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

III. SALT-FREE-TYPE IMIDAZOLINE AMPHOTERIC SURFACTANTS

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SUMMARY

Salt-free-type imidazoline amphoteric surfactants were analysed by reversed-phase high-performance liquid chromatography with ultraviolet and/or post-column detection. The active ingredients of the surfactants were isolated and identified directly by field desorption mass spectrometry and some specific chemical reaction techniques. Use of the method has clarified the reaction pathways by which the compounds are transformed and demonstrated the specificity of the proposed post-column detection in commercial products analysis. By this method, information on the alkyl-chain distribution of the orginal fatty acids, the degree of substitution by electrophilic reactants and the reaction process and conditions under which the surfactants were prepared can be obtained.

INTRODUCTION

Imidazoline-type amphoteric surfactants are used widely in hair conditioning shampoos, bath oils, permanent waves and some other toiletry products. Some papers and patents[1–21] have been published on their analysis. On the basis of these studies it is recognized that the main products of imidazoline amphoterics have structures containing amidoamine and carboxylate groups. However, incorrect structures (shown in Fig. 1) are to be found in many catalogues and in official reports.

Fig. 1. Conventional structures of imidazoline amphoteric surfactants. Left: derived from sodium chloroacetate; right: derived from ethyl acrylate and/or acrylic acid (salt-free type).

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In previous studies of amphoteric surfactants, we have developed a convenient and direct high-performance liquid chromatographic (HPLC) determination of alanine type amphoteric surfactants[22] and, as a first step towards HPLC analysis of imidazoline derivatives, imidazoline type amphoterics derived from sodium chloroacetate[23], using post-column detection.

In addition to those types of amphoterics, there are also the salt-free amphoteric imidazolines, derived from acrylic acid (AA) and/or ethyl acrylate (EA). They are required for all applications where sodium chloride is inconvenient.

In this report, salt-free type imidazoline amphoterics derived from AA and/or EA were analysed by HPLC.

EXPERIMENTAL

Materials

Salt-free type imidazoline amphoteric surfactants derived from AA and/or EA were synthesized according to the literature[1–10,20,21] and/or minor modifications thereof. Unless indicated otherwise, lauric acid derivatives were used for the structure identification and for the study of the reaction pathways by which the compounds were transformed.

Apparatus and procedures

Apparatus and procedures used were as described in the preceding paper[23] except as follows.

The packing materials tested were LiChrosorb RP-18 (5 μm, Merck,), Cosmosil C_{18} (5 μm; Nakarai Chemical Co., Japan), LS-410 (5 μm; Toyo Soda, Japan), Hitachigel 3057 (3 μm), Hypersil ODS (3 μm, Shandon) and Develosil ODS-3 (3 μm, Nomura Chemical Co., Japan).

As a recommended packing material, Develosil ODS-3 was slurry packed both in 150 × 4.6 mm I.D. columns and in 100 × 8 mm I.D. columns for analytical separations.

Ether bond determination by acid fusion of HBr–acetic acid. The isolated compounds were reacted in a screw-capped test-tube with HBr–acetic acid (1:1) according to the literature method[24]. A β-bromopropionic acid derived from the ether bond was identified by gas chromatography–mass spectrometry (GC–MS). GC–MS equipment for determination of the fragments of β-bromopropionic acid consisted of a JEOL JMS-D300 operated in electron ionization (EI) mode. The glass column (2 m × 2 mm I.D.) was packed with 25% FAL-M on Chromosorb W AW DMCS (80–100 mesh). The column temperature was maintained at 180°C. The carrier gas (helium) flow-rate was 40 ml min^{-1}.

RESULTS AND DISCUSSION

Reaction pathways and tentative identification

Here we describe the reaction pathways shown in Fig. 2, information on the reaction products being obtained by HPLC, IR spectra, etc. Paths A, C, D and E were suggested and/or confirmed previously[5,6,19–21].

Tentatively to identify the compounds in the liquid chromatogram, we re-

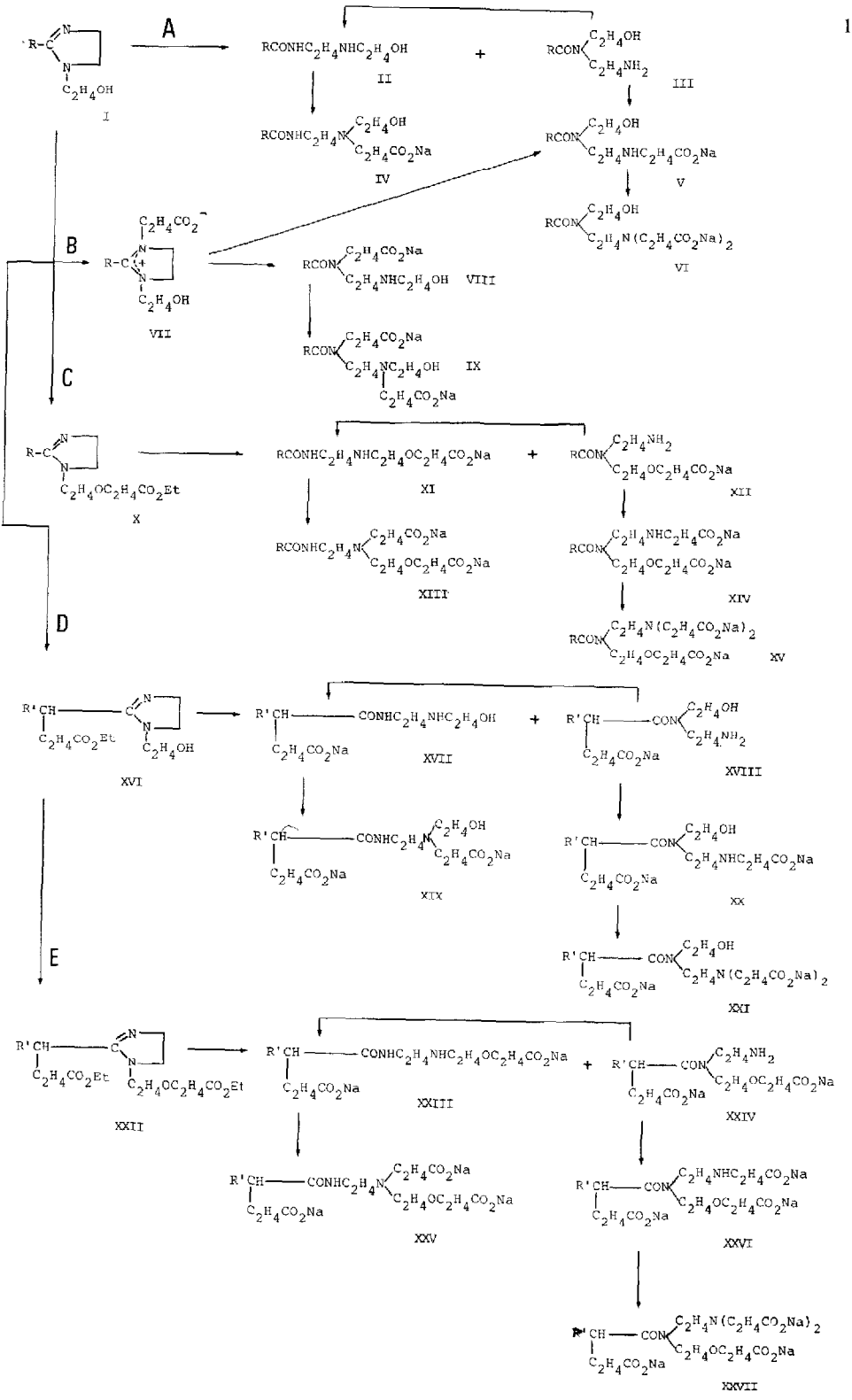
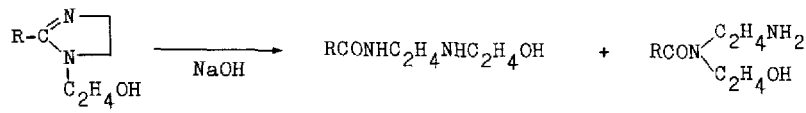


Fig. 2. Overall reaction pathways of salt-free type imidazoline amphoteric surfactants.

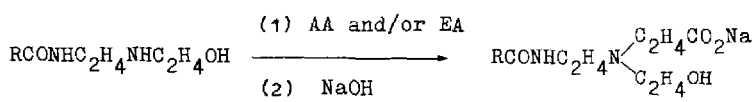
investigated the individual reaction pathways by use of HPLC in the manner described previously[23].

Path A. The reactions of path A proceeded with both the electrophilic reactants AA and EA, and were observed by HPLC with an eluent of 0.5 *M* sodium perchlorate in methanol–acetonitrile–deionized water (60:10:30):

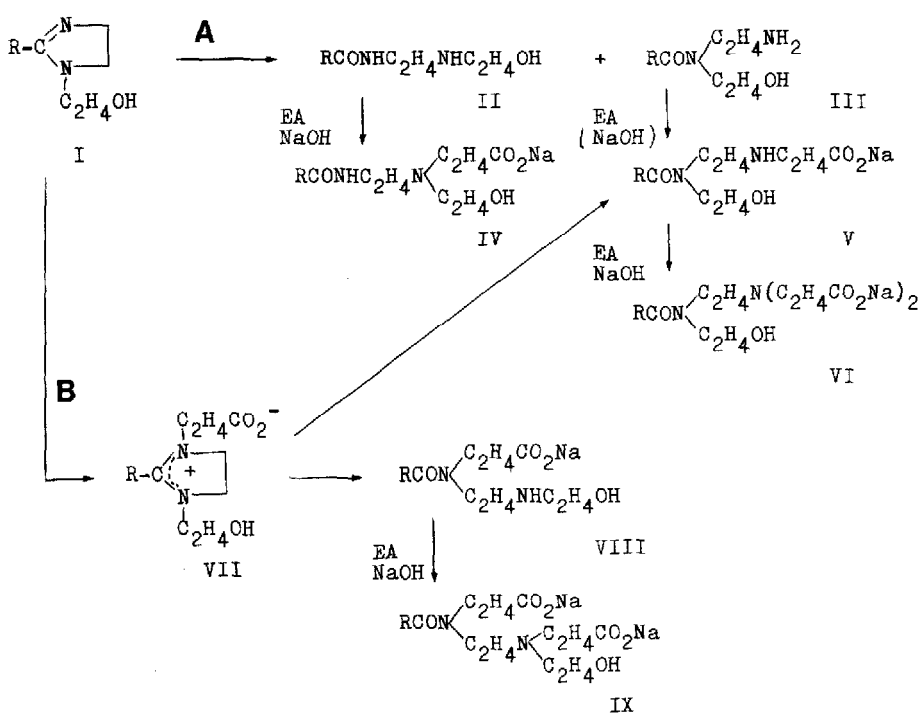


Scheme 1.

The imidazoline ring of I was opened in an alkaline medium (molar ratio $I/H_2O/NaOH = 1/3/0.03$) at 80–85°C for 2 h (Scheme 1) resulting in compound II as described previously[23]. Then compound II reacted with AA and/or EA at 65–85°C for about 4 h (molar ratio I/EA or I/AA = 1/1.1) and the resultant was saponified by sodium hydroxide to give compound IV (Scheme 2, Fig. 3).



Scheme 2.



Scheme 3.

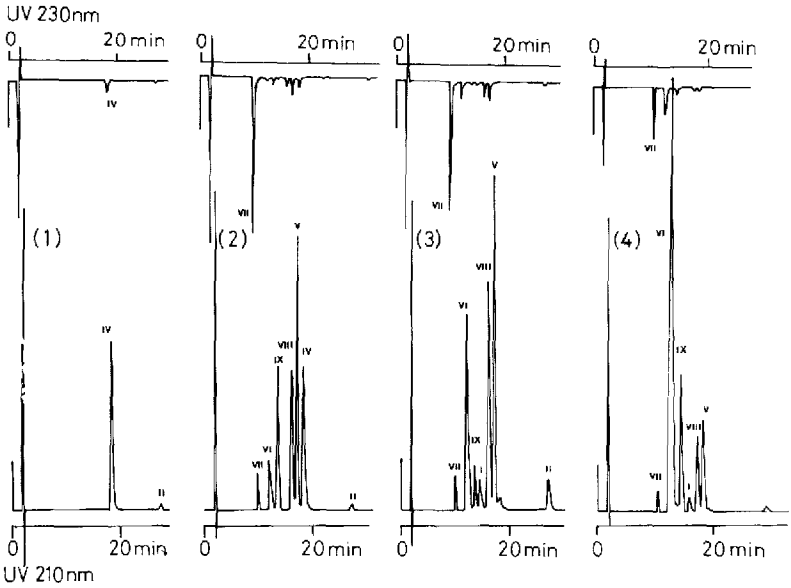


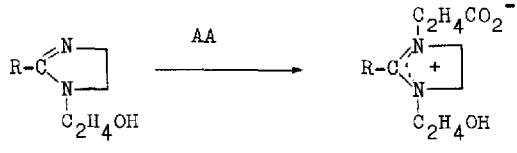
Fig. 3. Liquid chromatograms of reaction products in path A: (1) Scheme 2; (2) Scheme 3, (3) I/EA/H_2O/NaOH = 1/1.1/2/0.65; (4) I/EA/H_2O/NaOH = 1/2/2/0.65. Analytical conditions: column, Develosil ODS-3 (100 × 8 mm I.D.); eluent, 0.5 *M* $NaClO_4$ in methanol–acetonitrile–deionized water (60:10:30); flow-rate, 1.5 ml min^{-1}; UV detection.

In another reaction, the imidazoline ring was opened partially without a catalyst in a first step at 80–85°C for 2 h (molar ratio I/H_2O = 1/3) and the resultant was treated with EA and/or AA at 65–85°C for about 4 h (molar ratio I/EA = 1/1.1) then saponified by sodium hydroxide to give compounds II, IV–IX (Scheme 3, Fig. 3): Compound I was also treated with EA in an aqueous medium at 70°C for 2 h (I/EA/H_2O/NaOH = 1/1.1/2/0.65 and 1/2.0/2/0.65) and the resultant saponified by sodium hydroxide (Scheme 3, Fig. 3).

From the results of path A, the compounds I–VI were assigned tentatively on the basis of the literature[20,21]; trace levels of VII–IX were also detected. The UV absorbance at 210 nm of the latter compounds is probably quite high because the semi-preparative quantity of the compounds did not agree with the results of UV detection. The presence of VII–IX was later confirmed in path B, a reaction reported for the first time.

Under suitable conditions, it is thus possible to control the imidazoline ring opening.

Path B. The reaction of path B proceeded with AA mainly at temperatures higher than 100°C without solvent, resulting in a mixture of VII (λ_{max} at 240 nm) and I (Scheme 4, Fig. 4):



I VII

Scheme 4.

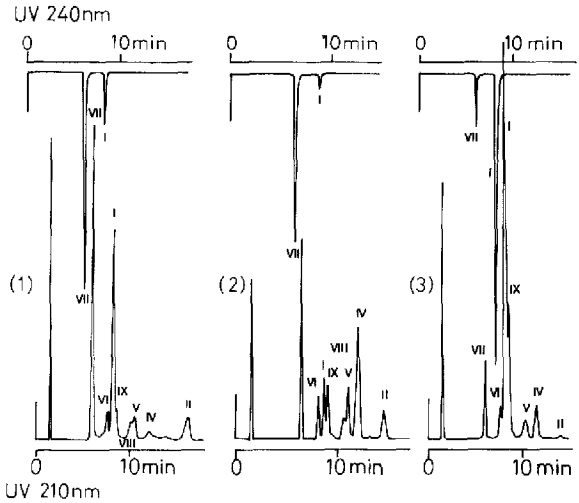
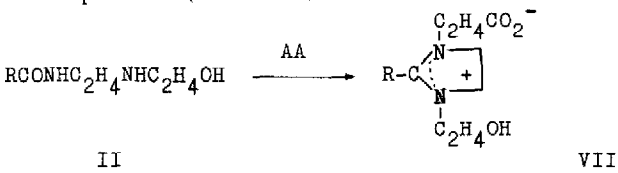


Fig. 4. Liquid chromatograms of path B: (1) Scheme 4 (I/AA = 1/1.1, 130–140°C for 2 h without solvent); (2) scheme 5 (II/AA = 1/1.5, 140 ± 5°C for 1 h without solvent); (3) I/AA = 1/1.1, 85–90°C for 6 h with deionized water as solvent. Analytical conditions: column, Develosil ODS-3 (150 × 4.6 mm I.D.); eluent, 0.5 *M* $NaClO_4$ in methanol–water (70:30); flow-rate, 1.0 ml min^{-1}.

In case of AA as an electrophilic reactant, the compounds X, XVI and XXI were not formed. Compound VII was also produced in the reaction of II and AA at higher reaction temperature (Scheme 5):

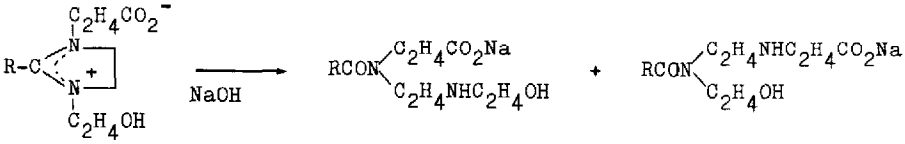


II VII

Scheme 5.

This reaction proceeded even in an aqueous medium but with lower yield.

Compound VII (very stable) was hydrolysed in an alkaline aqueous medium (molar ratio VII/NaOH = 1/0.7) to give compounds V and VIII (Scheme 6, Fig. 5):



VII VIII V

Scheme 6.

The reason why compounds VII–IX appeared in Scheme 3 is probably that the imidazoline ring of I did not open completely and that the minor reaction of Scheme 4 proceeded at the same time due to AA derived from the hydrolysis of EA in water without catalyst in the first step of the reaction.

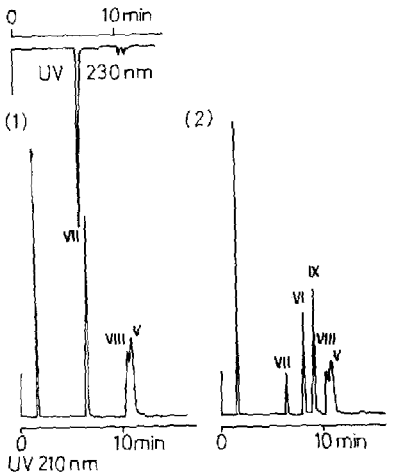
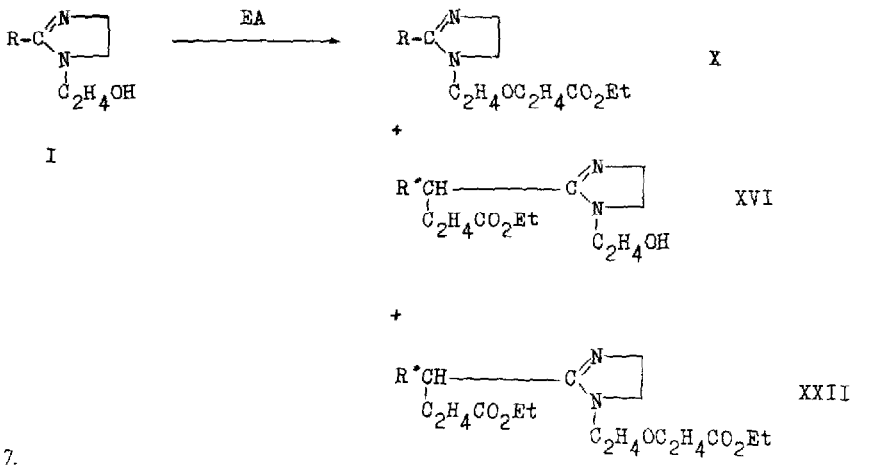


Fig. 5. Hydrolysis of VII and further reaction with EA: (1) Scheme 6; (2) tentative identification of IX (the reaction products in Scheme 6 were reacted further with EA and then saponified by NaOH). Analytical conditions as in Fig. 3.

Paths C–E. The reactions of paths C–E proceeded together in a non-aqueous medium in the first reaction step with the electrophilic reactant EA. Compound I reacted with EA at 60–65°C for 2 h without solvent (Scheme 7, molar ratio I/EA = 1/1, 1/2, 1/3):



Scheme 7.

The compounds I, XVI and XXII were observed by HPLC (Fig. 6), the analytical conditions being as indicated. Of these, X was a minor component in the reaction assuming that the UV (at 230 nm) responses of the compounds were identical. The results were supported by the literature[21].

In the second reaction step, the residual EA was removed by distillation and the resultant was saponified by sodium hydroxide [Fig. 7 (1,3)]. Alternatively, deionized water was added (molar ratio I/H_2O = 1/2), and the mixture was aged at 65–70°C for 2 h to open the imidazoline ring and the resultant was saponified [Fig. 7 (2, 4)].

The compounds in the chromatogram (Fig. 7) were tentatively assigned on the

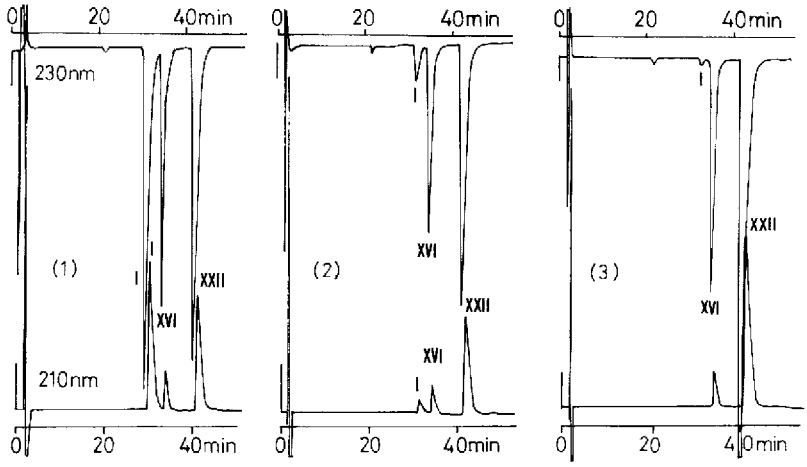


Fig. 6. Reaction of I and EA without solvent. Molar ratio I/EA = 1/1 (1), 1/2 (2) and 1/3 (3). Analytical conditions: column, Develosil ODS-3 (100 × 4.6 mm I.D.; eluent, 0.2 *M* $NaClO_4$ in acetonitrile–water (45:55) (pH 2.5); flow-rate, 1.0 ml min^{-1}; UV detection.

basis of the literature[21]. Only in the alternative step above, compound VII was observed by UV detection (210, 230 nm) as a minor component.

To identify compound XI, compound II (isolated and purified) was treated with EA with a sodium methoxide catalyst to give a mixture of II and XI.

From the chromatographic results the question arose as to why the relative ratio of primary amide/secondary amide compounds differs between the compounds derived from the α-substituted imidazolines (XVI and XXII) and those derived from unsubstituted imidazoline I, *i.e.*, ratios V + VI/II + IV and V + VI/II + IV + XVII + XIX + XXIII. There are three possibilities:

(1) The 1–2 position of the C–N bonds opens faster than the 2–3 position in the case of the α-substituted imidazolines (XVI and XXII) compared to the situation in compound I, when the imidazoline ring is opened in an aqueous medium without a catalyst (NaOH).

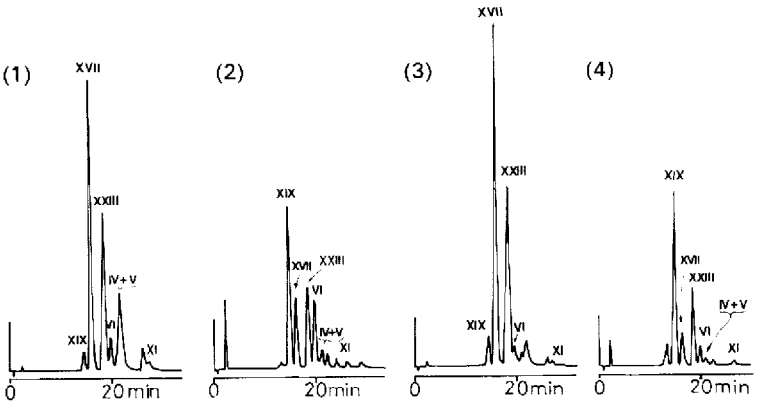


Fig. 7. Liquid chromatograms of paths C–E. Molar ratio I/EA = 1/2 (1, 2) and 1/4 (3, 4) (see text). Analytical conditions as in Fig. 5 except for the post-column detection.

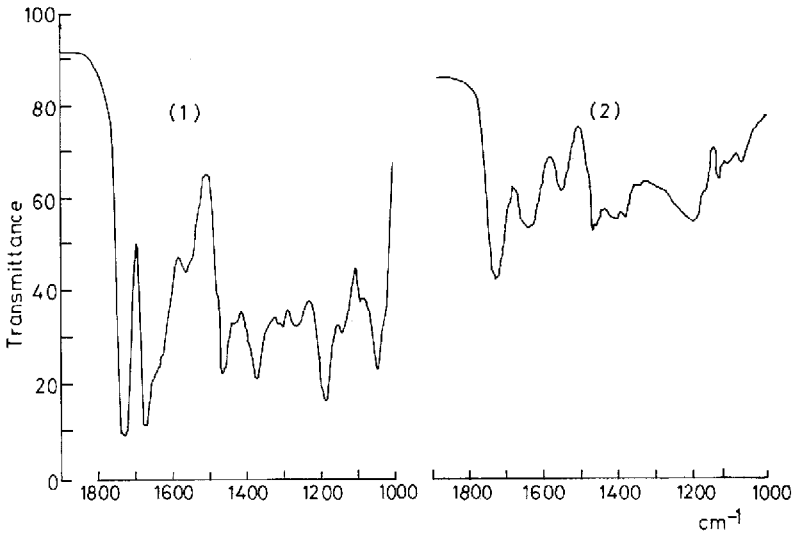


Fig. 8. IR spectra before (1) and after (2) saponification. IR spectra of sample 1 were recorded without any pre-treatment. Sample 2 was treated by HCl–2-propanol topping to obtain the spectra of the acidic forms.

(2) The rates of ring opening are equal, but the secondary amide compounds XII, XVIII, XX and XXIV decompose faster than the corresponding primary amide ones (XVII, XIX and XXIII) in the course of the reaction, due to the steric hindrance between the carboxyethyl group at the α-position and the secondary amide group.

(3) The secondary amide compounds XII, XVIII, XX and XXIV are transformed into the corresponding primary amide compounds XVII, XIX and XXIII in the course of saponification.

To resolve the problem, we made observations on the reaction products by IR spectroscopy of each individual process (Fig. 8), and the relative ratio of monobasic/dibasic fatty acid was compared for the native fatty acids derived from the amide decomposition in the course of reaction and those obtained after acid hydrolysis. The native acids in the reaction products were isolated by acid extraction and those present after hydrolysis were isolated according to the literature[21]; the relative ratio was determined by GC.

From the IR spectra of (1) and (2) in Fig. 8, the possibility 1 could be ruled out because secondary amide compounds in (b) disappeared after saponification (2). Therefore, possibilities 2 and 3 remain; the results of fatty acid analysis favoured 3.

Structure identification of isolated compounds

The active ingredients of the reaction products were isolated individually in their acidic forms by semi-preparative HPLC and by reversed-phase desalting.

The structures were identified by field desorption (FD) mass spectrometry, IR spectra, peak shifting[23] and fragment analysis.

FD mass spectra. The FD mass spectra of the isolated compounds are shown in Fig. 9. These spectra gave information on molecular weight, the molecular formula as determined by the nitrogen rule and the number of substituted carboxyethyl groups. Compound XXIII did not give quasi-molecular ions $[M + H]^+$, but the correspond-

ing methyl ester obtained by treatment with diazomethane gave $[M' + H]^+$. The FD spectra of acid fragments after hydrolysis of the isolated compounds with hydrochloric acid showed pure lauric acid for II, IV–IX, XI and dibasic acid (α-carboxyethyllauric acid) for XVII, XIX and XXIII, in agreement with the results given by Takano and Tsuji[21].

IR spectra. The IR spectra of the isolated compounds in their acidic forms distinguished between the structure of imidazolines ($\nu_{C=N}$ 1600 cm^{-1}), the carboxylic acid ($\nu_{C=O}$ of COOH at about 1710 cm^{-1}), the type of amide, *i.e.*, a primary amide ($\nu_{C=O}$ of CONH 1650–1620 cm^{-1}, δ_{NH} of CONH 1570–1520 cm^{-1}) or a secondary amide ($\nu_{C=O}$ of CON = 1650–1620 cm^{-1}), and the ether bond (ν_{C-O-C} 1100 cm^{-1}): Fig. 9.

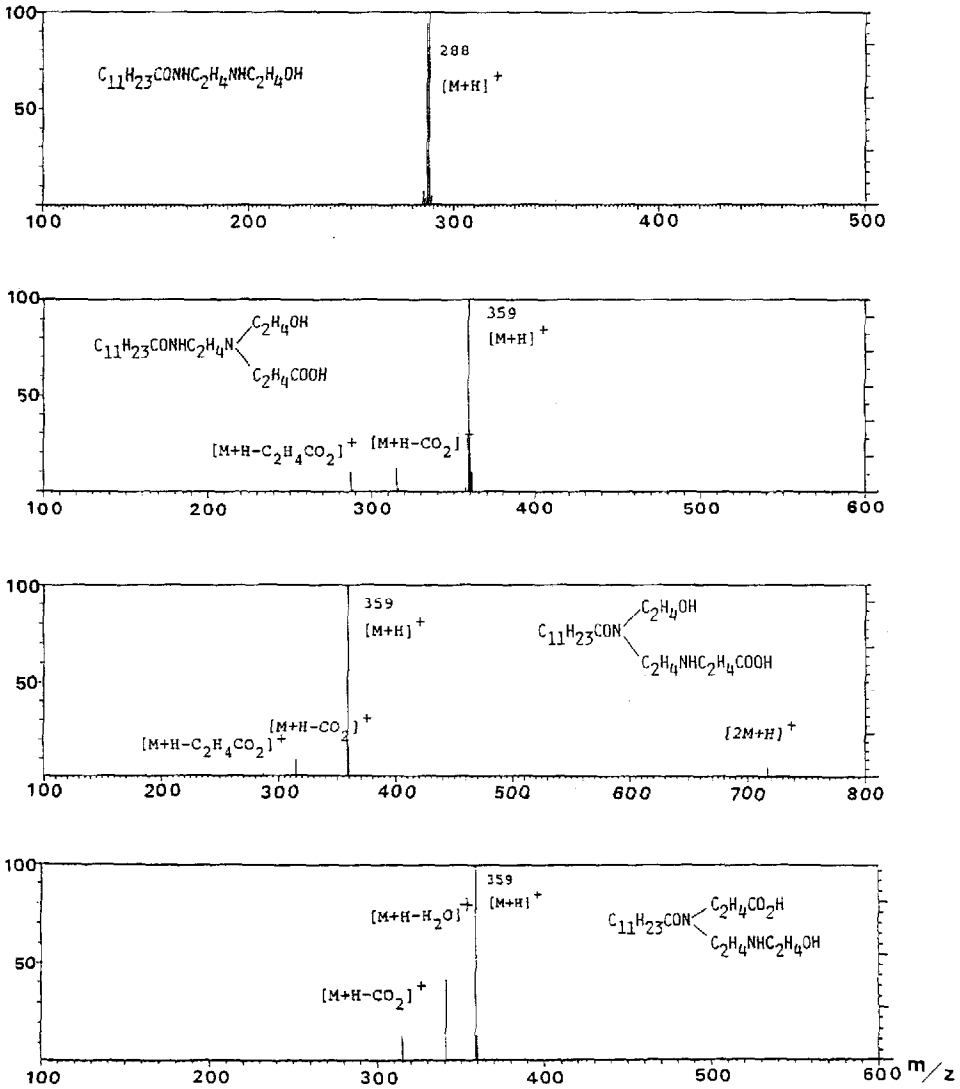


Fig. 9.

Peaks I and II: as described previously[23]

Peak IV: 1720 (weak), 1660, 1540 cm^{-1} (inner salt, chloroform solution); 1720, 1650, 1540 cm^{-1} (acid form after HCl–2-propanol topping, chloroform solution)

Peak V: 1710 (weak), 1650 cm^{-1} (inner salt, chloroform solution); 1720, 1650 cm^{-1} (acid form after HCl–2-propanol topping, chloroform solution)

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

Peak XI: 1660, 1560, 1140 cm^{-1} (inner salt, chloroform solution); 1710, 1660, 1560 cm^{-1} (acid form after HCl–2-propanol topping, chloroform solution)

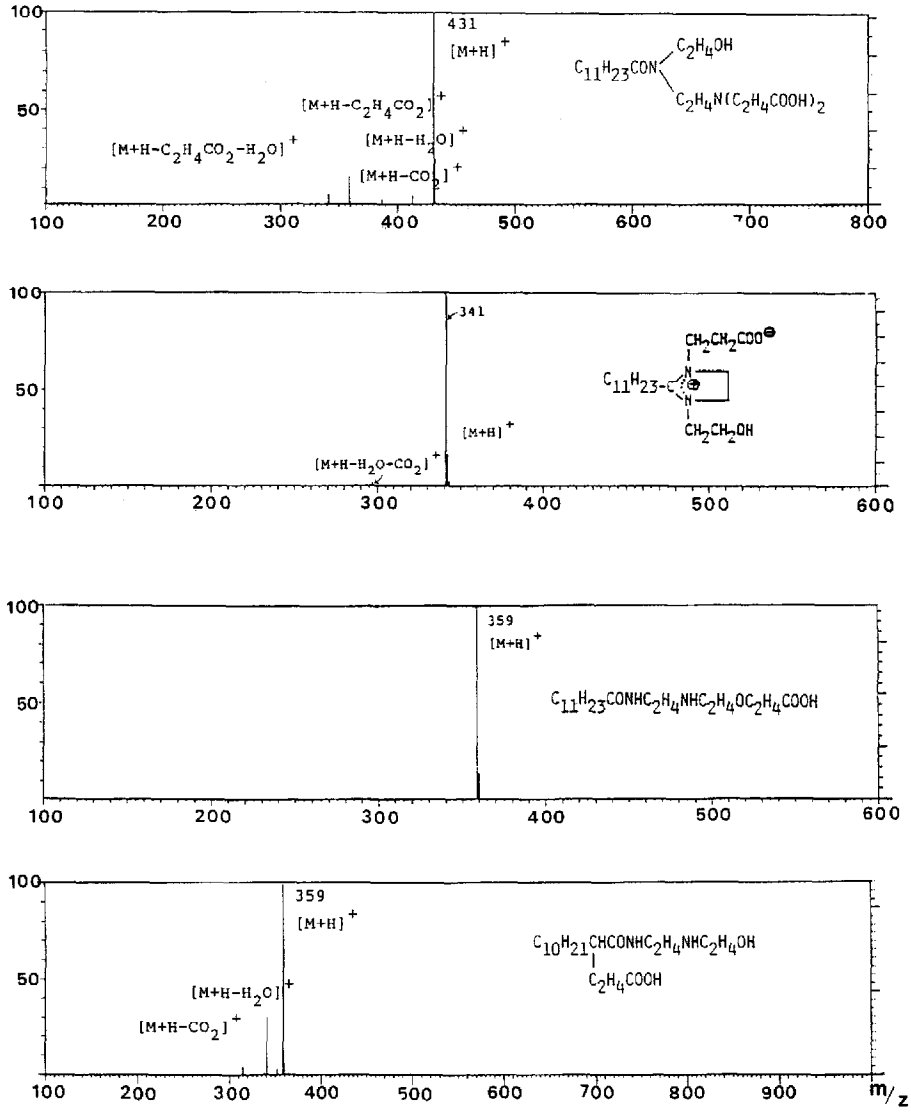


Fig. 9.

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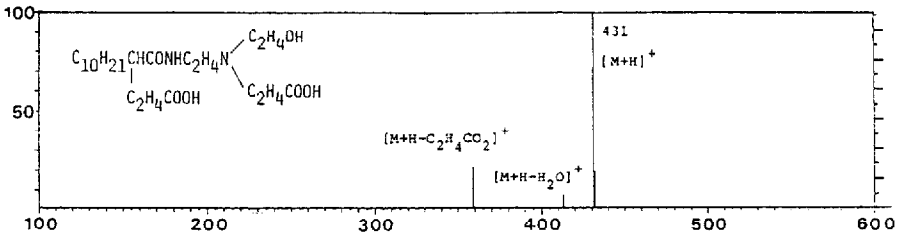
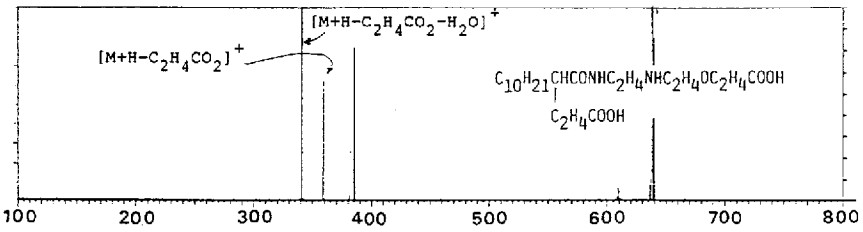
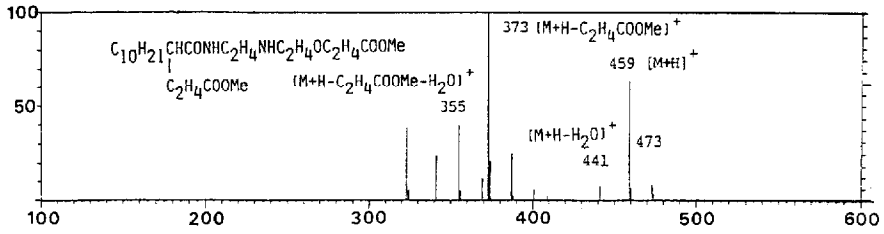
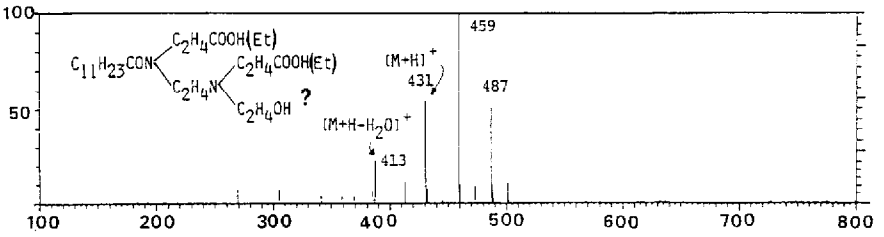
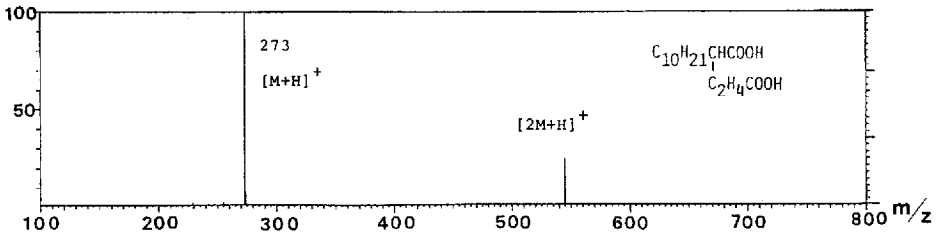

100
50
$C_{10}H_{21}CHCONHC_2H_4N$
C_2H_4OH
C_2H_4COOH
C_2H_4COOH
C_2H_4COOH
431
$[M+H]^+$
$[M+H-C_2H_4CO_2]^+$
$[M+H-H_2O]^+$
100 200 300 400 500 600


$[M+H-C_2H_4CO_2-H_2O]^+$
$[M+H-C_2H_4CO_2]^+$
$C_{10}H_{21}CHCONHC_2H_4NHC_2H_4OC_2H_4COOH$
C_2H_4COOH
100 200 300 400 500 600 700 800


100
50
$C_{10}H_{21}CHCONHC_2H_4NHC_2H_4OC_2H_4COOMe$
C_2H_4COOMe
$[M+H-C_2H_4COOMe-H_2O]^+$
355
373 $[M+H-C_2H_4COOMe]^+$
459 $[M+H]^+$
$[M+H-H_2O]^+$
441
473
100 200 300 400 500 600


100
50
$C_{11}H_{23}CON$
$C_2H_4COOH(Et)$
$C_2H_4COOH(Et)$
C_2H_4N
C_2H_4OH
?
$[M+H]^+$
431
459
487
$[M+H-H_2O]^+$
413
100 200 300 400 500 600 700 800


100
50
273
$[M+H]^+$
$C_{10}H_{21}CHCOOH$
C_2H_4COOH
$[2M+H]^+$
100 200 300 400 500 600 700 800
m/z

Peak XVII: 1640, 1550 cm^{-1} (inner salt, chloroform solution); 1720, 1650, 1550 cm^{-1} (acid form after HCl–2-propanol topping, chloroform solution)

Peak XIX: 1730, 1650 cm^{-1} (acid form, chloroform solution)

Peak XXIII: 1710, 1670, 1560, 1060 cm^{-1} (acid form, chloroform solution)

Peak VII: 1600 cm^{-1} (inner salt, chloroform solution); 1720, 1680, 1600, 1550 cm^{-1} (acid form after trifluoroacetic acid–2-propanol topping, chloroform solution)

Peak VIII: 1720, 1640 cm^{-1} (acid form after HCl–2-propanol topping, chloroform solution)

Peak IX: 1720, 1650 cm^{-1} (acid form after HCl–2-propanol topping, chloroform solution)

Ether bond identification by acid fusion of HBr–acetic acid. The ether bonds were determined by acid fusion of HBr–acetic acid as described in the Experimental. A β-bromopropionic acid was found in the reaction products of both XI and XXIII, and not in those of any other compounds. The results support the structure presented.

Amine structure identification by peak shifting. In the peak shifting method mentioned previously[23], peaks II, V, VIII, XVII and XXIII almost disappeared. The results are in accord with the amine structures presented.

From the spectral data and the results of the chemical reactions, the structures of the isolated compounds were confirmed as those presented in Fig. 2.

Post-column detection of reaction products by HPLC

Each compound in Fig. 2 except for VII can be detected by the post-column detection system developed previously[22]. In this method, the relative molar responses of secondary amide compounds and primary amide compounds can be regarded as identical. Further, the amine structure of unknown compounds can be determined by observing the pH and temperature profiles of the compounds in the post-column reaction. The only disadvantage of the detection system is the influence of the eluent used, *i.e.*, type of organic modifiers, water content and pH. The detection system could be employed with the limited eluent described previously[22], but in some cases this eluent probably would not give satisfactory chromatographic separations.

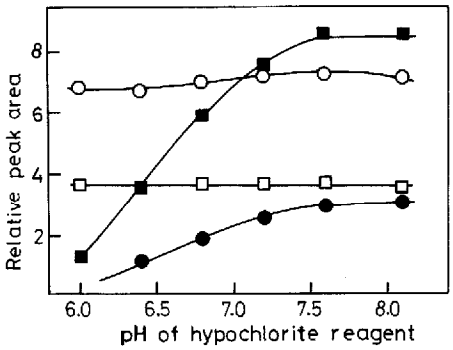


Fig. 10. Effects of pH of hypochlorite reagent on the sensitivities of II (□), IV (■), V (○) and VI (●).

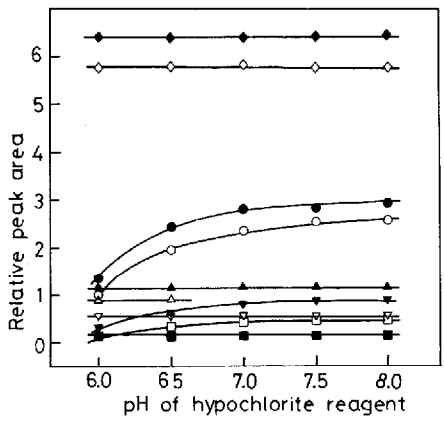
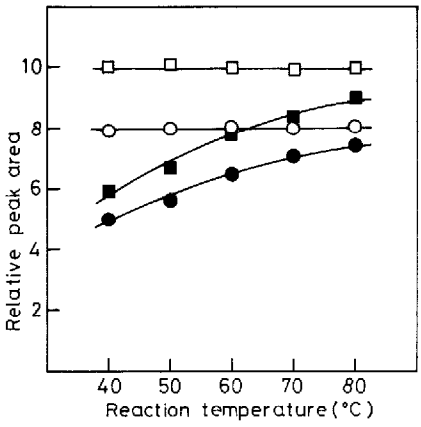


Fig. 11. Effects of pH of hypochlorite reagent on the sensitivities of XVII (◆), XIX (○), XXIII (◇), VI (▼), IV + V (●), II (△) and XI (▽). □, ■ and ▲ are unidentified compounds corresponding to peaks e, f and g, respectively, in Fig. 14.



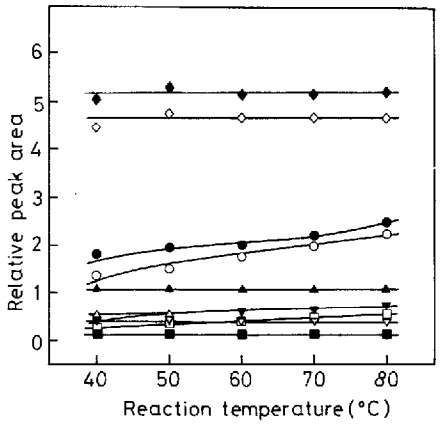


Fig. 12. Effects of reaction temperature on the sensitivities. Compounds as in Fig. 10.

Fig. 13. Effects of reaction temperature on the sensitivities. Compounds as in Fig. 11.

In the analysis of the compounds listed in Fig. 2, the separation of IV, V and VIII could not be achieved with the eluent employed for the post-column detection. However, this separation was not very important in the analysis of commercially available surfactants.

The pH and temperature profiles of the compounds in the post-column reaction (Figs. 10–13) supported the amine structures presented. The recommended post-column conditions were as described previously[23]: pH of hypochlorite reagent, 7.5; reaction temperature, 60°C.

Under the optimum conditions, the calibration curve was completely linear for each compound. Thus the content of each compound can be determined by summing the corresponding peak areas.

Chromatographic separation of reaction products

The reversed-phase separation of the reaction products in Fig. 1 was achieved with two eluents. Among the packing materials tested, Develosil ODS-3 gave excellent separations in both cases.

Products derived from paths A and B. The reaction products were completely separated as indicated in Figs. 2–4, under the following optimum conditions: analytical column, Develosil ODS-3 (100 × 8 mm I.D.); column temperature, 40°C; eluent 0.5 *M* sodium perchlorate in methanol–acetonitrile–deionized water (60:10:30); flow-rate, 1.5 ml min^{-1}; UV detection. The elution order was VII, VI, IX, I, VIII, V, IV and II. A minor variation of the eluent, such as 0.5 *M* sodium perchlorate in methanol–water (70:30), altered the order of I and IX (Fig. 4). The above eluent was not suitable for the post-column detection; instead, 0.2 *M* sodium perchlorate in 45–60% aqueous acetonitrile (pH 2.5) is recommended. However, with this eluent, the separations of IV, V and VIII and of V and IX could not be achieved.

Products derived from paths C–E. The reaction products from paths C–E were separated as indicated in Figs. 6 and 7, under the following optimum conditions: analytical column, Develosil ODS-3 (150 × 4.6 mm I.D.); column temperature, 40°C; eluent, 0.2 *M* $NaClO_4$ in acetonitrile–deionized water (45:55) buffered at pH

2.5 by phosphoric acid; flow-rate, 1.0 ml min^{-1}; post-column detection and/or UV detection. The elution order was XIX, XVII, XXIII, VI, IV + V, II, VII (UV detection), XI, I, XVI and XXII.

Analysis of commercially available surfactants with post-column detection

The commercially available imidazoline amphoterics derived from AA and/or EA could be classified approximately into three types according to their methods of preparation:

Type 1 Scheme 1 → Scheme 2
Type 2 Scheme 3
Type 3 Scheme 7 → ring opening, saponification, etc.

Representative chromatograms of these three types of compound are shown in Fig. 14. At the same time, UV detection was also performed (Fig. 15, Types 1 and 2). From the results, the reaction process and the conditions under which the surfactants were prepared can be guessed. For example, the surfactants C and D belong to Type 3, and D would be prepared at a higher molar ratio of EA to I and the content of

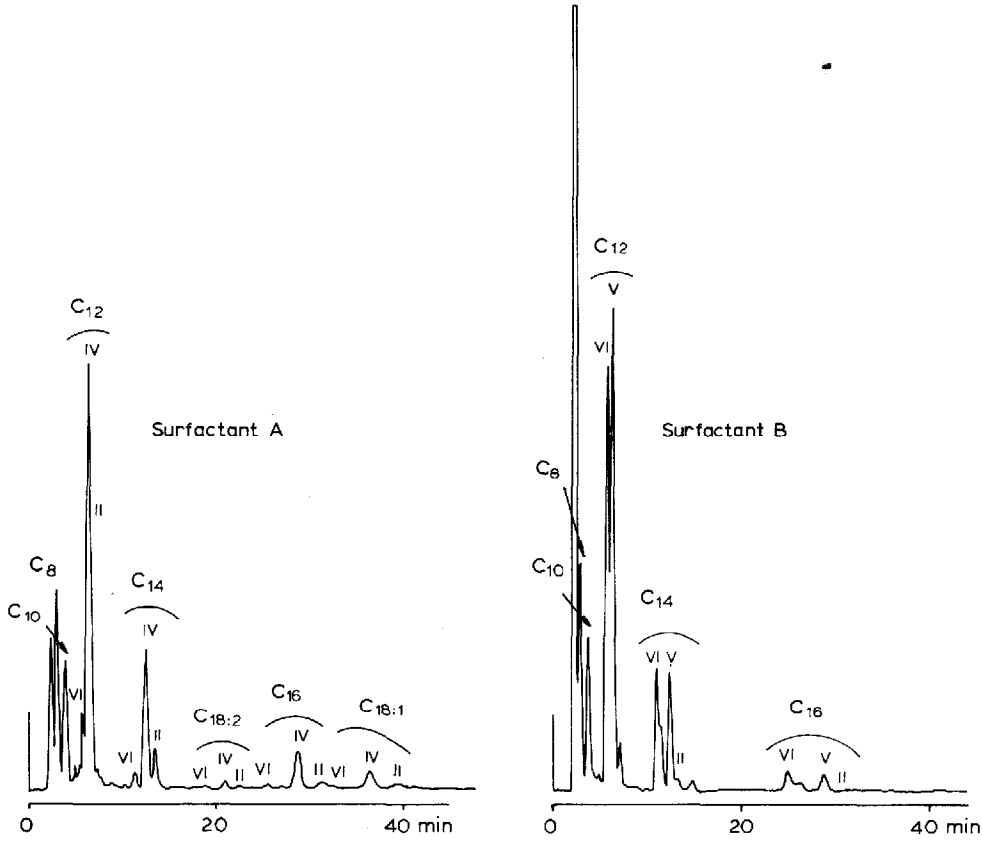


Fig. 14.

(Continued on p. 164)

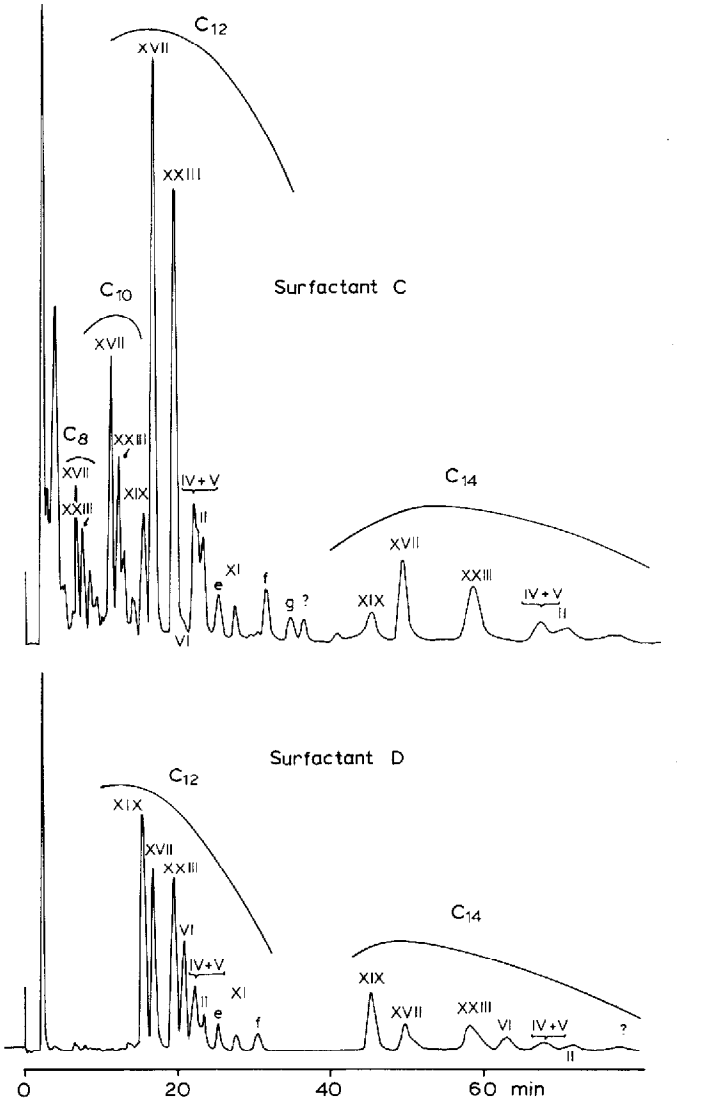


Fig. 14. Representative chromatograms of commercially available surfactants (post-column detection) of types 1 (A), 2 (B), and 3 (C, D). Analytical conditions: column, Develosil ODS-3 (100 × 4.6 mm I.D.); post-column detection; eluent, 0.2 *M* $NaClO_4$ in acetonitrile–water (60:40) (pH 2.5) for surfactants A and B, 0.2 *M* $NaClO_4$ in acetonitrile–water (50:50) (pH 2.5) for surfactants C and D.

secondary amide compounds (V + VI + VIII) would be higher, compared to surfactant C.

The chromatograms shown in Figs. 14 and 15 also gave information on the alkyl chain distribution of the original fatty acids and the degree of substitution by the electrophilic reactants. With respect to the distribution of the alkyl chain, the results of the proposed post-column detection agreed with that of a conventional GC method[21], as found previously[23].

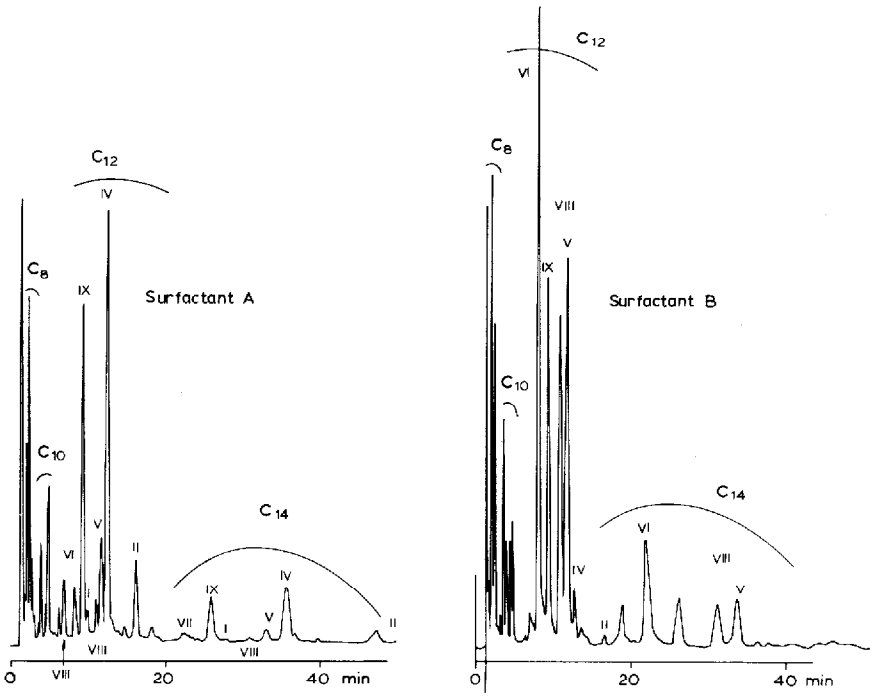


Fig. 15. Representative chromatograms of the above surfactants A and B with UV detection (210 nm). Analytical conditions: column, Develosil ODS-3 (100 × 8 mm I.D.); eluent, 0.5 *M* $NaClO_4$ in methanol–acetonitrile–deionized water (60:10:30).

The information obtained from the post-column detection was unaffected by presence of other components in commercial products.

Commercial products analysis

The precision and accuracy of the method were tested by adding known amounts of the surfactants A–D to commercial products. Table I shows the results obtained, and demonstrates that the method can be applied to commercial products analysis.

TABLE I

DETERMINATION OF SALT-FREE-TYPE IMIDAZOLINE AMPHOTERIC SURFACTANTS IN TOILETRY PRODUCTS

Samples: A = shampoo; B = permanent wave. Added (%) was involatile matter (%) of the surfactants. Found (%) was calculated by summing the peak areas of the alkyl chains.

Sample	*Surfactants*	*Added (%)*	*Found (%)*	*n*	*Coefficient of variation (%)*	*Recovery (%)*
A	A	5.0	4.86	4	2.6	97.2
A	B	5.0	4.90	4	1.8	98.0
A	D	5.0	4.84	4	2.3	96.8
B	D	3.0	2.89	3	2.4	96.3

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