1580, 1290, 1170, 1060; $^1\text{H-NMR}$ (ppm; solvent, CDCl_3) 0.90 (3H, t, $J=7\text{Hz}$; CH_2CH_3), 1.65 (2H, sextet, $J=7\text{Hz}$; CH_2CH_3), 2.85 (2H, m), 3.20–3.85 (12H), 4.00 (2H, t, $J=7\text{Hz}$; COOCH_2); $^{13}\text{C-NMR}$ (ppm; solvent, $^{12}\text{CD}_3\text{OD}$) (ethyl ester) 10.7 (q), 23.0 (t), 49.0 (t), 50.3 (t), 57.1 (t), 58.0 (t), 60.3 (t), 67.4 (t), 169.2 (s), 171.6 (s); MS m/e 244 (M^+ ; found 244.1427, calcd. for $\text{C}_{11}\text{H}_{20}\text{N}_2\text{O}_4$ 244.1422).

Lactam Xb. IR (neat, cm^{-1}) 3450, 1740, 1650, 1240, 1190, 1040; $^1\text{H-NMR}$ (ppm; solvent, CDCl_3) 0.90 (3H, t, $J=7\text{Hz}$; CH_2CH_3), 1.64 (2H, sextet, $J=7\text{Hz}$; CH_2CH_3), 2.03 (3H, s; Ac), 2.55–2.90 (4H, m), 3.20–4.65 (4H), 3.85–4.25 (6H); $^{13}\text{C-NMR}$ (ppm; solvent, $^{12}\text{CD}_3\text{OD}$) (ethyl ester) 10.7 (q), 20.8 (q), 22.9 (t), 48.8 (t), 50.5 (t), 56.3 (t), 57.7 (t), 62.5 (t), 67.9 (t), 169.8 (s), 170.2 (s), 172.6 (s); MS m/e 286 (M^+ ; found 286.1522, calcd. for $\text{C}_{13}\text{H}_{22}\text{N}_2\text{O}_5$ 286.1527).

ANALYSIS OF IMIDAZOLINES (II)

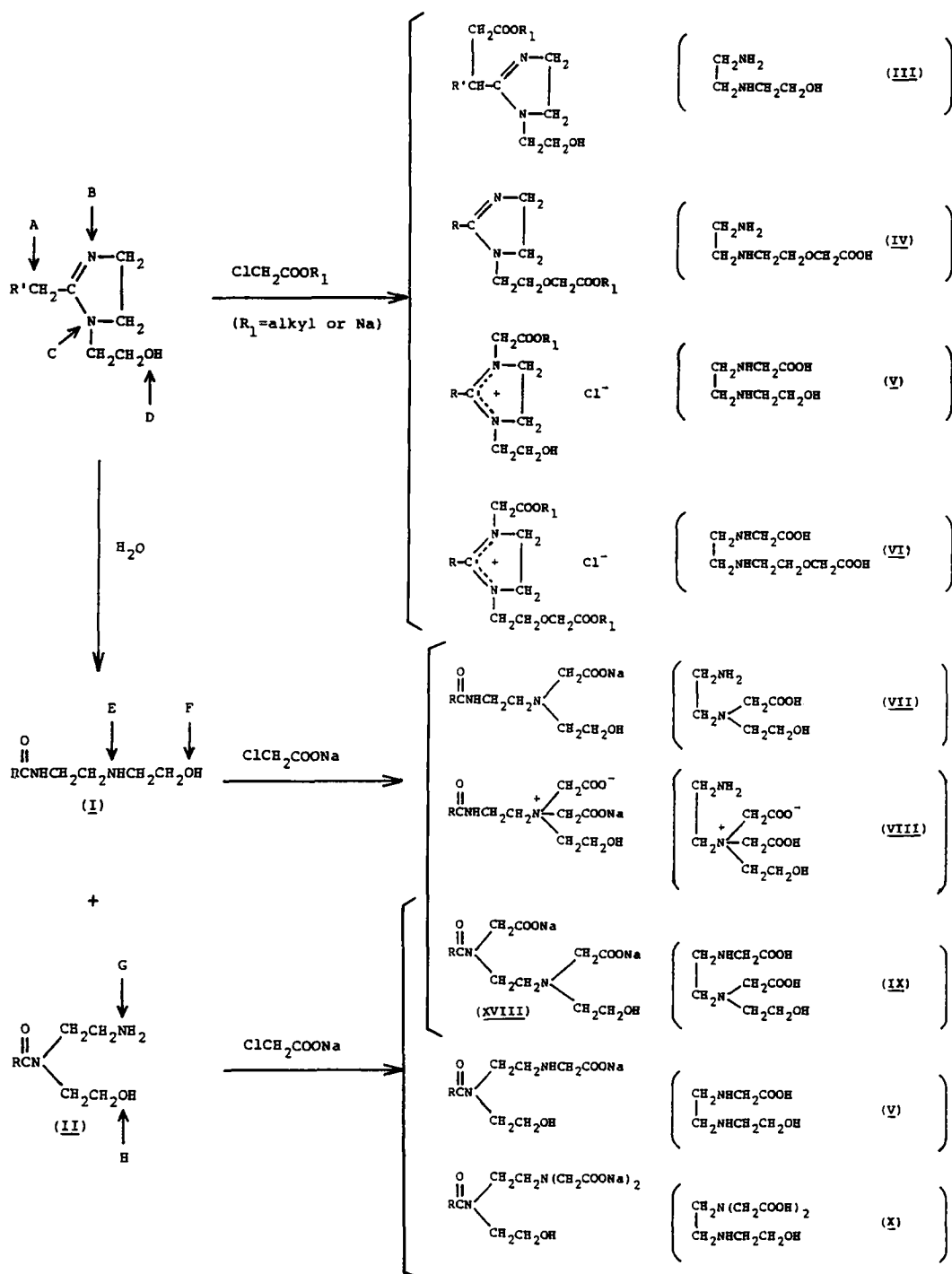


FIG. 2. Scheme for syntheses of diamine derivatives.

RESULTS AND DISCUSSION

Estimated Products from the Reaction of HEAI with Monochloroacetate Derivatives

Based upon the results of previous studies (4,5), products by reaction of HEAI with monochloroacetate derivatives could be estimated as shown in Figure 2.

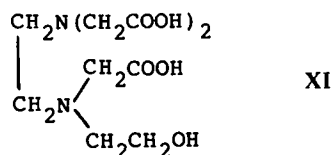
Attack of monochloroacetate derivatives to HEAI may occur at four positions, A–D, as indicated by the arrows in Figure 2. Since ethyl acrylate reacts at the carbon atom alpha to an imidazoline ring (5), monochloroacetate ester may attack at site A. Also, etherification at site D may be

observed. It has been found (4, 5) that quarternization of an imidazoline ring selectively occurred at site B, and so reaction of monochloroacetate derivatives at site C will not occur. Thus, reaction of HEAI with monochloroacetate derivatives in the absence of water may produce the products as shown in Figure 2. Hydrolysis of these reaction products gives diamines, III–VI, in parentheses.

In the case of the reaction of HEAI with monochloroacetate derivatives in the presence of water, a ring-opening reaction occurs to give amides, I and II. Reaction of monochloroacetate derivatives with these amides may occur at four sites, E–H, indicated by the arrows in Figure 2. Since

the reaction of ethyl acrylate at F and H is not observed under ordinary conditions (5), monochloroacetate derivatives also will not react. Therefore, the reaction products shown in Figure 2 can be estimated, and hydrolysis of these products gives diamines, VII–X, in parentheses.

These diamines, III–X, could be isolated and identified from the various reaction products by preparative TLC on silica gel after the treatment as described in the experimental section. Furthermore, diamine derivative XI indicated below was identified in most of the reaction products.



Syntheses of Standard Diamine Derivatives

Various diamine derivatives were synthesized by the scheme as shown in Figure 1, however III and XI were obtained commercially. In addition, VIII was not synthesized in this study, since quaternization by sodium monochloroacetate did not occur under ordinary conditions.

On acetylation of X in order to apply GC analysis, cyclization of X to lactams Xa and Xb occurred as shown below. The structure of these lactams was confirmed as described below.

Under these conditions, lactam Xb was chiefly formed, and this compound was isolated by preparative TLC on silica gel. Reduction of Xb with lithium aluminum hydride in ether afforded piperazine derivative XII, which was identified by comparing various spectral data with those of authentic sample (Scheme 1).

On the other hand, IX and X cannot be separated by GC under the conditions described in the experimental section. Diamine IX is derived from amide XVIII as shown in Figure 2; however, this product is estimated to be scarcely formed, as will be discussed later. Therefore, the presence of XI could be neglected in the following study.

Reduction of Lactam Xb

Lactam Xb (200 mg, 0.74 mmol) was dissolved in 20 mL of anhydrous ether, and a little excess of lithium aluminum hydride was added and refluxed for 3 hr. After cooling, a small amount of ethyl acetate was carefully added to de-

compose excess lithium aluminum hydride, and then a small amount of 6N NaOH was added to form precipitate. Concentration of the supernatant solution gave 86 mg of unreacted lactam Xb. Extraction from precipitate with chloroform gave 73 mg of N,N'-bis-(2-hydroxyethyl)-piperazine (56.7% yield), which was identified by comparing various spectral data with commercially available sample (Aldrich).

Transformation of XI to XIa

n-Propyl ester of XI (0.2 g) dissolved in 50 mL of pyridine was refluxed for 4 hr to afford XIa quantitatively.

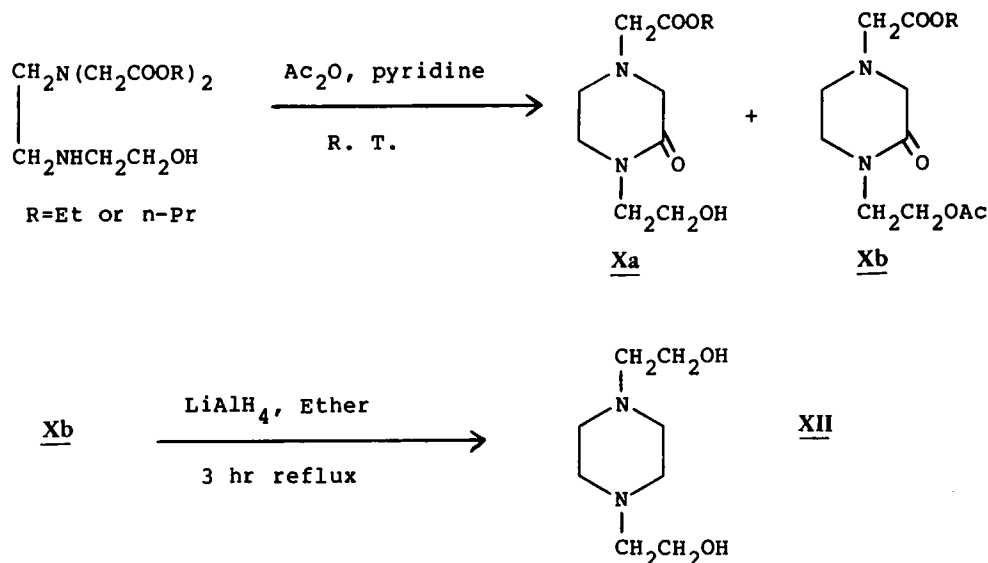
IR (neat, cm^{-1}) 1740, 1240, 1190, 1140, 1060; $^1\text{H-NMR}$ (ppm; solvent, CDCl_3) 0.92 (6H, t, $J=6\text{Hz}$; CH_2CH_3), 1.62 (4H, sextet, $J=6\text{Hz}$; CH_2CH_3), 2.40–3.00 (6H; NCH_2), 3.40–3.65 (6H; CH_2COO), 3.99 (4H, t, $J=6\text{Hz}$; COOCH_2), 4.30 (2H, t, $J=5\text{Hz}$; $\text{NCH}_2\text{CH}_2\text{O}$); MS m/e 344 (M^+ ; found 344.1948, calcd. for $\text{C}_{16}\text{H}_{28}\text{N}_2\text{O}_6$ 344.1948).

Analysis of Diamine Derivatives by GC

After similar treatment as described in the previous study (4), various diamine derivatives were analyzed under the same GC conditions. However, III and VII could not be separated under these conditions. Therefore, esterification with *n*-propanol instead of ethanol was carried out, and these diamine derivatives (propyl esters) were separated completely as shown in Figure 3.

Figure 3 shows the typical gas chromatogram of diamine derivatives. Assignment of each peak was carried out by comparing retention time with that of standard samples and by GC-MS analyses. As shown in Figure 3, each diamine derivative was completely separated, and satisfactory repeatability, 3–7% of standard deviation, was obtained. In addition, the ratio of Xa to Xb varied with the reaction products.

Since gas chromatographic peak eluted at 12.7 min revealed parent ion peak at m/e 344 by GC-MS analysis, three structures XIa–XIc indicated below were conceivable. This compound was found to be formed from XI by acetylation after esterification, and could be isolated by preparative TLC on silica gel. The structure of this compound was deduced as XIa by the absence of amide absorption band on its IR spectrum. Furthermore, reflux of *n*-propyl ester of XI in pyridine afforded XIa quantitatively. From these results, the structure of this compound was established as XIa, which was considered to be formed by



SCHEME 1

ANALYSIS OF IMIDAZOLINES (II)

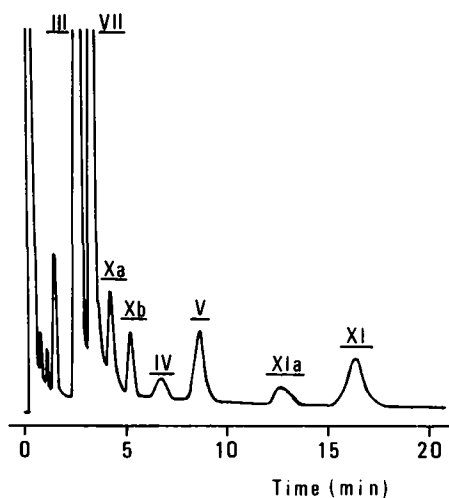
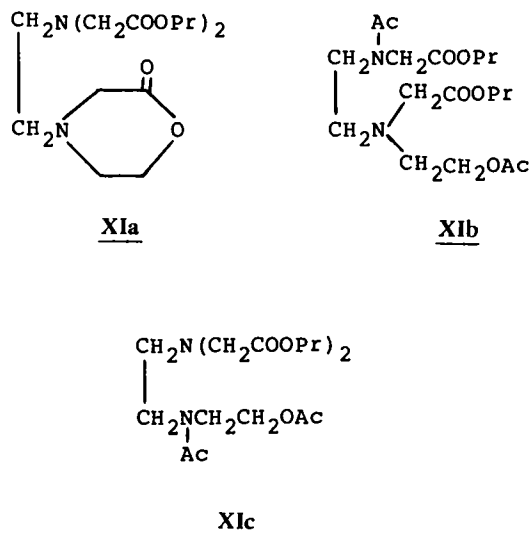


FIG. 3. Typical gas chromatogram of diamine derivatives.



lactonization of XI during acetylation.

Reaction of HEAI with Monochloroacetate Derivatives in the Absence of Solvent

Dibasic acid was not detected from any reaction products. This result indicated that attack of monochloroacetate derivatives at the carbon atom alpha to an imidazoline ring did not occur.

HEAI ($R=C_{11}H_{23}$) was allowed to react with 1–3 equivalent mol of ethyl or sodium monochloroacetate at 60–65 C for 4 hr in the absence of solvent, and the reaction products were treated and analyzed as described in the experimental section. As shown in Table I, all reaction products gave chiefly diamine V.

On the assumption described below, reaction products and each content were estimated as shown in Table II. (a) Each content is calculated on the basis of GC peak area percent in Table I. (b) Diamine III is all derived from unreacted HEAI. (c) Diamines VII and X are derived from the products by the reaction of the amide, I or II, with monochloroacetate derivatives. (d) Diamines IV and V are assigned to imidazoline remaining compounds XIII and XIV, respectively; however, it is considered that ring-opening products are also present in the case of sodium monochloroacetate.

In the case of the reaction of HEAI with ethyl monochloroacetate, it attacked preferentially at the 3-nitrogen of an imidazoline ring to give XIa as estimated from the

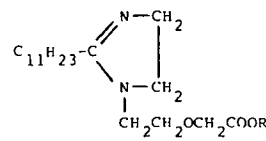
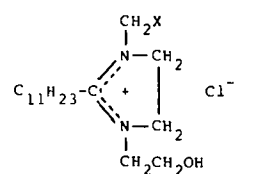
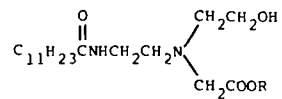
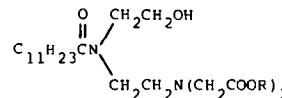
TABLE I

Results of GC Analysis of the Products Obtained by the Reaction of HEAI with Ethyl or Sodium Monochloroacetate in the Absence of Solvent

Compound	GC peak area %					
	ClCH ₂ COOEt			ClCH ₂ COONa		
	1.0	2.0	3.0	1.0	2.0	3.0
	(mol)			(mol)		
$\begin{array}{c} \text{CH}_2\text{NH}_2 \\ \\ \text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH} \end{array}$ (III)	36.7	21.8	8.9	22.0	25.1	
$\begin{array}{c} \text{CH}_2\text{NH}_2 \\ \\ \text{CH}_2\text{N} \end{array}$ $\begin{array}{l} \text{CH}_2\text{CH}_2\text{OH} \\ \text{CH}_2\text{COOH} \end{array}$ (VII)	4.4	5.1	1.5	18.0	20.6	
$\begin{array}{c} \text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2 \\ \\ \text{CH}_2\text{OCH}_2\text{COOH} \end{array}$ (IV)	3.8	11.1	9.5	8.1	8.8	
$\begin{array}{c} \text{CH}_2\text{NHCH}_2\text{COOH} \\ \\ \text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH} \end{array}$ (V)	55.2	62.0	80.1	49.1	40.2	
$\begin{array}{c} \text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2 \\ \\ \text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH} \end{array}$ (X)	-	-	-	2.8	5.3	

TABLE II

Estimated Products from the Reaction of HEAI with Ethyl or Sodium Monochloroacetate in the Absence of Solvent

Compound	ClCH ₂ COOEt			ClCH ₂ COONa		
	1.0	2.0	3.0	1.0	2.0	
	(mol)			(mol)		
HEAI (R=C ₁₁ H ₂₃)	36.7	21.8	8.9	22.0	25.1	
	R=Et (XIIIa)	3.8	11.1	9.5	8.1	8.8
	R=Na (XIIIb)					
	X=COOEt (XIVa)	55.2	62.0	80.1	49.1	40.2
	X=COO ⁻ (XIVb)					
	R=Et (XV a)	4.4	5.1	1.5	18.0	20.6
	R=Na (XV b)					
	R=Et (XVI a)	-	-	-	2.8	5.3
	R=Na (XVI b)					

results of previous studies (4,5). As shown in Table II, the yield of XIVa increased with the increase of ethyl monochloroacetate, and reaction of 3 mol equivalent of ethyl monochloroacetate with HEAI gave XIVa in 80% yield. Also, etherification of hydroxyethyl group was observed in 10% yield; however, the extent of etherification was rather lower than that of ethyl acrylate (5). On the other hand, reaction of ethyl monochloroacetate at 3-nitrogen and at hydroxyethyl group (sites B and D in Fig. 2) did not occur simultaneously, since diamine VI was not detected. This result suggested that the reactivity of an imidazoline ring is changed by the reaction of ethyl monochloroacetate at 3-nitrogen or at hydroxyethyl group. It may be considered that the reaction at 3-nitrogen lowers acidity of the hydroxy proton of hydroxyethyl group.

The reaction of HEAI with sodium monochloroacetate in the absence of solvent was heterogeneous system, and gave diamines VII and X in high yields, which indicated that ring-opening reaction proceeded appreciably during the reaction. As shown in Table II, a main product was also XIVb which showed that quaternization occurred selectively at 3-nitrogen atom.

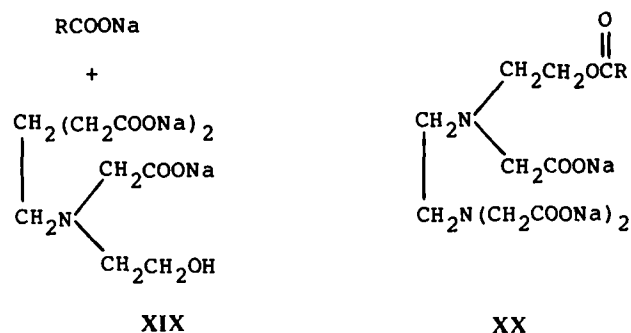
Consequently, it was found that the main reaction products in the absence of solvent were XIVa and XIVb.

Reaction of HEAI with Sodium Monochloroacetate in the Presence of Water

In the case of the reaction of HEAI with sodium monochloroacetate, water is required in the reaction system because of its poor solubility to organic solvent. This reaction can be divided into two typical types as described below.

(a) HEAI is hydrolyzed under alkaline condition, and then is reacted with sodium monochloroacetate (type I).
(b) HEAI is allowed to react with sodium monochloroacetate in the presence of water (type II).

The products synthesized under various conditions were treated and analyzed as described in the experimental section, and the results were shown in Table III. It was found that appreciable amount of diamine III was observed, and that any etherified diamine IV was not detected. In addition, it is also characteristic that the considerable amount of XI was detected from all reaction products. This compound was estimated to be formed by the reaction of sodium monochloroacetate with free diamines, which were formed by hydrolysis of amides during the reaction. It also can be estimated that diamine XI is derived from ester derivative XX, however it seems reasonable that most of diamine XI is derived from XIX.



ANALYSIS OF IMIDAZOLINES (II)

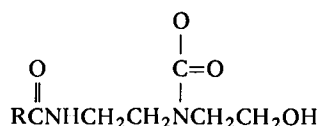
TABLE III

Results of GC Analysis of the Products Obtained by the Reaction of HEAI with Sodium Monochloroacetate (SMA) in the Presence of Water

Compound	Sample No.	GC peak area %								
		Type-I			Type-II					
		1	2*	3*	4		5		6*	
	1.0	2.0			1.0	2.0	3.0	2.0		
		(SMA mol)			(SMA mol)					
$\begin{array}{c} \text{CH}_2\text{NH}_2 \\ \\ \text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH} \end{array}$	(III)	25.6	22.8	31.6	2.1	15.6	5.9	7.0	10.4	5.8
$\begin{array}{c} \text{CH}_2\text{NH}_2 \\ \\ \text{CH}_2\text{N} \begin{array}{l} \text{CH}_2\text{CH}_2\text{OH} \\ \text{CH}_2\text{COOH} \end{array} \end{array}$	(VII)	62.0	68.1	53.3	86.1	63.4	49.4	50.2	39.0	43.9
$\begin{array}{c} \text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2 \\ \\ \text{CH}_2\text{OCH}_2\text{COOH} \end{array}$	(IV)	-	-	-	-	-	-	-	-	-
$\begin{array}{c} \text{CH}_2\text{NHCH}_2\text{COOH} \\ \\ \text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH} \end{array}$	(V)	4.0	0.1	2.2	0.7	8.6	0.6	0.7	4.3	1.2
$\begin{array}{c} \text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2 \\ \\ \text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH} \end{array}$	(X)	2.8	0.6	0.6	1.1	11.0	33.5	27.1	38.0	36.5
$\begin{array}{c} \text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2 \\ \\ \text{CH}_2\text{N} \begin{array}{l} \text{CH}_2\text{CH}_2\text{OH} \\ \text{CH}_2\text{COOH} \end{array} \end{array}$	(XI)	5.7	8.4	10.0	10.0	1.4	10.6	15.0	8.3	12.8

* Commercial imidazolinium amphoteric surfactants.

On the assumption described below, the reaction products and each content were estimated as shown in Table IV. (a) Each content is calculated on the basis of peak area percent in Table III. (b) Under these conditions, an imidazoline ring is completely hydrolyzed to give amides. (c) Diamine III is all derived from amide I, since amide II isomerizes to I under alkaline conditions (2, 3). However, the diamide indicated below may be present in the reaction mixture.



(d) All reaction products except XIX are indicated as amides, however a small part of these amides are considered to be derived from soap and free diamines as described in the previous paper (5).

In the case of type I, monosubstituted amide XVb was predominantly formed in 60–70% yields, since hydrolysis of HEAI was carried out under alkaline condition. As shown in Table IV, increase of sodium monochloroacetate resulted in increase of XIX, which suggested that it only promoted hydrolysis of amides. In addition, it is noteworthy that sample 3 shows the highest yield of XVb in 86% among these products.

On the other hand, type II contained appreciable amounts of disubstituted amides, XVIIb, XVII and XVIII, as shown in Table IV. It was also observed that increase of

sodium monochloroacetate brought the increase of disubstituted amide XVIIb with remarkable decrease of XVII.

Since diamine IX and X can not be separated by GC under the proposed conditions as described previously, amides, XVIIb and XVIII, are indistinguishable. It may be estimated from the results of the previous section that XIVb is formed in rather high yields in the case of type II, since HEAI is allowed to react directly with sodium monochloroacetate. However, any etherified products are not detected from the reaction products synthesized under various conditions. This fact suggests that hydrolysis reaction of HEAI preferentially occurs. Thus, it may be estimated that amide XVIII is formed from XVII by amide exchange reaction (Fig. 4). However, this amide exchange reaction was not observed in the reaction of HEAI with ethyl acrylate (5). Therefore, it can be estimated that XVIII is scarcely formed.

Since the ratio of mono- to disubstituted amides varies with the reaction conditions as shown in Table IV (sample 4 and 5), it seems possible to obtain disubstituted amides in higher yield as type III described in the previous paper (5).

The scheme for the reaction of HEAI with monochloroacetate derivatives was summarized in Figure 4. The reaction in the absence of solvent proceeds through path A to give XIVb as a main product, and also gives etherified product XIIIb in 10% yield.

The reaction products in the presence of water divided into two typical types as follows.

Type I. The reaction proceeds through path A. Hydrolysis

TABLE IV
Estimated Products from the Reaction of HEAI with
Sodium Monochloroacetate (SMA) in the Presence of Water

Compound	Sample No.	Composition %								
		Type-I			Type-II					
		1	2*	3*	4	5	6*			
	1.0	2.0		1.0	2.0	3.0	2.0			
		(SMA mol)			(SMA mol)					
$\begin{array}{c} \text{O} \\ \\ \text{RCNHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH} \end{array}$ (I)		25.6	22.8	31.6	2.1	15.6	5.9	7.0	14.0	5.8
$\begin{array}{c} \text{O} \\ \\ \text{RCNHCH}_2\text{CH}_2\text{N} \begin{array}{l} \nearrow \text{CH}_2\text{CH}_2\text{OH} \\ \searrow \text{CH}_2\text{COONa} \end{array} \end{array}$ (XVb)		62.0	68.1	53.3	86.1	63.4	49.4	50.2	39.0	43.9
$\begin{array}{c} \text{O} \\ \\ \text{RCN} \begin{array}{l} \nearrow \text{CH}_2\text{CH}_2\text{OH} \\ \searrow \text{CH}_2\text{CH}_2\text{NHCH}_2\text{COONa} \end{array} \end{array}$ (XVII)		4.0	0.1	2.2	0.7	8.6	0.6	0.7	4.3	1.2
$\begin{array}{c} \text{O} \\ \\ \text{RCN} \begin{array}{l} \nearrow \text{CH}_2\text{CH}_2\text{OH} \\ \searrow \text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COONa})_2 \end{array} \end{array}$ (XVIb) or XVIII		2.8	0.6	0.6	1.1	11.0	33.5	27.1	38.0	36.5
$\begin{array}{c} \text{RCOONa} \\ + \\ \text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2 \\ \\ \text{CH}_2\text{N} \begin{array}{l} \nearrow \text{CH}_2\text{CH}_2\text{OH} \\ \searrow \text{CH}_2\text{COOH} \end{array} \end{array}$ (XIX)		5.7	8.4	10.0	10.0	1.4	10.6	15.0	8.3	12.8

* Commercial imidazolinium amphoteric surfactants.

ANALYSIS OF IMIDAZOLINES (II)

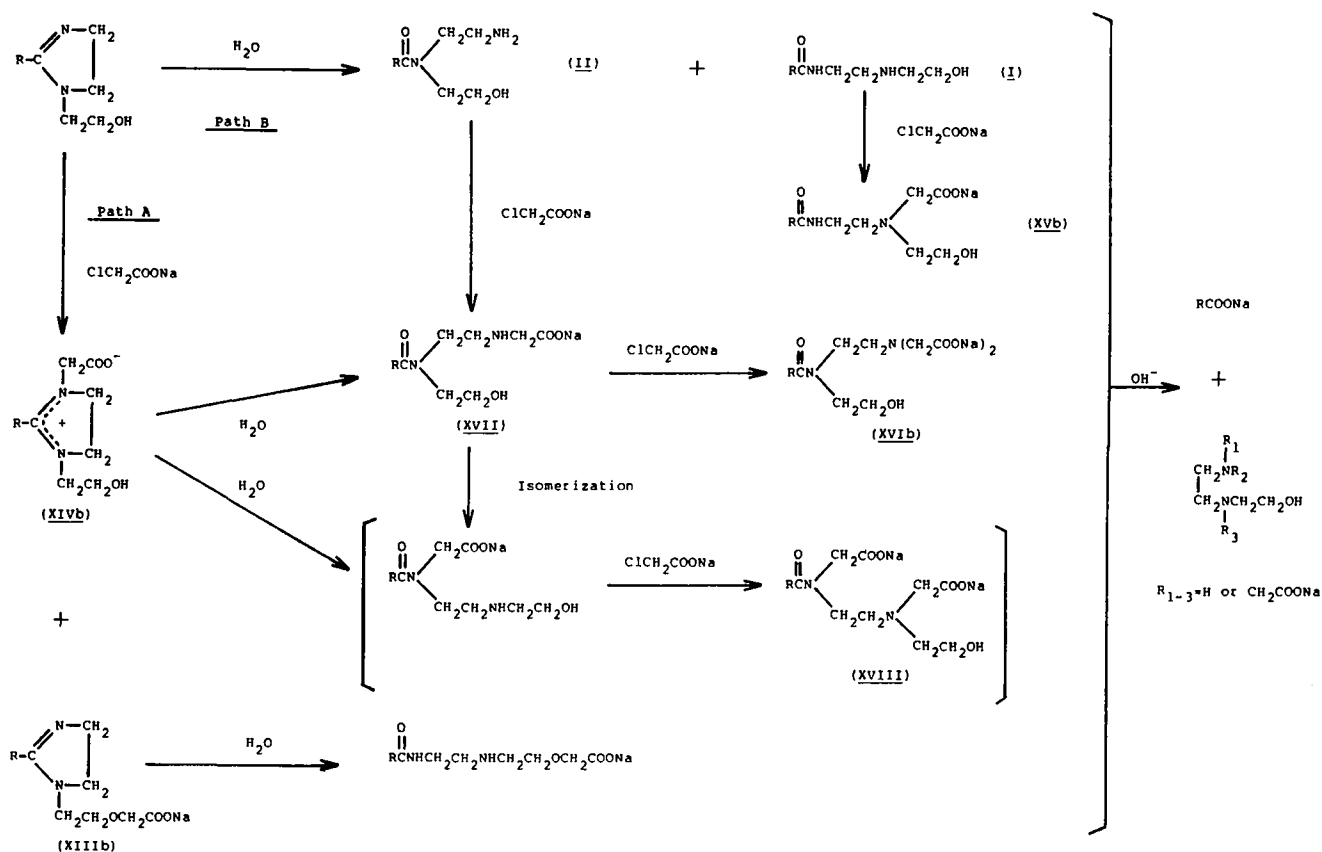


FIG. 4. Reaction pathways and products.

of an imidazoline ring is carried out under alkaline condition, and the main reaction product was monosubstituted amide XVb.

Type II. The reaction proceeds through both paths A and B. The reaction products contain appreciable amounts of disubstituted amides. However, the reaction proceeds mainly through path B, since any etherified products can not be detected.

The reaction products had simpler composition compared with those of ethyl acrylate (5); however, it is characteristic that appreciable amounts of hydrolysis products of amides, soap and free diamine XI are detected.

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