Analysis of Cationic and Amphoteric Surfactants II: Determination of Their Homolog Distributions by Reaction Gas Chromatography on the Basis of the Hofmann Degradation

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ABSTRACT AND SUMMARY

Pyrolysis and reaction gas chromatography (GC) methods have been investigated for the homolog distribution analysis of cationic and amphoteric surfactants containing a quaternary ammonium group. Pyrolysis GC was found to be inapplicable to the analysis of amphoteric surfactants because of the formation of the nonvolatile compounds as the main products. However, when cationic and amphoteric surfactants dissolved in a 3% potassium hydroxide methanolic solution were injected into a gas chromatograph, Hofmann degradation occurred at the injection port of a gas chromatograph (reaction GC), and we obtained about the same products as were formed by the older DMF-Methylate method. Under optimum conditions, various cationic and amphoteric surfactants were degraded almost quantitatively, and the reproducibility of this method was satisfactory. Furthermore, the homolog distribution of surfactants found by the reaction GC method closely agreed with that of the starting alkyldimethylamines used. Thus, reaction GC analysis was applicable to the homolog distribution analysis of these surfactants. The reaction GC method surpassed the DMF-Methylate method with regard to the simplicity and reproducibility of the determination.

INTRODUCTION

In the preceding work (1), the homolog distribution of cationic and amphoteric surfactants had been determined by the DMF-Methylate method applied to the Hofmann degradation, and we confirmed that the main degradation of these surfactants proceeded by way of the elimination of a β-hydrogen atom.

Many papers have been published on the homolog determination of cationic surfactants by means of pyrolysis gas chromatography (pyrolisis GC) (2-4). This method has the advantage of simplicity of analysis, however, nothing has been reported on pyrolysis GC of amphoteric surfactants. The present authors attempted to determine the homolog distribution of both types of surfactants by pyrolysis GC. In the case of cationic surfactants, similar results as those reported by Metcalfe (2) and Uno et al. (3) were obtained except that alkylbenzyldimethylammonium chlorides gave 9% alkylbenzylmethylamine in addition to 91% alkyldimethylamine. It became apparent, however, that pyrolysis GC was inapplicable to the analysis of amphoteric surfactants because of the formation of nonvolatile compounds as the main products.

TABLE I

Abbreviations of Cationic and Amphoteric Surfactants

Surfactant	Abbreviation
$RN^+(CH_3)_3\ C1^-$	ATMA
$R(R')N^+(CH_3)_2\ C1^-$	DDMA
$RN^+(CH_3)_2\ CH_2\ C_6\ H_5\ Cl^-$	BDMA
$RN^+(CH_3)_2\ CH_2\ COO^-$	DAMC
$RN^+\ (CH_3)_2\ CH_2\ CH_2\ COO^-$	DAEC
$RN^+(CH_3)_2\ CH_2\ CH_2\ SO_3^-$	DAES
$RN^+\ (CH_3)_2\ CH_2\ CH_2\ CH_2\ SO_3^-$	DAPS
$RN^+\ (CH_3)_2\ CH_2\ CH_2\ CH_2\ CH_2\ SO_3^-$	DABS

On the other hand, if Hofmann degradation at the injection port of a gas chromatograph (reaction GC) is possible, both types of surfactants should give volatile degradation products (1), and reaction GC would have the advantage of simplicity of analysis over the DMF-Methylate method. Therefore, reaction GC was investigated by way of a modification of the Hofmann degradation. It was found that under optimum conditions both types of surfactants could be quantitatively degraded to give about the same volatile products as those obtained by the DMF-Methylate method.

EXPERIMENTAL PROCEDURES

The apparatus was similar to that previously described (1). Table I shows the structures and abbreviation code used for the surfactants of this study. They were prepared in the same way as described earlier (1).

A solution containing 4.65 g of methanol and 0.15 g of potassium hydroxide (3 wt % in the final solution) was added to a sample, about 0.2 g (4 wt% in the final solution), in a test tube, and it was stoppered with a rubber septum. Then, 1 μl of the sample solution was withdrawn through the rubber septum with a syringe and injected into a gas chromatograph. It is desirable that the sample be prepared and analyzed as soon as possible.

A Shimadzu 4BM-PF gas chromatograph equipped with a dual flame ionization detector was used for all experiments. The column was Pyrex glass, 1 m long, 3 mm ID, packed with Gas Chrom Q (80-100 mesh) coated with 3% w/w JXR-Silicone. A Pyrex glass tube (reaction zone), 9 cm long, 3 mm ID, was inserted into the injection port and connected with the column. The column temperature was linearly programmed from 100 to 300 C at a rate of 10 C per min. The injection port and detector temperatures were set at 170 C. Helium was used as the carrier gas at a rate of 50 ml per min. All peak areas were computed by a Hitachi Datalyzer-002 (mini-computer online system).

The pyrolysis GC experiment was carried out in a similar way as described above except that the sample solution did not contain potassium hydroxide and that the injection port and detector temperatures of the gas chromatograph were held at 290 C.

RESULTS AND DISCUSSION

Pyrolysis GC of Amphoteric Surfactants

Table II shows the extent of degradation of five amphoteric surfactants subjected to pyrolysis GC. The extent of degradation of all amphoteric surfactants except DAEC was fairly low. The results of pyrolysis GC of cationic surfactants reported by Metcalfe (2) and Uno et al. (3) indicated that the benzyl and methyl groups attached to the quater-

TABLE II

Extent of Degradation of Amphoteric Surfactants in Pyrolysis Gas Crhomatography (GC)

Surfactant	Extent of degradation (%)
DAMC	56
DAEC	75
DAES	33
DAPS	37
DABS	33

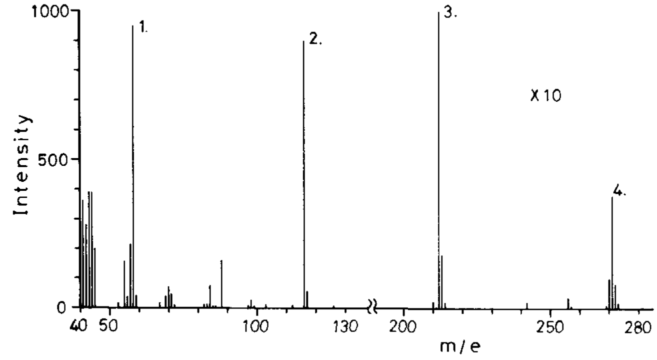

FIG. 1. Gas chromatograph-mass spectrometry (GC-MS) spectrum of dodecylmethyl(methoxycarbonylmethyl)amine obtained from pyrolysis GC of C_{12}-DAMC. Peak 1: m/e 58, $[CH_2=N(CH_3)_2]^+$; Peak 2: m/e 116, $[CH_2=N(CH_3)CH_2\text{-}COOCH_3]^+$; Peak 3: m/e 212, $[CH_2=N(CH_3)C_{12}H_{25}]^+$; Peak 4: m/e 271, $[C_{12}H_{25}N(CH_3)CH_2COOCH_3]^+$.

nary nitrogen atom were easily eliminated. Since the amphoteric surfactants have a polar substituent on the nitrogen atom, their pyrolysis products, formed by the elimination of a methyl group, are nonvolatile. Therefore, elimination of a methyl group was presumably the primary reaction occurring in the pyrolysis GC of amphoteric surfactants.

In order to confirm this assumption, DAMC was esterified with n-propyl alcohol with hydrogen chloride as catalyst, and the product was then injected into a gas chromatograph. The n-propyl ester of DAMC was almost quantitatively degraded to give a 40% yield of alkyldimethylamine and 60% alkylmethyl(propoxycarbonylmethyl)amine, which would be formed by the elimination of a methyl group. Furthermore, in the pyrolysis GC of all amphoteric surfactants except DAMC, the volatile product which showed up on the gas chromatogram was only alkyldimethylamine.

DAMC gave α-olefin, alkyldimethylamine, and alkylmethyl(methoxycarbonylmethyl)amine, whose GC-MS spectrum was shown in Figure 1, in 17, 25, and 14% yields, respectively. The last product apparently was formed by partial methyl ester formation of the nonvolatile product formed by the elimination of a methyl group. The formation of α-olefin also indicated that partial elimination of the β-hydrogen atom occurred, whereas pyrolysis GC of the n-propyl esters of DAMC and other surfactants gave no α-olefin. These facts suggest the participation of carboxylate ion in the elimination of the β-hydrogen atom and also hint at differences in steric conformation between DAMC and the other surfactants.

Reaction GC of Cationic and Amphoteric Surfactants

It thus seemed undesirable to apply pyrolysis GC to amphoteric surfactants because of the formation of nonvolatile compounds as the main products. Since in the Hofmann degradation of cationic and amphoteric surfactants volatile products were formed almost quantitatively as described in the preceding paper (1), modification of the Hofmann degradation at the injection port of a gas chromatograph (reaction GC) was investigated in this study. Potassium hydroxide was used as the strong base required for the Hofmann degradation, and methanol was selected as the solvent since it dissolved both potassium hydroxide and the surfactants (5).

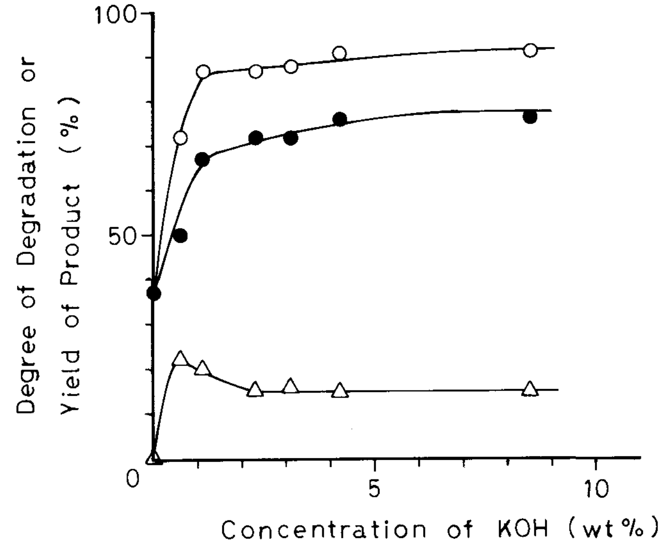

FIG. 2. Effect of the concentration of potassium hydroxide on the extent of degradation and the yields of degradation products of C_{16}-DABS. —○— = Extent of degradation; —●— = yield of dimethylhexadecylamine; —△— = yield of 1-hexadecene.

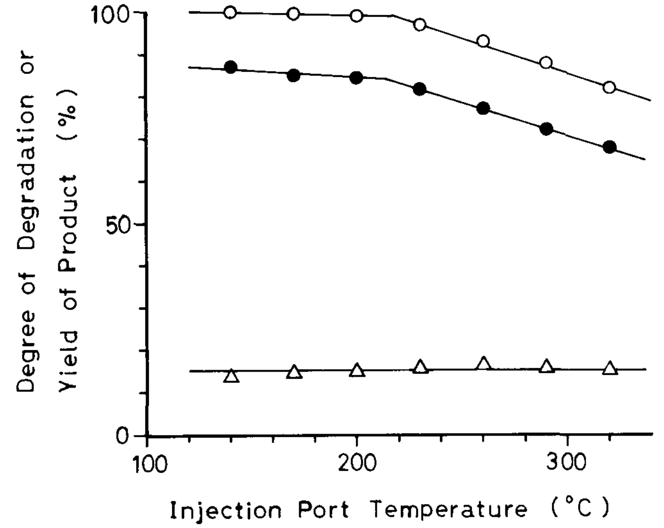

FIG. 3. Effect of the injection port temperature on the extent of degradation and the yields of degradation products of C_{16}-DABS. —○— = extent of degradation; —●— = yield of dimethylhexadecylamine; —△— = yield of 1-hexadecene.

In a study of optimization of reaction conditions, DABS was used as a standard sample (1), and its concentration was adjusted as 4% for reasons of solubility. The extent of degradation and the yield of each product were determined with the aid of tetradecyldimethylamine as an internal GC standard.

Figure 2 shows the extent of degradation of DABS in methanol and the yields of degradation products as a function of the concentration of potassium hydroxide. The

TABLE III

Extent of Degradation and Yield of Degradation Products of Cationic and Amphoteric Surfactants in Reaction Gas Chromatography (GC)

Surfactant	Yield (%)					
	α-Olefin	Alkyldimethylamine	Dialkylmethylamine	Alkylbenzylmethylamine	Rearrangement products	Extent of degradation (%)
ATMA	40	57	---	---	---	97
DDMA[a]	70	72	28	---	---	99
BDMA	29	55	---	15	6	105
DAMC	52	39	---	---	---	91
DAEC	---	97	---	---	---	97
DAES	---	96	---	---	---	96
DAPS	2	96	---	---	---	98
DABS	14	85	---	---	---	99

[a] DDMA gives α-olefin and alkyldimethylamine simultaneously.

TABLE IV

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

Surfactant		Homolog distribution (peak area, %)				
		C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
ATMA	Original	0.1	1.8	1.0	17.7	79.5
	Found	---	1.4	2.2	17.5	79.0
DDMA	Original	---	0.1	0.3	34.1	65.5
	Found	---	---	0.8	33.4	65.8
BDMA	Original	0.3	3.5	62.3	32.6	1.2
	Found	---	3.4	63.2	31.2	2.2
DAMC	Original	0.1	3.8	63.5	31.4	1.2
	Found	---	3.1	64.8	31.2	0.9
DAEC	Original	0.3	57.2	34.4	7.7	0.4
	Found	---	57.6	35.1	7.0	0.4
DAES	Original	0.2	57.4	34.2	7.8	0.6
	Found	0.1	57.7	34.3	7.5	0.4
DAPS	Original	0.4	33.4	65.1	0.9	0.2
	Found	0.6	34.0	64.2	0.8	0.4
DABS	Original	0.1	3.8	63.5	31.4	1.2
	Found	---	3.5	65.1	30.5	0.9

temperature of the injection port of a gas chromatograph was kept at 290 C. The extent of degradation rapidly increased with an increase in concentration of potassium hydroxide and reached nearly constant value above 3%, and the concentration of potassium hydroxide was thus fixed at 3%.

The extent of degradation of DABS dissolved in 3% potassium hydroxide methanolic solution was then determined as a function of the injection port temperature (140 to 320 C) as shown in Figure 3. The extent of degradation was over 99% up to 200 C, and the injection port temperature was thus fixed at 170 C. Under these conditions, the extent of degradation was little affected by flow rate of helium carrier gas and sample volume injected. We arbitrarily set the flow rate of helium at 50 ml/min and the sample volume at 1 μl.

As Figure 3 shows, a change in slope in a plot of the extent of degradation vs. the injection port temperature was observed near 220 C, and above this point the extent of degradation decreased linearly with an increase in temperature. This suggests that the amount of nonvolatile compounds formed by elimination of a methyl group increases with an increase in temperature above 220 C.

In summary, the optimum conditions for reaction GC are those described in the experimental section. Table III shows the extent of degradation and the yields of the products obtained from various cationic and amphoteric surfactants under optimum conditions.

All surfactants except DAMC are almost quantitatively degraded, and the resulting data closely agree with those obtained by the DMF-Methylate method (1), which indicates that Hofmann degradation occurred at the injection port of the gas chromatograph. The standard deviations in the measurement of the extent of degradation were 1-5%.

Determination of Homolog Distribution by Reaction GC

Cationic and amphoteric surfactants having a known homolog distribution were synthesized from mixtures of alkyldimethylamines as described in the preceding paper (1). Table IV shows a comparison of the homolog distribution of the original alkyldimethylamines with that of corresponding quaternary ammonium compounds.

The agreement between both distributions was satisfactory, and the standard deviation in the determination was within 3%. Therefore, the reaction GC method should also be applicable to the determination of the homolog distributions of various cationic and amphoteric surfactants containing a quaternary ammonium group. The present reaction GC method surpasses the older DMF-Methylate method with regard to simplicity and reproducibility.

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[Received January 11, 1977]