Rapid Quantitative HPLC Analysis of Polyethoxylated Nonionics

Haruo Yoshimura, Toyoki Sugiyama and **Toshio Nagai**
Analytical Research Center, Lion Corporation 13-12, 7 Chome, Hirai Edogawa-ku, Tokyo, Japan

A rapid quantitative HPLC method for alkylethoxylate was studied. According to theoretical considerations based on the plate theory, it was expected that alkylethoxylate could be separated to give one chromatographic peak regardless of the carbon number distribution in hydrophobic moiety and adducted number of ethylene oxide by using a back flush technique.

As expected, a single peak with good shape for quantitative use was obtained. Quantitative analytical methods were developed for (i) unconverted alkylethoxylate in alkylethoxysulfate, and (ii) alkylethoxylate nonionics formulated with anionics in detergents.

As anionics generally were retained less than alkylethoxylates under the condition in which ODS-column and a methanolic aqueous eluent were used, a single peak for alkylethoxylates was obtained by back flushing after anionics were eluted from the column. In the case of a heavy duty detergent, an additional column was needed to remove the interferences owing to co-existing more retained species.

In alkylethoxysulfate (AES), one of the most commonly used anionic surfactants, there always remains a small amount of unconverted alkylethoxylate (AE). A reliable and rapid analytical method for determining unconverted AE would be useful in maintaining the quality of the end products. Unconverted AE has been determined by using columns packed with anion and cation exchange resins. Unconverted AE could be obtained as an eluted nonionic when an alcoholic solution of AES was passed through the columns, and determined by weighing after the removal of the alcoholic eluent. This method, however, is very time consuming.

As the use of high performance liquid chromatography (HPLC) seems adequate for analyzing AE, many analytical works by means of this technique have been published (1-5). AE is ordinarily a complicated mixture with a distribution of carbon numbers in its hydrophobic moiety and/or adducted number of ethylene oxides. Most reports have concerned analyses of the distribution of either the adducted number of ethylene oxide (1-3) or the carbon number in its hydrophobic moiety (4). These HPLC methods would be difficult for the quantitative analysis of a small amount of AE, because many peaks of separated AE were observed in most of them.

According to Dijk et al. (6), when an alcoholic solution of AES is introduced to a mixed-bed ion exchange column with H^+-form strong cation and OH^--form strong anion resins, unconverted AE could be determined by means of a differential refractometer. As the separated AE shows a single peak regardless of the distribution of the hydrophobic moiety or the adducted number of ethylene oxide, this method was thought suitable for determining a small amount of unconverted AE in AES. However, accumulation of ionic species in the column, which requires column regeneration or renewal in a very short time, makes it difficult to apply this method to a routine analysis.

AE also have been used as nonionics in a household detergent together with anionics. The determination of AE in this case has been important to maintain the quality of the product. However, the same difficulties as described above are involved.

The study described here was carried out in order to develop a HPLC method suitable for determining a small amount of AE, first in AES and then in a detergent formulation.

EXPERIMENTAL

Apparatus. The instrument used in this study consists of a high pressure liquid pump (LC-3A, Shimadzu Corp., Kyoto, Japan) with six-port injection valve (Model 7125, Rheodyne Inc., Contati, California); a differential refractometer (SE-11, Showa Denko Co. Ltd., Tokyo, Japan); four-port timer-controlled switching valve (NP4V; Gasukuro Inc., Tokyo, Japan), and data processor (SIC 7000A, System Instruments Corp., Tokyo, Japan). Figure 1 shows a schematic diagram of the instrumentation of this study. An NMR spectrometer (XL-200; Varian Instruments Ltd., Palo Alto, California) and a gas chromatograph (GC-4B; Shimadzu Corp.) also were used in this study.

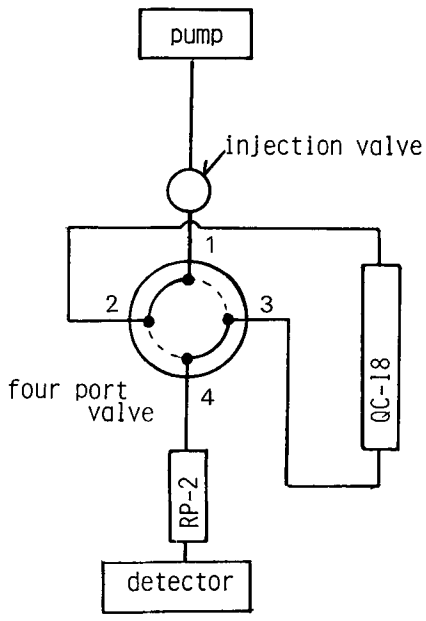

FIG. 1. Schematic diagram of system. Eluent flow: before backflushing, 1 → 2 → 3 →4; after backflushing, 1 → 3 → 2 → 4.

Materials. All AEs and AESs used in this study were obtained by ethoxylation of synthetic alcohols (DOBANOL 23(C_{12-14}), DOBANOL 25(C_{12-15}), Mitsubishi Oil Co. Ltd., Tokyo, Japan; DIADOL 13(C_{13}), Mitsubishi Chem. Co. Ltd., Tokyo, Japan, and nonylphenol (NP), Mitsui Toatsu Chem. Inc., Tokyo, Japan) and following sulfation in our company. All other reagents were of analytical reagent grade. Columns used here were 150 mm × 4.6 mm i.d. and 50 mm × 4.6 mm i.d. packed with Unisil QC-18(10 μ, ODS-modified silica; Gasukuro Inc.) and LiChrosorb RP-2 (5 μ, E. Merck, Darmstadt, German Federal Republic) respectively by a slurry method (7). These columns will be referred to as QC-18 or RP-2.

The samples were dissolved in methanol, and 50 μl of them were injected into the chromatographic system. Only 85% (v/v) methanolic aqueous solution was used as eluent throughout this study.

RESULTS AND DISCUSSION

A reverse phase chromatographic technique was used in this study, because it would be suitable for a sample containing a considerable amount of water as AES slurry, and a column used would be easy to handle.

Figure 2 shows an AES separation obtained by reverse phase chromatography using a column packed with an ODS-modified silica and methanolic aqueous eluent. The unconverted AE could be separated from AES with many peaks, which seemed difficult for quantitative use. Accordingly, we tried to make this chromatography suitable for quantitative use.

At first, the distribution of AE in the column was considered. At arbitrary time between about 5.5 min and 7.0 min of the chromatogram in Figure 2, only the AE was thought to exist in the column. The distribution was considered by dividing the column into imaginary r segments according to the continuous flow model (8). The distribution of the species whose capacity factor is k' can be expressed by:

$$m(t;n) = m_0 \times (at)^n \times \exp(-at)/(n!) \qquad [1]$$

where $a = 1/(1+k')$; $m(t;n)$ represents the amount of species in the n-th segment from the inlet side of the column at the time t, and m_0 represents the total amount of the species injected. When the flow direction of eluent in the column is switched to reverse, namely back flushed at time t_1, the amount of the species eluted from the column at time t [m(t)] can be expressed by:

$$m(t) = \sum_{n=1}^{n=r} m(t_1;n) \times [a(t-t_1)]^n \times \exp[-a(t-t_1)]/(n!) \qquad [2]$$

A plot according to Eqn. (2) with respect to t means a chromatogram of the species with k' of capacity factor. Figure 3 shows the simulated chromatograms with $r = 1000$ and $k' = 9$ and 19, respectively, in Eqn. (2). The retention times thus obtained are the same regardless of the value of k', though the peak width increases with the increase of k'. These results suggested that a single peak could be obtained for the AE using the back flush technique.

As shown in Figure 4, the peaks due to the unconverted AE in Figure 2 were reduced to a single peak by the back flush. Figure 5 shows a chromatogram of another AES whose hydrophobic moiety was different.

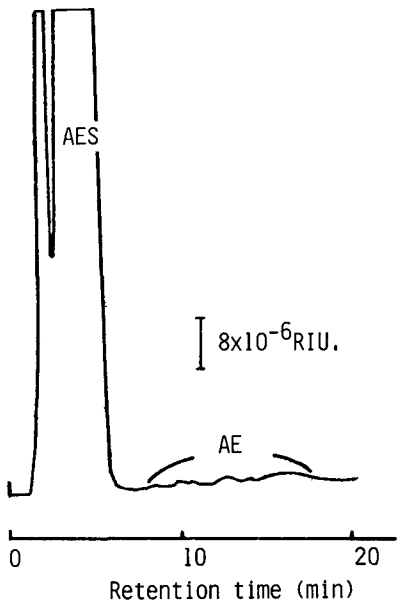

FIG. 2. HPLC separation of AES. Conditions: column, Unisil QC-18 150 mm long × 4.6 mm i.d.; eluent, MeOH/H_2O, 85/15 (v/v); flow rate, 1 ml/min; column temp, ambient; injected volume, 50 μl. Sample, $C_{12-15}(OC_2H_4)_pOSO_3Na$(p=3) ca. 9% (w/v) in MeOH.

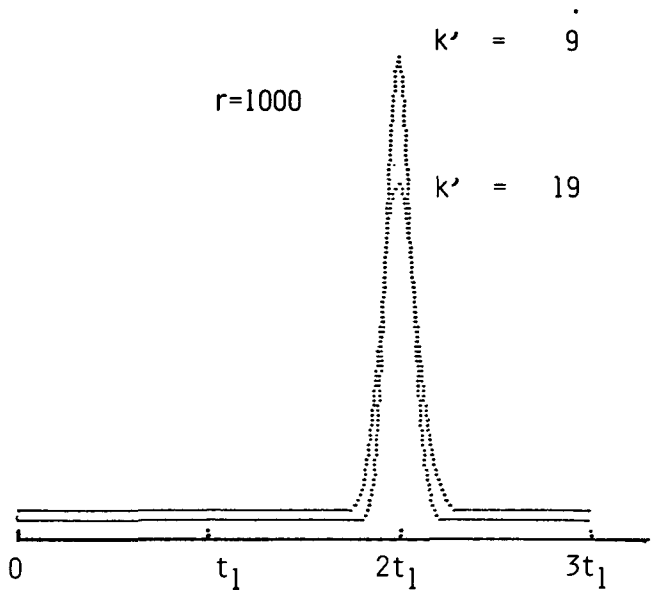

FIG. 3. Simulated chromatograms.

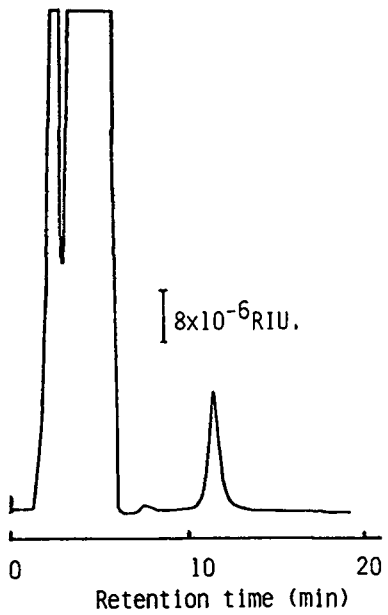

FIG. 4. Separation of AES(1). Conditions: column, Unisil QC-18 150 mm long × 4.6 mm i.d.; eluent MeOH/H_2O, 85/15 (v/v); flow rate, 1 ml/min; column temp, ambient; injected volume, 50 μl; back flush time, 5.5 min. See Fig. 2 for sample.

Although there existed only a very small amount of unconverted AE, the peak seemed good enough for quantitative use. The eluted fraction corresponding to this peak was collected and analyzed by ^{1}H-NMR and gas chromatography. With respect to the distribution of the carbon number and the averaged adducted number of ethylene oxide, the AE thus obtained was almost identical to the original AE.

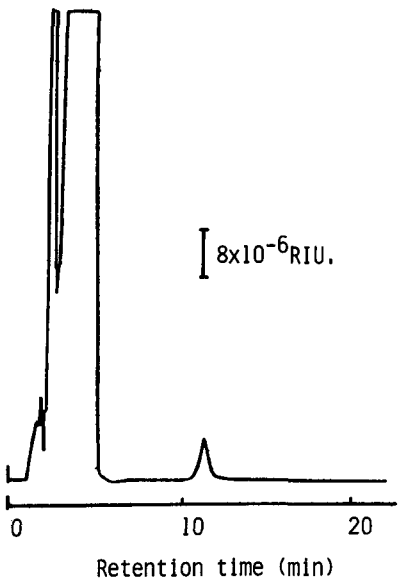

FIG. 5. Separation of AES(2). Conditions, see Fig. 4. Sample, C_{12-14} $(OC_2H_4)_{\bar{p}}OSO_3Na(\bar{p}=3)$ ca. 9% (w/v) in MeOH.

The relationship between the injected amount of AE and the peak area was studied, and good linearity was obtained up to 50 μg as shown in Figure 6. Recoveries of AE in AES were tested, and good results were obtained as indicated in Table 1. Determinations of unconverted AE in AES were carried out, comparing this method with the conventional ion exchange method. The analytical results are listed in Table 2. Good accordance was obtained, and repeatability of this method was much superior to that of the conventional one.

TABLE 1

Recoveries of AE in AES

Alkylethoxylate	Added (mg)	Found (mg)	Recovery (%)
C_{12-14} $(OC_2H_4)_{\bar{p}}OH$	0	31.6	—
$(\bar{p}=3)$	41.4	72.7	99.6
	62.1	94.0	100.3
C_{12-14} $(OC_2H_4)_{\bar{p}}OH$	0	37.3	
$(\bar{p}=5)$	46.9	83.4	99.0
	70.4	108.7	100.9

Sample: C_{12-14} $(OC_2H_4)_{\bar{p}}OSO_3Na$ ca. 7% (w/v) in MeOH, $(\bar{p}=3$ or 5).

TABLE 2

Comparison of Analytical Results for Unconverted AE in AES

Original Alkylethoxylate	Unconverted AE HPLC (%)	Unconverted AE Conventional (%)
C_{12-14} $(OC_2H_4)_{\bar{p}=2}OH$	0.54[a]	0.49[b]
C_{12-14} $(OC_2H_4)_{\bar{p}=3}OH$	1.23	1.18
C_{12-14} $(OC_2H_4)_{\bar{p}=5}OH$	0.72	0.76
C_{12-15} $(OC_2H_4)_{\bar{p}=3}OH$	1.42	1.39
C_{13} $(OC_2H_4)_{\bar{p}=3}OH$	1.64	1.54

Sample: ca. 5-10% (w/v) of AES in MeOH.
[a]CV. 0.6%, n=8.
[b]CV. 4.0%, n=6.

As the back flush technique was found to be suitable for the determination of AE, this method was extended to a more general case. AE has been used together with anionics in household detergents because of their co-operative effects on detergency. Table 3 shows one example of granular heavy duty detergents which contain AE. The applicability of this method to the determination of the AE in this formulation was tested. When the methanol extract of the formulation [alkylethoxylate; C_{12-14} $(OC_2H_4)_{\bar{p}=7}$-OH] was injected, the chromatogram as shown in Figure 7 was obtained. This chromatogram seemed good enough. However, the amount of AE determined was about 0.3% higher than expected. This discrepancy might be due to interferences of more-retained co-existing species, for example unconverted α-olefin or alkylbenzene.

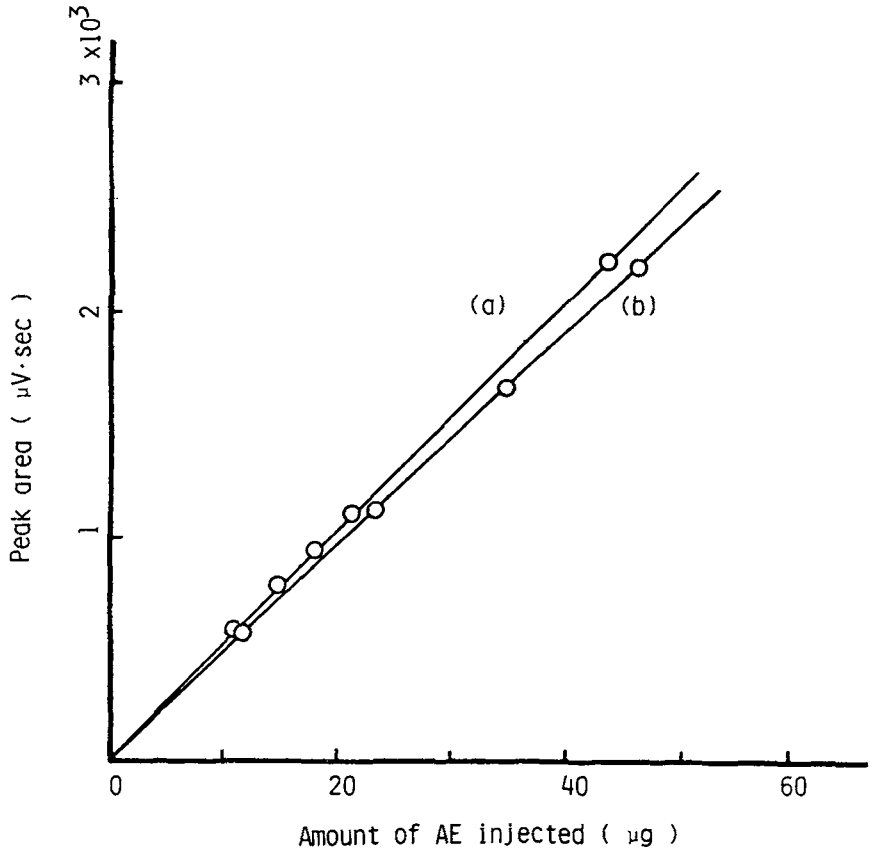

FIG. 6. Calibration curve. Conditions, see Fig. 4. Samples, $C_{12-14}(OC_2H_4)_{\bar{p}}OH$ in MeOH; (a) $\bar{p}=3$; (b) $\bar{p}=5$.

As all the species in the column were eluted simultaneously, this method had the disadvantage of being easily disturbed by the more-retained co-existing species; thus, it gave positive error. Therefore, further separation of the AE from interfering species without mutual separation among the AE was required. This separation was considered possible by passing all the species eluted simultaneously by the back flush through an appropriate additional column.

A short column packed with LiChrosorb RP-2 was found to be fit for this purpose, according to the following consideration. The elution behavior of fatty

TABLE 3

Detergent Formulation

Components	Ratio (%)
Anionic surfactants (LAS, AOS, Soap)	20
Alkylethoxylate	1-3
Perfume additives	0.2
Fluorescent dyes	0.2
Alkali builder (Na_2CO_3, $Na_2O \cdot nSiO_2$)	20
Zeolite	15
Sodium sulfate	balance

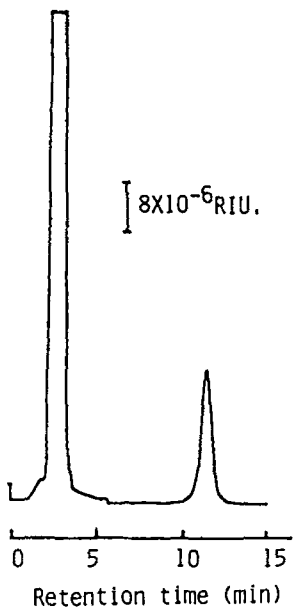

FIG. 7. Separation of AE in detergent formulation. Conditions, see Fig. 4. Sample, methanol extract of 3 g detergent formulation.

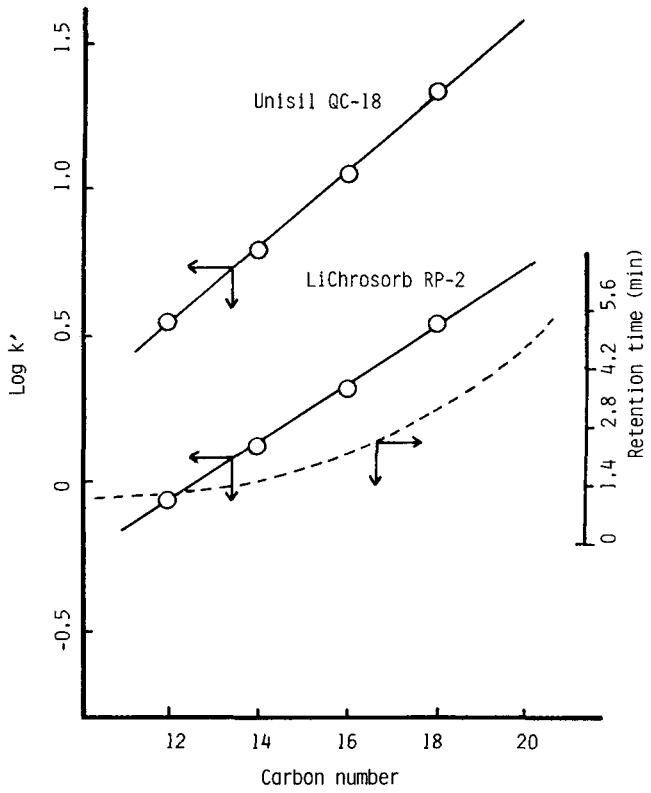

FIG. 8. Elution behavior of fatty alcohol. Conditions: eluent, flow rate, column temp and injected volume, see Fig. 4. Samples, ca. 1,000 ppm of fatty alcohol in MeOH.

alcohols with respect to the carbon number is indicated in Figure 8. Under this chromatographic condition, as AE and a fatty alcohol with the same alkyl radical show almost the same elution, fatty alcohols were used as model substances in order to estimate the elution of AE. In Figure 8, the retention time by the 5-cm RP-2 column is also indicated by a dotted line. As the RP-2 had much less ability than the QC-18 to retain a hydrophobic species, a fatty alcohol with carbon number from 12 to 14, consequently AE with the same alkyl radical was hardly retained. Therefore, significant separation among the AE whose hydrophobic moiety is distributed from 12 to 14 would not occur by passing through the RP-2. On the other hand, the species more hydrophobic than octadecylalcohol would be retained significantly, and separated from the AE.

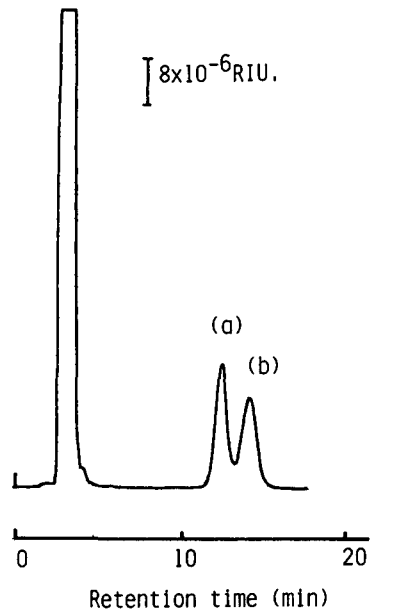

FIG. 9. Separation of AE from octadecyl alcohol. Conditions: column, Unisil QC-18 150 mm long × 4.6 mm i.d.; LiChrosorb RP-2 50 mm long × 4.6 mm i.d.; eluent, flow rate, column temp, injected volume and backflush time, see Fig. 4. Samples, (a) ca. 3,000 ppm of C_{12-14} $(OC_2H_4)_{\bar{p}}OH$ ($\bar{p}$=3); (b) ca. 3,000 ppm of octadecyl alcohol.

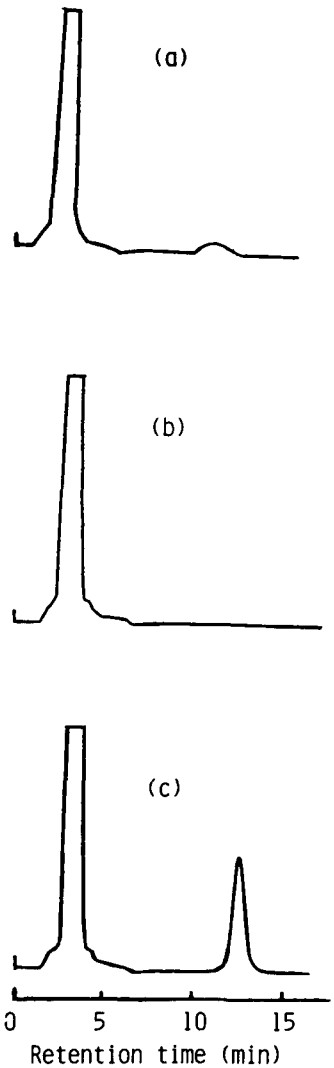

FIG. 10. Effect of RP-2 on separation of AE in detergents, (a) without RP-2 for detergent containing no AE; (b) with RP-2 for detergent containing no AE; (c) with RP-2 for detergent containing AE. Conditions, See Fig. 4(a) and Fig. 9(b,c).

TABLE 4

Recoveries of AE in Detergent Formulations

Alkylethoxylate	Added (mg)	Found (mg)	Recovery (%)
$C_{12-14}(OC_2H_4)_{\bar{p}=7}OH$	34.5	35.5	102.9
	68.9	68.3	99.1[a]
$C_{13}(OC_2H_4)_{\bar{p}=15}OH$	37.4	36.9	98.7
	74.7	73.7	98.7
$NP(OC_2H_4)_{\bar{p}=6}OH$	31.7	32.1	101.3
	63.5	64.9	102.2
$NP(OC_2H_4)_{\bar{p}=30}OH$	36.0	36.7	101.9
	72.0	74.1	102.9

Injected sample: methanol-extract of 3 g detergent.
[a]CV. 1.5%, n=6.

The model separation for the mixture of the AE and octadecylalcohol was carried out by the system in which the RP-2 column was placed between the detector and four-port valve in Figure 1. As shown in Figure 9, the AE still showed a single peak and was almost completely separated from octadecylalcohol.

The effect of the RP-2 on the separation of the AE in detergent was examined. When the separation was carried out for the detergent which did not contain any AE, a small peak was observed at the position of the AE under the condition without the RP-2 as shown in Figure 10(a), whereas no peak was observed under the condition with the RP-2 as in Figure 10(b). With respect to the formulation containing AE, a single peak with good shape for a quantitative use was obtained, as in Figure 10(c). A linear relationship between the peak area and the amount of AE injected also was obtained. Then recoveries were tested. As indicated in Table 4, good results were obtained.

Determination of AE was made possible in other cases. For instance, AE formulated together with cationics also could be determined in the same manner. Although a hundred analyses have been carried out, noticeable degradation of the column has not yet been observed.

In conclusion, we think this method would be useful especially for a routine analysis, because it is simple and faster than the conventional one.

ACKNOWLEDGMENT

Akira Mori, Executive Vice President of Lion Corporation, allowed us to publish this paper.

REFERENCES

1. Aserin, A., M. Frenkel and N. Garti, *J. Am. Oil Chem. Soc. 61*:805 (1984).
2. Nakamura, K., and I. Matsumoto, *Nippon Kagaku Kaishi 1975*:1342 (1975).
3. Nozawa, A., and T. Ohnuma, *J. Chromatogr. 187*:261 (1981).
4. Kudoh, M., *J. Chromatogr. 291*:327 (1984).
5. Kudoh, M., H. Ozawa, S. Fudano and K. Tsuji, *J. Chromatogr. 287*:337 (1984).
6. van Dijk, J.H., R.R. Lamping, C. Slagt and A.W.J. Raaijmakers, *Tenside Detergents 12*:261 (1975).
7. Liao, J.C., and J.L. Panzo, *J. Chromatogr. Sci. 20*:14 (1982).
8. Fritz, J.S., and D.M. Scott, *J. Chromatogr. 271*:193 (1983).

[Received June 26, 1986]