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Note

Determination of poly(ethylene glycols) in non-ionic surfactants by preparative high-performance liquid chromatography

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Ethoxylated non-ionic surfactants are widely used as detergents and emulsifying agents. These surfactants contain poly(ethylene glycols) (PEG) as the by-product of ethoxylation. Methods reported for the determination of PEG in ethoxylated non-ionic surfactants are mainly chromatographic, such as paper chromatography[1], thin-layer chromatography[2,3], liquid chromatography[4,5], and gas chromatography[6]. Solvent extraction and sedimentation of PEG have also been reported[7–10]. The determination of PEG in ethoxylated non-ionic surfactants by high-performance liquid chromatography (HPLC)[11–13] and its development have been reported, and optimum conditions of separation have been established. Unfortunately, these methods have poor accuracy and precision because of the lack of an adequate detector. As PEG has no UV absorption, a refractometer (RI detector) must be used. This detector is a universal type, but the response factor varies with the molecular weight of the PEG. It is also sensitive to differences in the solvent composition. Therefore, the results of PEG determination using the RI detector are not quantitative because PEG is a mixture of homologous polymeric compounds with various molecular weights, and in reversed-phase HPLC, PEG elutes at the solvent front where the solvent peak appears. To overcome the problems of inaccuracy associated with the RI detector, Henke[14] reported the determination of PEG in ethoxylated non-ionic surfactants by means of preparative HPLC. Good accuracy and precision were achieved when a gravimetric method was used to determine the weight of PEG. However, Henke's method is only applicable to relatively hydrophilic samples and requires a long analysis time (more than 3 h).

The present paper describes the precise determination of PEG in ethoxylated non-ionic surfactants by preparative HPLC. The long analysis time associated with preparative HPLC was reduced by using a back-flush elution method. The method was extended to ethoxylated fatty alcohols, ethoxylated alkylphenols, and ethoxylated alkylamines of various degrees of polymerization.

EXPERIMENTAL

Chemicals

Ethoxylated non-ionic surfactants were purchased from Kao-Atlas Co.Ltd.

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(Tokyo, Japan) and were used without further purification. PEG 400 and PEG 4000 were obtained from Wako (Osaka, Japan).

Preparative HPLC apparatus and procedure

Chromatographic separation of PEG in non-ionic surfactants was carried out with an instrument consisting of an HPLC pumping system (Tri Rotar, Jasco, Tokyo, Japan) and a Waters Model R-403 differential refractometer. A loop injector with 7.87-ml sample loop was used for sample injection. The column used in this study was a 500 × 20 mm I.D. stainless-steel column packed with LiChroprep RP-18 (Merck, Darmstadt, G.F.R.) by a dry method. Stainless-steel tubing (0.8 mm I.D., 1/16 in. O.D.) was used for all connections of the chromatographic system. The change of flow path in the back-flush elution method was done by a six-port high-pressure valve (Shimadzu, Kyoto, Japan). Acetone–water mixture was used as mobile phase and the flow-rate was 9 ml/min. As the solubility of ethoxylated non-ionic surfactants in the eluent varies with the alkyl chain length, the proportion of acetone was increased to 100%, depending upon the solubility of samples. For ethoxylated lauryl alcohols, octylphenols, and nonylphenols, acetone–water (55:45, v/v) was used. For ethoxylated cetyl alcohols, oleyl alcohols, and stearyl alcohols, acetone–water (80:20, v/v) was used. Acetone–water (60:40, v/v) was used for ethoxylated alkylamines, except for ethoxylated stearylamine with an average of two moles of ethylene oxide (EO) which was eluted with 100% acetone.

To determine the amounts of PEG, the eluate containing PEG was collected manually with the aid of the RI detector. After complete elution of PEG, the back-flush elution method was employed to shorten the time for eluting ethoxylated non-ionic surfactant. After the eluate containing PEG had been collected, the solvent was evaporated to dryness on a hot plate and the weight of PEG was obtained by gravimetry.

RESULTS AND DISCUSSION

A typical chromatogram showing the separation of PEG in ethoxylated lauryl alcohol of average 3 EO is shown in Fig. 1; PEG elutes first and ethoxylated lauryl alcohol next. The retention volume of PEG is almost independent of the molecular weight because of its hydrophilic nature. However, the degree of ethoxylation influences the retention volume of the ethoxylated non-ionic surfactant, which approach-

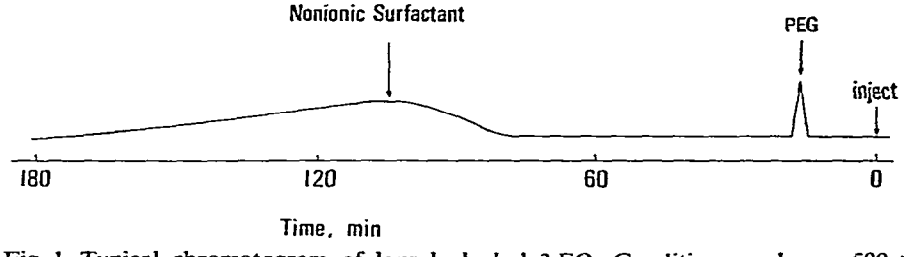

Fig. 1. Typical chromatogram of lauryl alcohol–3 EO. Conditions: column, 500 × 20 mm I.D.; packing, LiChroprep RP-18; eluent, acetone–water (55:45); monitor, R-403 (RI detector); flow-rate, 9 ml/min.

es that of PEG as the degree of ethoxylation becomes large and the hydrophilicity increases. As ethoxylated non-ionic surfactants are a mixture of molecules with different degrees of ethoxylation and different compositions of alkyl chain, a relatively broad peak occurs in Fig. 1. Complete elution took *ca.* 3 h. The long analysis time is a problem in the partical use of preparative HPLC. In order to overcome the problem, a back-flush elution method was employed after elution of PEG.

Fig. 2 shows a chromatogram of the same sample as Fig. 1, obtained using the back-flush elution method. The analysis time was shortened by employing the back-flush elution method after elution of PEG. The elution of PEG and ethoxylated product was complete within 1 h.

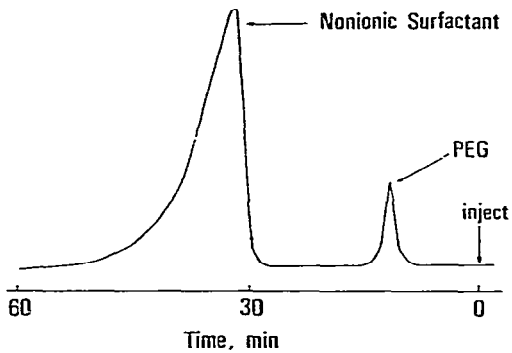

Fig. 2. Chromatogram of lauryl alcohol–3 EO using the back-flush elution method. Sample and conditions as in Fig. 1.

PEG in other samples, such as more hydrophobic ethoxylated fatty alcohols, ethoxylated alkylphenols and ethoxylated alkylamines, was separated using the back-flush elution method.

The recovery of PEG was examined in order to confirm that PEG in ethoxylated non-ionic surfactants was completely recovered from the column. The content of PEG in ethoxylated non-ionic surfactants was determined before and after the addition of known amounts of PEG. The examination of the recovery was repeated three times, and the result in every test was over 99% and there was no adsorption of PEG in the separation column.

The procedure described here includes the process of solvent evaporation on a hot plate. The low-molecular-weight PEG might evaporate with solvent and cause an error in the determination. The weight loss during solvent evaporation was examined in the following way. PEG of average molecular weight (*ca.* 400) was weighed in a small beaker, and heated on a hot plate for 3 h. After cooling, the beaker plus PEG were weighed again. This procedure was repeated three times. The difference in three determinations was less than 1.0 mg: hence the weight loss during solvent evaporation is negligible.

Table I shows the reproducibility of the determination of PEG. Four samples were chosen from ethoxylated alcohols and ethoxylated amines. Each sample was determined five times and the standard deviation and coefficient of variation (C.V.) were calculated. The result was satisfactory.

TABLE I

REPRODUCIBILITY OF DETERMINATIONS

Sample	*PEG content (%)*	*Standard deviation*	*C.V. (%)*
Lauryl alcohol–3 EO	1.41	0.052	2.47
Lauryl alcohol–50 EO	4.66	0.023	0.50
Laurylamine–10 EO	5.72	0.080	1.40
Oleylamine–15 EO	3.63	0.022	0.63

TABLE II

DETERMINATION OF PEG IN ETHOXYLATED ALCOHOLS AND ALKYLPHENOLS

Sample	*PEG content (%)*
Lauryl alcohol–3 EO	1.4
Lauryl alcohol–50 EO	4.7
Cetyl alcohol–10 EO	1.5
Stearyl alcohol–6 EO	2.4
Stearyl alcohol–20 EO	5.4
Oleyl alconol–2 EO	3.8
Oleyl alcohol–30 EO	9.8
Octylphenol–3 EO	*
Octylphenol–50 EO	8.8
Nonylphenol–3 EO	*
Nonylphenol–50 EO	4.0
Nonylphenol–85 EO	8.1

* Not detected.

Tables II and III show the results of the determination of PEG in ethoxylated alcohols and ethoxylated amines by preparative HPLC.

There was no apparent decrease of column effiiciency by changing the path of flow in the back-flush elution method after 6 months' use.

TABLE III

DETERMINATION OF PEG IN ETHOXYLATED ALKYL AMINES

Sample	*PEG content (%)*
Laurylamine–2 EO	*
Laurylamine–5 EO	1.5
Laurylamine–10 EO	5.7
Stearylamine–2 EO**	*
Stearylamine–4 EO	0.7
Stearylamine–50 EO	5.0
Oleylamine–2 EO	*
Oleylamine–15 EO	3.6
Oleylamine–20 EO	13.6

* Not detected.
** Eluent, 100% acetone.

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