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ANALYSIS OF AMPHOTERIC SURFACTANTS BY LIQUID CHROMATOGRAPHY WITH POST-COLUMN DETECTION

II. IMIDAZOLINE-TYPE AMPHOTERIC SURFACTANTS DERIVED FROM SODIUM CHLOROACETATE

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SUMMARY

A convenient and direct high-performance liquid chromatographic (HPLC) determination of imidazoline-type amphoteric surfactants derived from sodium chloroacetate, using post-column detection, is described. The active ingredients of the surfactants were isolated by semi-preparative HPLC and identified directly by using both field desorption mass spectra and some specific chemical reaction techniques. The post-column detection system was based on a specific reaction with the amine structures of the surfactants, developed previously. The proposed method gave information on alkyl chain distribution of the original fatty acids, the degree of N-substitution by an electrophilic reactant, the reaction mechanism and conditions under which the surfactants were prepared. The method was applied successfully to toiletry products analysis.

INTRODUCTION

Imidazoline-type amphoteric surfactants can be classified according to the electrophilic reactants used in their production, *e.g.*, sodium chloroacetate, acrylic acid, ethyl acrylate and β-propiolactone. Some papers and patents[1–21] have been published on their structural analysis, but a clear-cut analytical method has not yet been reported. Problems lie in the lack of knowledge of the reaction mechanism, and in the variety of products resulting from the different preparation methods.

Recent investigations in this laboratory enabled Takano and Tsuji[21] to suggest structures for imidazoline amphoterics, by analysing the fragments produced upon acid hydrolysis, such as fatty acids and hydrophilic groups. But the structures and the composition of the active ingredients were not always reliable, because both hydrolysed products from amide compounds and adducts of an aminoethylethanolamine with electrophilic reactants are present.

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In this research the isolation and structural identification of the individual active ingredients is of primary importance, We have previously reported[22] a new approach for convenient and direct high-performance liquid chromatographic (HPLC) determination of alanine-type amphoteric surfactants, using post-column detection.

At a first step towards HPLC analysis of imidazoline amphoterics, here we report a method for convenient and direct determination of such compounds derived from sodium chloroacetate using post-column detection. During the course of this study, the active ingredients of the reaction products were separated and isolated by HPLC, their structures identified by both field desorption mass spectrometry (FD-MS) and some specific chemical reactions. Furthermore, the reaction pathways by which the compounds were transformed were investigated by using the novel post-column detection system developed previously[22]. The method was applied successfully to determine these compounds in commercial products.

EXPERIMENTAL

Materials

Imidazoline-type amphoteric surfactants derived from sodium chloroacetate were synthesized according to the literature procedures and/or minor modifications thereof[7,8,10–20]. Unless indicated otherwise, the lauric acid derivatives were used for the structure identification and the study of the reaction pathways. Those commercially available were kindly supplied by the manufacturers.

Apparatus

The HPLC equipment consisted of a Hitachi 635 pump for eluent delivery, a Hitachi variable-sample injector, a Haarke D1L water-bath for column temperature control (40°C), a UVIDEC III and a Hitachi 635M multi-wavelength monitor for UV detection and the post-column detection system developed previously[22]. A Shimadzu Chromatopac E1A integrator was used for the calculation of peak areas. Of the packing materials used, Develosil ODS-3 (3 μm; Nomura Chemical Co., Seto, Japan) was slurry packed in 150 × 4.6 mm I.D. columns for analytical separation and in 250 × 8 mm I.D. columns for semi-preparative separation. Cosmosil C_8 (5 μm; Nakarai Chemical Co., Japan) was slurry packed in 100 × 8 mm I.D. columns for desalting of preparatively separated compounds at low pH values.

The analytical and preparative separations were done with isocratic elution at 1.0 ml min^{-1} and 2.0 ml min^{-1}, respectively. The eluted compounds were detected by UV absorbance (generally at 210 or 230 nm) or post-column detection[22].

UV spectra were recorded using a Hitachi 200-10 scanning detector designed for HPLC on-line detection. IR spectra were determined using an Hitachi Model 260-50 instrument. Field desorption mass spectra were recorded using a Hitachi Model M-80 instrument. Tungsten wires (10 μm) activated with benzonitrile were used as FD emitters. The emitter was heated by a d.c. current of 0–40 mA.

Reversed-phase isolation of reaction products

The compounds in Fig. 1 were separated preparatively on a Develosil ODS-3 column with an eluent of acetonitrile–water (45:55) containing 0.2 *M* sodium per-

chlorate buffered at pH 2.5 by phosphoric acid. The collected fractions were neutralized by sodium carbonate and dried with a rotary evaporator at 50°C. Then the residues were dissolved in deionized water and desalted by reversed-phase chromatography on a Cosmosil C_8 column with trifluoroacetic acid–water (0.1:99.9) as eluent to obtain the acid form. The compounds were finally eluted with methanol and dried with a rotary evaporator at 50°C.

Peak shifting method with specific chemical reaction

To identify the structure of amines on the chromatogram, *i.e.*, secondary and tertiary amines, a specific chemical reaction with secondary amines was tested. The reaction mixture of compound I and sodium chloroacetate in aqueous solution with a sodium hydroxide catalyst in the molar ratio of 1/3/3(I/$ClCH_2CO_2Na$/NaOH) was lyophilized. The dry residue was treated with N-succinimidyl-*p*-nitrophenyl acetate in dry tetrahydrofuran (THF) at 50°C for 1 h. Then the solution was injected into an analytical column to observe the peak shift on the chromatogram.

Fragments determination after acid hydrolysis

The isolated compounds were hydrolysed in a screw-capped test-tube with 12 *M* hydrochloric acid according to the literature method[21]. The acid fragments were extracted by diethyl ether and dried by using a rotary evaporator. The acid structures were determined by FD-MS.

RESULTS AND DISCUSSION

Reaction pathways and tentative structure identification

Heiner *et al.*[19] and Takano and Tsuji[21] suggested the reaction pathways shown in Fig. 1. Except for the compounds I, II, III and X, the structures were not identified directly, only the suggested ones from the results of IR spectra, primary, secondary and tertiary amine content determined by titration and/or the hydrolysed fragments' determination of the reaction product mixtures.

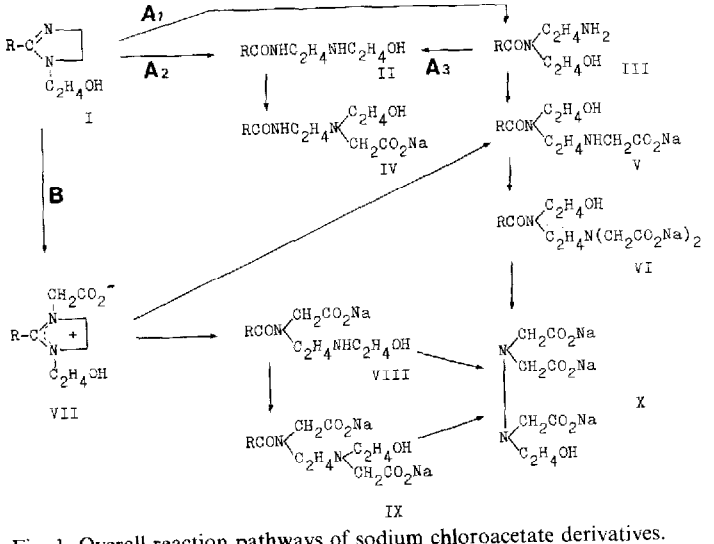
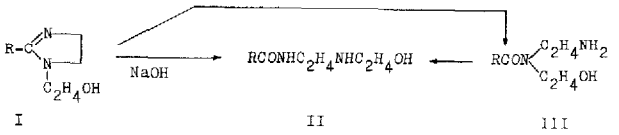


Fig. 1. Overall reaction pathways of sodium chloroacetate derivatives.

We reinvestigated the reaction pathways and the products of lauric acid derivatives by HPLC.



Scheme 1.

Hydrolysis of I (Scheme 1). Compound I, under alkaline conditions (molar ratio $I/H_2O/NaOH = 1/3/0.03$), gave the hydrolysed products II and III (Fig. 2) following the reaction pathways $A_{1,2,3}$ as described previously[20]. At higher reaction temperatures (80–85°C), compound III was unstable and was finally replaced by the diamine compound, $H_2NC_2H_4NHC_2H_4OH$, at the void volume in the chromatogram.

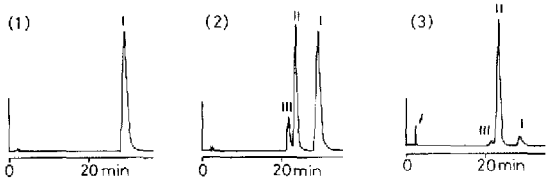
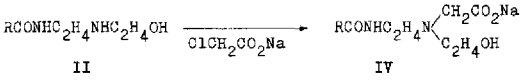


Fig. 2. Hydrolysis of I in an alkaline medium (Scheme 1): (1) just after the reaction (at room temperature); (2) 10 min after (at room temperature); (3) 2 h after (at 80–85°C). The diamine compound $H_2NC_2H_4NHC_2H_4OH$ is indicated with an arrow. Analytical conditions: eluent, 0.2 *M* $NaClO_4$ in 45% acetonitrile (pH 2.5); post-column detection.



Scheme 2.

Reaction of II and sodium chloroacetate (Scheme 2). Compound II reacted with sodium chloroacetate in aqueous solution at 80–85°C and different molar ratios ($I/ClCH_2CO_2Na/NaOH = 1/1/1$, 1/2/2, 1/3/3) to give the compound IV (Fig. 3).

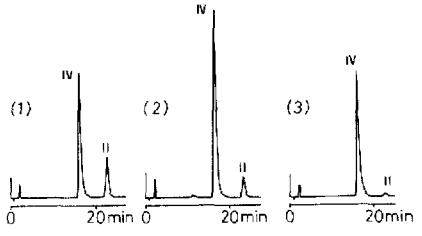
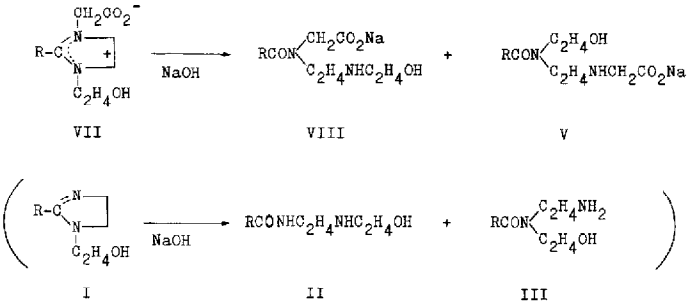


Fig. 3. Reaction of II and sodium chloroacetate (Scheme 2). Molar ratio $I/ClCH_2CO_2Na/NaOH = 1/1/1$ (1), 1/2/2 (2) and 1/3/3 (3). Analytical conditions as in Fig. 2.

Reaction of I and sodium chloroacetate without solvent (Scheme 3). Compound I (λ_{max} 230 nm) reacted at a 1/1 molar ratio of sodium chloroacetate to give the compound VII. The UV spectrum of compound VII showed λ_{max} at 240 nm in the weakly acidic medium of the eluent (0.2 *M* $NaClO_4$ in 50% acetonitrile, pH 2.5).

Scheme 3.



Scheme 4.

Hydrolysis of VII (Scheme 4). The reaction mixtures were hydrolysed under alkaline conditions (molar ratio VII + I/NaOH = 1/1.03) at 70–75°C to give the products II, III, V and VIII (Fig. 4). The presence of IV, VI and IX is due to the residue of sodium chloroacetate from path B. The hydrolysis of VII may yield one or

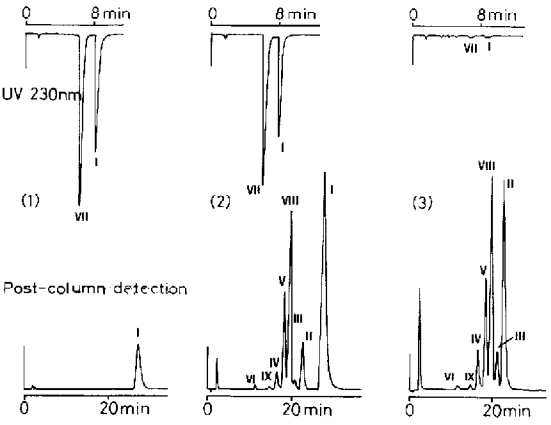


Fig. 4. Hydrolysis of I and VII in an alkaline medium; (1) just after the reaction; (2) 10 min after; (3) 30 min after. Analytical conditions: upper chromatograms, eluent 0.2 *M* $NaClO_4$ in 50% acetonitrile (pH 2.5), detection UV 210 nm; lower chromatograms, eluent 0.2 *M* $NaClO_4$ in 45% acetonitrile (pH 2.5), post-column detection.

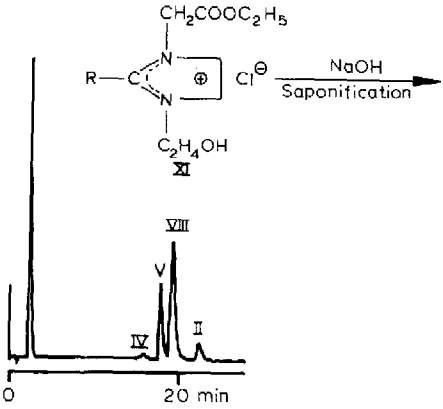


Fig. 5. Tentative identification of V and VIII.

both the isomers V and VIII as product. The reaction shown in Fig. 5 confirmed that V and VIII are derived from VII (Compound XI was stable and could be isolated by HPLC.) Compounds V and VIII were assigned in the chromatogram from their peak area ratio, provided that 1–2 cleavage of the imidazoline ring predominated over 2–3 cleavage[20].

Reaction of I and sodium chloroacetate in aqueous solution (see Fig. 1). Compound I was treated with sodium chloroacetate (molar ratio 1/1) in aqueous solution without addition of sodium hydroxide at 70–75°C for 6 h. The compounds I–IV, VI and VII were observed and the reaction was in equilibrium at all stages except for the decomposition of sodium chloroacetate leading to lower pH and stabilization of compounds I and VII (Fig. 6). On the other hand, when compound I was treated with different molar ratios of sodium chloroacetate with addition of sodium hydroxide ($I/ClCH_2CO_2Na/NaOH$ = 1/1/1, 1/2/2, 1/3/3) at 70–75°C for 4 h (Fig. 7), paths A and B proceeded simultaneously. With increasing molar ratio of sodium chloro-

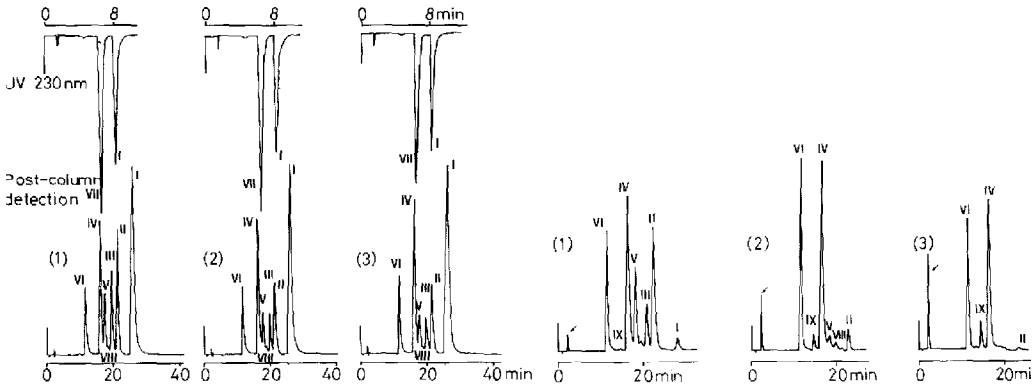
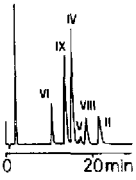


Fig. 6. Reaction of I and sodium chloroacetate in an aqueous solution without a catalyst: (1) just after the reaction; (2) 3 h after; (3) 6 h after. pH of 1% aqueous solution of the reaction mixture: 9.72 (1); 7.40 (2); 7.05 (3). Analytical conditions as in Fig. 4.

Fig. 7. Reaction of I and sodium chloroacetate in an aqueous solution with a catalyst of sodium hydroxide. Molar ratio $I/ClCH_2CO_2Na/NaOH$ = 1/1/1 (1); 1/2/2 (2) and 1/3/3 (3). Analytical conditions as in Fig. 2.

acetate, the decomposition of secondary amide compounds, *i.e.*, III, VI, VIII and IX, relative to primary amide IV increased resulting in the corresponding diamine derivatives and/or a product of further reaction such as X. Otherwise, the content of IX increased gradually. The tentative assignment of IX was based on its subsequent reaction (Fig. 8).

Stability of reaction products. Fig. 9 shows the effects of both the reaction temperature and the alkalinity on the stability of the reaction products. From the results, the secondary amide compounds were less stable than the primary amide ones, especially in an alkaline medium.



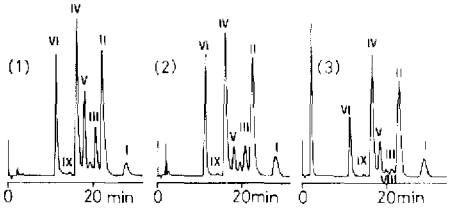


Fig. 8. Reaction of VII and sodium chloroacetate in an alkaline medium. A reaction mixture of I and VII as in Scheme 3 was treated with sodium chloroacetate in an alkaline medium (molar ratio I + VII/$ClCH_2CO_2Na$/NaOH = 1/1/1). Analytical conditions as in Fig. 2.

Fig. 9. Stability of reaction products: (1) untreated sample [same as in Fig. 8(1)]; (2) refluxed for 2 h in methanol; (3) left overnight at room temperature after adding one drop of 2 *M* sodium hydroxide solution. Analytical conditions as in Fig. 2.

Structure identification of isolated compounds

Takano and Tsuji[21] suggested structures of the reaction products by analysing the fragments of acid hydrolysis of the reaction products, *i.e.*, the fatty acids and the hydrophilic groups were determined by gas chromatography.

Here the active ingredients of the reaction products were isolated individually in acidic form by semi-preparative HPLC and by reversed-phase desalting. Compounds V and VIII were isolated together; III and VII were too unstable to be isolated, but the existence of III in Scheme 1 had already been verified by Tomidokoro *et al.*[20] and that of VII in Scheme 3 by Takano and Tsuji[21].

The structures of the isolated compounds were identified by FD-MS, IR spectra, peak shifting and fragment analysis after acid hydrolysis.

FD-MS. The FD mass spectra of the isolated compounds gave their quasi-molecular ions, $[M + H]^+$, and their fragments, *i.e.*, $[M + Na]^+$, $[M + H - CO_2]^+$, $[M + H - H_2O]^+$, $[M + H - CH_2CO_2]^+$, $[M + H - 2CO_2]^+$ and $[M + H - CO_2 - CH_2CO_2]^+$ (Fig. 10). The effects of inorganic salts on the spectra were studied by adding sodium perchlorate–methanol solution to isolated compounds such as IV and VI in their acidic forms. The intensities of the fragment ions varied with the amount of salt added (Fig. 11). From this, information on molecular weight, molecular formula determined by the so-called "nitrogen rule" and the number of carboxymethyl group substituents could be obtained. The FD mass spectra of IX and a mixture of V and VIII gave complicated fragments at higher m/z values, but the methyl esters obtained by treatment with diazomethane gave clear-cut spectra. All FD mass spectra of fragments obtained after hydrolysis of the isolated compounds with hydrochloric acid showed pure lauric acid, but a dibasic acid described previously[21] was absent.

IR spectra. The IR spectra of the isolated compounds as their acidic forms distinguished between the structures of imidazolines ($\nu_{C=N}$ 1600 cm^{-1}), carboxylic acids ($\nu_{C=O}$ for COOH at about 1710 cm^{-1}) and the type of amide, *i.e.*, primary ($\nu_{C=O}$ for CONH 1650–1620 cm^{-1}, δ_{NH} for CONH 1570–1520 cm^{-1}) or secondary ($\nu_{C=O}$ for CON = 1650–1620 cm^{-1}).

No ether bond was found in the spectra of isolated compounds:

Peak I: 1607 cm^{-1} (base form, chloroform solution of starting material)

Peak II: 1635, 1560 cm^{-1} (base form, chloroform solution)

Peak IV: 1720, 1650, 1540 cm^{-1} (acid form, chloroform solution)

Peak VI: 1710, 1620 cm^{-1} (acid form, chloroform solution)

Peak IX: 1720, 1630 cm^{-1} (acid form, chloroform solution)

Peak V and VIII: 1710 (weak), 1640 (acid form or inner salt, chloroform solution); 1740, 1640, 1080 cm^{-1} (methyl esters, chloroform solution)

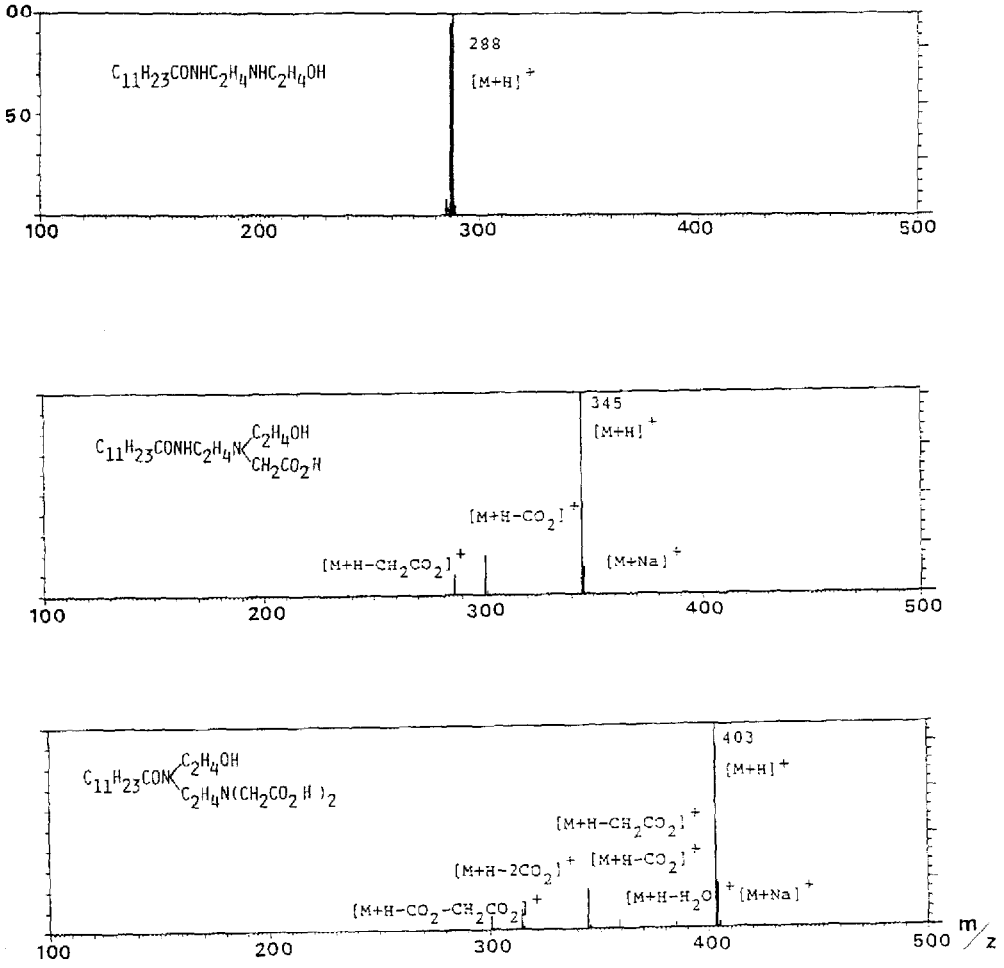


Fig. 10.

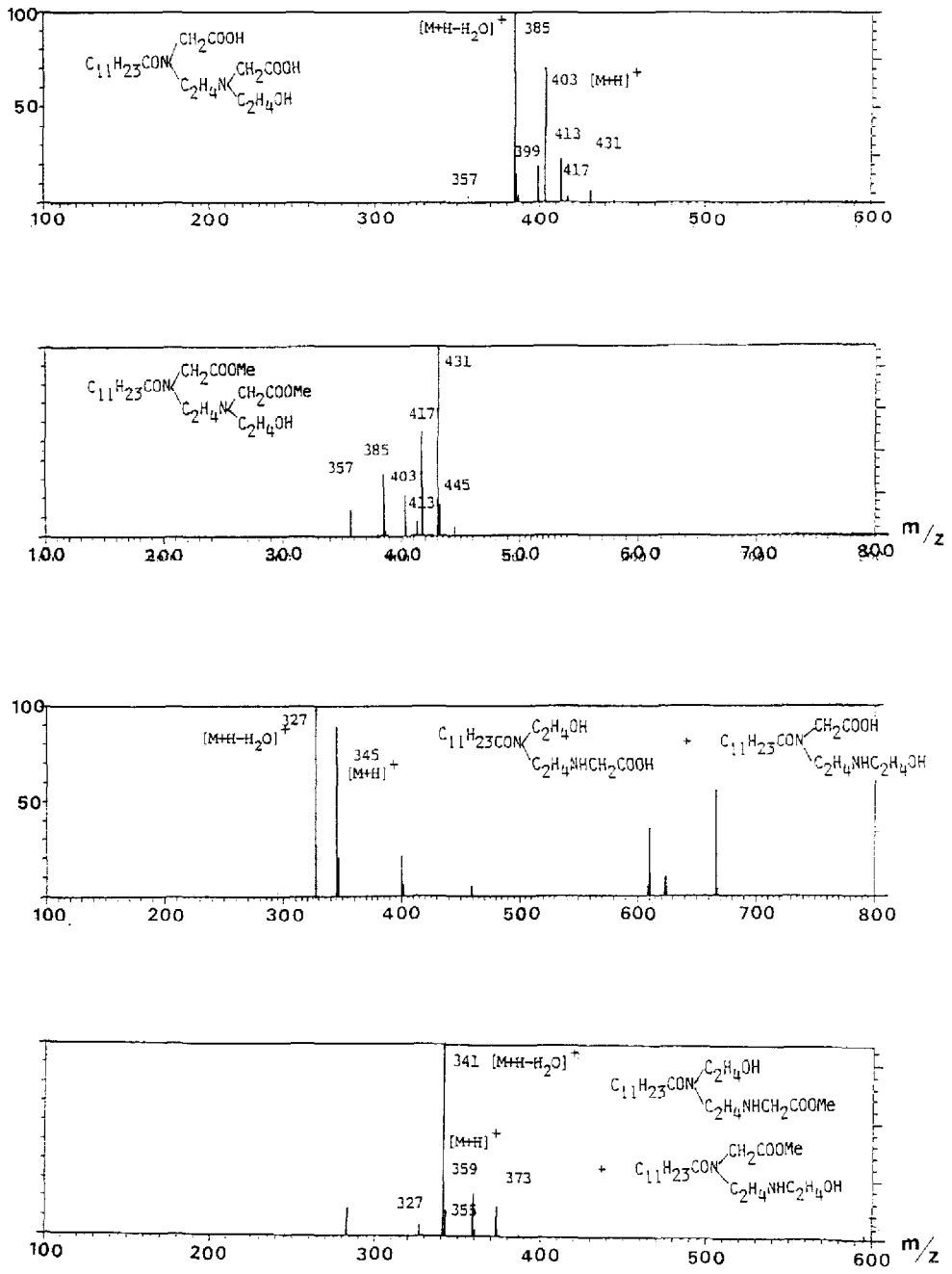


Fig. 10. FD mass spectra of isolated compounds.

Amine structure by peak shifting. In the peak shifting method mentioned previously, peaks II, III, V and VIII almost disappeared. The results suggested that the structures of the compounds were as follows:

Peaks II, III, V and VIII: primary or secondary amine
Peaks I, IV, VI and IX: tertiary amine

From the spectral data and the results of the chemical reactions, the structures of the isolated compounds were confirmed as those in Fig. 1, except that no unambiguous distinction could be made between V and VIII. The results support the structures and reaction pathways given by Takano and Tsuji[21], where the existence of VIII and IX was not confirmed.

Post-column detection of reaction products by HPLC

Each compound in Fig. 1 can be detected directly with the UV detector at 210 nm. However, the relative molar responses are quite different, *i.e.*, the responses of secondary amide compounds were more than ten times higher than that of primary amides. Therefore, in some cases, a small amount of active ingredient of lower response was liable to escape detection (Fig. 12).

On the other hand, the post-column detection system developed previously[22] can detect all sorts of amine structures, except for a quaternary one. In the previous section, the active ingredients of imidazoline amphoterics derived from sodium chloroacetate have been proved to be primary, secondary and/or tertiary amines, except for compound VII which has a betaine structure. The stable active ingredients in the commercially available surfactants were almost always the compounds II, IV, VI and IX, the amine structures of which are secondary or tertiary ones. In the proposed post-column detection, the relative responses of secondary and tertiary amine compounds could be regarded as identical[22], but a quaternary amine such as VII gives no response at all in the method. Fortunately, intermediate VII would be

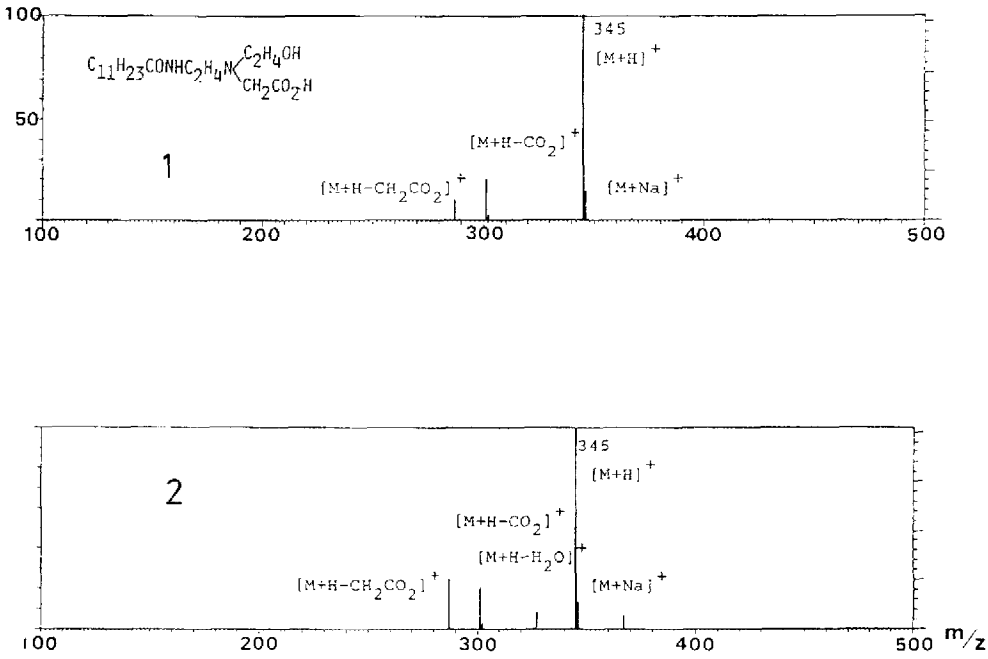


Fig. 11.

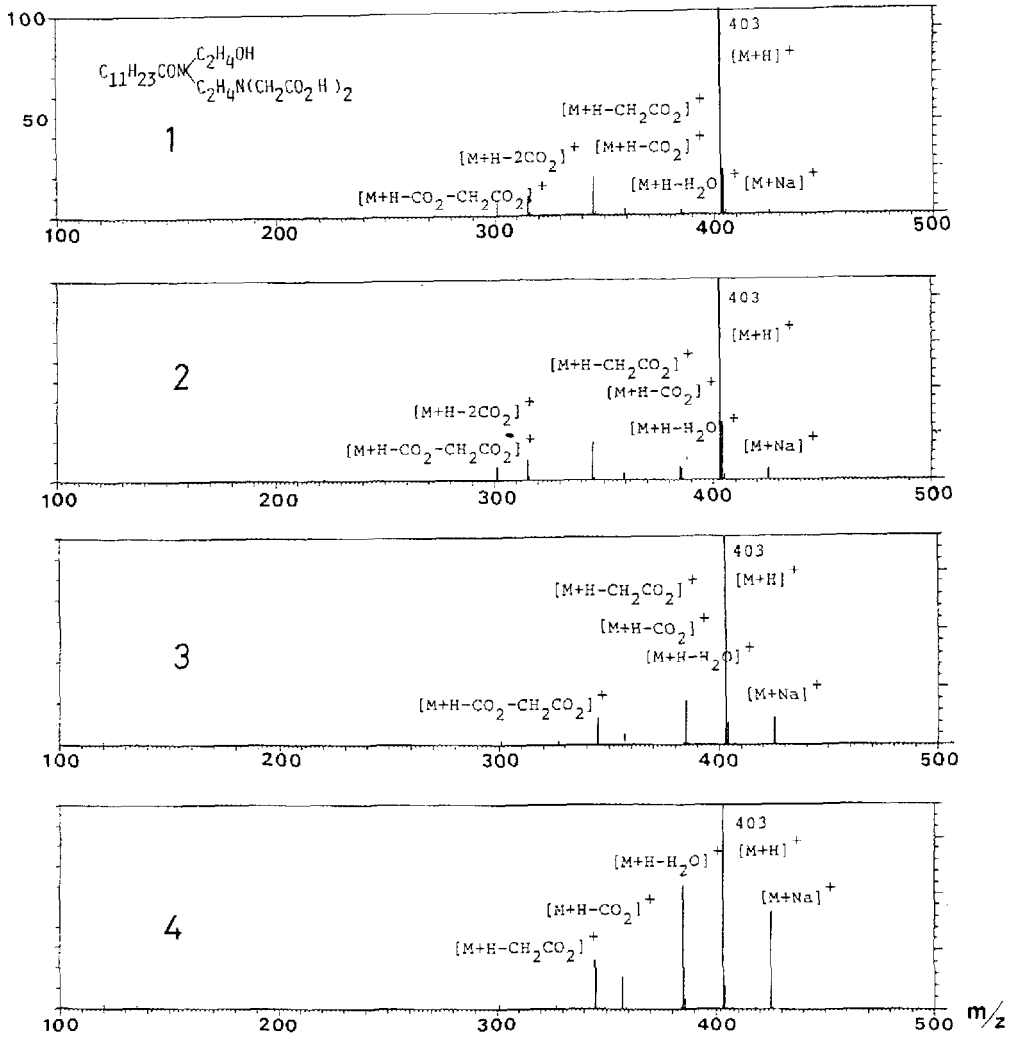


Fig. 11. Effects of inorganic salts on the FD spectra. Numbers 1–4 indicate an increase in the salt added.

too unstable to be present in the commercially available surfactants and has not yet been found by direct UV detection at 230 nm.

The mechanism of the post-column detection was the same as described previously[22]. Here the effects of both pH of the hypochlorite reagent and reaction temperature on the detection of compounds II, IV, VI and IX were examined. The eluent used was that recommended in the Experimental section.

Effects of pH of hypochlorite reagent. Fig. 13 shows that the sensitivity of secondary amine compound II was fairly constant over the range examined, whereas that of tertiary amine compounds IV and VI increased gradually with increasing pH of the hypochlorite reagent.

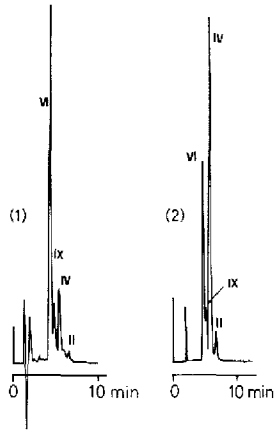


Fig. 12. Comparison of the relative responses of the reaction products: (1) detected directly at UV 210 nm; (2) post-column detection. Analytical conditions: eluent, 0.2 *M* $NaClO_4$ in 60% acetonitrile (pH 2.5). The relative molar ratio of VI/IV was determined as about 4/6 from the corresponding calibration curves of the isolated compounds.

Effects of reaction temperature. Fig. 14 shows the effects of reaction temperature on the sensitivities. The sensitivity of secondary amine compound II was fairly constant over the range examined, whereas that of tertiary amine compounds IV and VI increased with increasing reaction temperature.

With regard to the amine structure, the results obtained were similar to those for alanine type amphoteric surfactants[22]. Therefore the structure of unknown amines could be determined by observing both the pH and temperature profiles of the compounds in the post-column detection. The information obtained supports the structures of II, IV and VI as presented. The structure of the minor component IX could not be distinguished by the results.

From the results, the recommended post-column conditions are as follows: pH of hypochlorite reagent, 7.5; reaction temperature, 60°C.

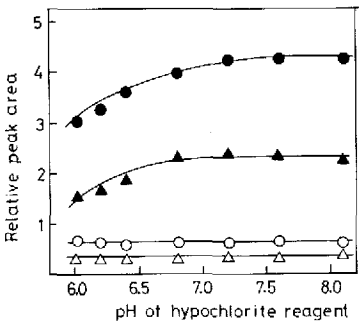


Fig. 13. Effects of pH of hypochlorite reagent on the sensitivity of II (○), IV (●), VI (▲) and IX (△).

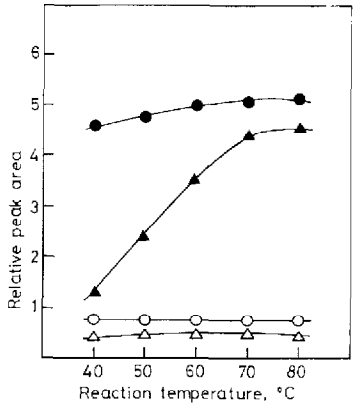


Fig. 14. Effects of reaction temperature on the sensitivity. Compounds as in Fig. 13.

Reversed-phase separation of reaction products

The separation of imidazoline type amphoterics derived from sodium chloroacetate was achieved with an acidic eluent containing inorganic salts and an organic modifier as mentioned previously. Fig. 15 shows the effects of eluent pH on the capacity factor, k'. The capacity factor of amidoamine II was fairly constant in the range pH 3–5.0 and below pH 3.0 the k' value decreased gradually as the result of neutralization in the eluent. The capacity factors of IV, VI and IX increased with increasing acidity of the eluent. These results can be explained in terms of the suppressing effects of H^+ on carboxylic acid dissociation. On the other hand, the peak shapes of the compounds worsened with increasing eluent pH. Thus, an eluent pH of 2.5 was adopted. The elution order was VI, IX, IV and II, independent of the eluent pH. The recommended eluent is 0.2 *M* sodium perchlorate in 45–60% acetonitrile (pH 2.5). The column temperature chosen was 40°C.

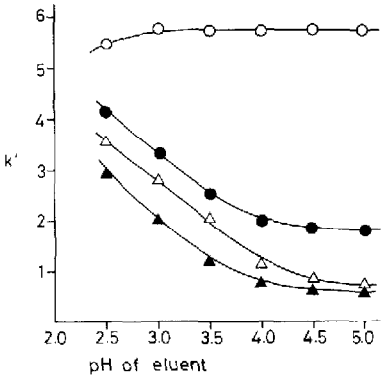


Fig. 15. Effects of eluent pH on the capacity factor. Compounds as in Fig. 13. Analytical conditions: eluent, 0.2 *M* $NaClO_4$ in acetonitrile–water (45:55) (pH 2.5–5.0).

Analysis of commercially available surfactants with post-column detection

Type analysis. The commercially available imidazoline amphoterics derived from sodium chloroacetate were classified into three types according to their methods of preparation:

Type 1	Scheme 1 → Scheme 2	Molar ratio $I/ClCH_2CO_2Na \approx 1/1$
Type 2	Scheme 1 → Scheme 2	$I/ClCH_2CO_2Na \approx 1/2$
Type 3	See Fig. 1	$I/ClCH_2CO_2Na \approx 1/2$

Representative chromatograms of these three types of compound are shown in Fig. 16. The low-molecular-weight diamine derivatives appeared at the void volume, indicating decomposition of amide structures in the course of reaction. So the high content of the diamine derivatives in Fig. 16D suggests that the surfactant D would be

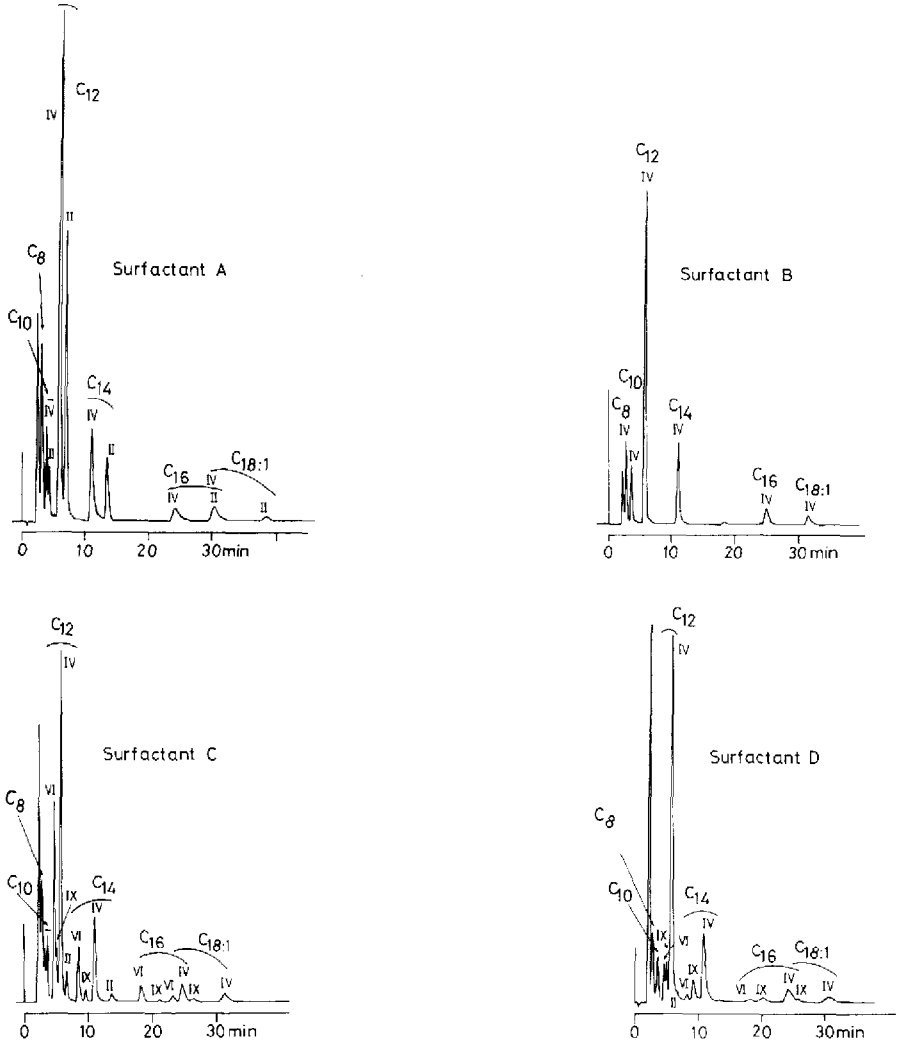


Fig. 16. Representative chromatograms of the commercially available surfactants A (Type 1), B (Type 2) and C and D (Type 3). Analytical conditions as in Fig. 12.

prepared under the conditions of Type 3, but the more unstable compound VI would be decomposed in the course of reaction to give the corresponding fatty acids and low-molecular-weight diamine derivatives. This suggestion is supported by determination of the residual fatty acids. Thus the reaction process and conditions under which the surfactants were prepared can be guessed from the chromatograms.

Determination of alkyl chain distribution. The chromatograms shown in Fig. 16 also gave information on both the alkyl chain distribution and degree of N-substitution of the surfactants, provided that almost identical molar responses were yielded regardless of the alkyl chain length.

With respect to the alkyl chain distribution analysis, the results of the proposed post-column detection are compared in Table I with those of conventional gas chro-

TABLE I

COMPARISON OF THE PROPOSED HPLC METHOD AND A CONVENTIONAL GC METHOD IN THE ALKYL CHAIN DISTRIBUTION ANALYSIS OF ORIGINAL FATTY ACIDS

Surfactants A and C belong to Types 1 and 3 respectively.

	*HPLC method** mol%		*GC method***			
			wt.%		*mol%*	
	A	*C*	*A*	*C*	*A*	*C*
C_8	9.55	9.22	5.79	6.34	8.25	8.98
C_{10}	9.34	9.92	7.06	7.29	8.41	8.65
C_{12}	50.28	51.19	53.08	53.05	54.39	54.09
C_{14}	18.41	17.25	20.58	20.34	18.49	18.20
C_{16}	7.67	8.20	8.99	9.44	7.20	7.52
$C_{18:1}$	4.74	4.20	4.50	3.54	3.27	2.56
Average molecular weight	205.7	205.3			205.3	204.3

* Sample solutions diluted in deionized water were injected. Mol % calculated by summing the peak area (%) of II, IX, XI and VI providing that identical molar responses were yielded regardless of the alkyl chain length.

** Described by Takano and Tsuji[21]. Sample preparation procedure: acid hydrolysis; extraction of the acids by diethyl ether; esterification with diazomethane; GC analysis. The wt. % was calculated from the FID response and hence the mol %.

matographic (GC) method described by Takano and Tsuji[21], which needed cumbersome sample preparation. The agreement between the methods is good and the distribution of the original fatty acids can be calculated directly by the proposed method.

Commercial products analysis

In the proposed post-column detection, the calibration curve gave a completely linear response for each alkyl chain of the compounds. For example, the calibration curves for both IV and VI of C_{12} alkyl chain were linear in the range of 0.5–18 μg. Thus the content of the surfactants in commercial products can be determined by summing the peak areas for each alkyl chain. The precision and accuracy of the method were tested by adding known amounts of three types of surfactants in a standard shampoo. Table II shows the results demonstrating that the method can be applied to commercial products analysis.

TABLE II

DETERMINATION OF IMIDAZOLINE AMPHOTERICS DERIVED FROM SODIUM CHLOROACETATE IN A STANDARD SHAMPOO

Surfactant	*Added (%)*	*Found (%)*	*n*	*Coefficient of variation*	*Recovery (%)*
A	5.00	5.02	4	2.1	100.4
B	5.00	4.93	4	2.5	98.6
C	5.00	4.97	4	2.7	99.4

* Calculated by summing the peak areas for C_8–C_{18} alkyl chains.

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