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Short communication

Simultaneous determination of nonionic and anionic industrial surfactants by liquid chromatography combined with evaporative light-scattering detection

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Abstract

LC/ELSD was used for the simultaneous and rapid analysis of various anionic and nonionic surfactants. Eight surfactants (APG, LAE7, CDE, NPE7, LAE9-cap, SLS, AOS, AOT) were separated within 30 min in one LC run on C18-bonded silica column with a methanol–water gradient condition, using ELSD detection. The ELSD could be used efficiently for the detection of the surfactants not detectable by UV absorbance. Calibration plots of peak area vs. injected mass were linear in the range of 0.4–140 μg injected per 20 μL, with a log–log slope of 1.4–2.4. Several commercial products were analyzed to demonstrate the practicality of the procedure.

Keywords: Evaporative light-scattering detection; Surfactants; Anionic surfactant; Nonionic surfactant

1. Introduction

Chemical products, widely used in modern ordinary life such as cosmetics, medicines and household goods, contain surfactants as important ingredients. In terms of product quality control and environment protection, the analysis of surfactants is important.

LC has been the most popular method in the analysis of surfactants, because of its superiority in precision and accuracy. The analysis of surfactant mixtures, however, is very complicated, especially when the properties of the constituents differ significantly from each other. Recently, the advent of evaporative light-scattering detector (ELSD), detecting surfactants without any chromophore, has been one of the possible solutions in the analysis of surfactants of various types [1–5].

In spite of such a technical development, a simultaneous and rapid analysis of mixtures of surfactants of various types has been challenging. Generally, a mixture of various surfactants is chromatographically analyzed using several LC methods appropriate for each constituent [6–10]. Thus, a proper LC method is needed to separate various surfactants, at least, for screening purpose at the product control level.

In this work, we demonstrate an LC/ELSD combination for a simultaneous and rapid analysis of various anionic and nonionic surfactants with one LC run.

2. Experimental

2.1. Reagents and chemicals

The studied surfactants were as follows: alkyl poly glucoside (APG, R = C8, C10, monoglucoside, LG Chemical Ltd., South Korea), sodium lauryl sulfate (SLS, Ekyung Ltd., South Korea), alpha olefin sulfonate (AOS, Ekyung Ltd., South Korea), coconut diethanol amide (CDE, I.C. Chemical Ltd., South Korea), methyl capped lauryl alcohol 9 mol ethoxylate (LAE9-cap, average n = 9, I.C. Chemical Ltd.,

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South Korea), aerosol OT (AOT, R: Octyl, Fluka, Japan), lauryl alcohol 7 mol ethoxylate (LAE7, average $n = 7$, Hannong Chemical Ltd., South Korea), nonylphenyl 7 mol ethoxylate (NPE7, average $n = 7$, Hannong Chemical Ltd., South Korea).

2.2. Chromatographic conditions

The LC apparatus consisted of Hewlett-Packard 1050 Chemstation with an autosampler (100 μL loop), a quaternary gradient pump system and a reverse phase J'sphere ODS-H80 column (250 mm × 4.6 mm, 4 μm particle size). The detection was performed utilizing an Alltech 500 ELSD whose signal was integrated to a Hewlett-Packard Chemstation via an Agilent 35900E interface. The ELSD was warmed up for 20 min prior to each run, and was operated at 90 °C. The optimum flow rate of the nebulizing gas (N_2, 99.99%) was 2.60 L/min.

The composition and flow rate of the employed eluent were programmed for simultaneous and rapid separation. At the moment of injection of a 20 μL sample, the eluent consisted of 70% methanol (HPLC grade, Fisher Scientific Co., USA) and 30% water (>18 MΩ cm, Mili-Q, USA), and its flow rate was 0.8 mL/min. After holding the initial flow for 6 min, the content of methanol was increased linearly from 70 to 100% for the next 14 min. This particular condition was maintained for more 4 min, and then the flow rate was increased to 1 mL/min for 2 min to keep the chromatographic peaks sharp. After cleaning the column with the flow rate of 0.8 mL/min for 2 min, all the variables concerning the eluent was resumed to the initial ones for the next injection.

2.3. Preparation of standard and sample solutions

Stock solutions of each surfactant under study were prepared in 50% methanol aqueous solvent, and the working solutions for calibration were implemented by successive dilutions of the stock solutions with the solvent. The concentration ranges of the working solutions were selected based on the solubility limit and the tolerance in column loading amount of each surfactant.

Sample solutions were prepared by dissolving accurately weighed four commercial products (one toothpaste, two detergents and one body cleanser) in the 50% methanol aqueous solvent, and their final volumes were 50 mL. After keeping the solutions calm for 3 h, only the clear upper layers of the sample solutions were allowed to pass through membrane filters. Without any further treatment, the filtered solutions were injected into the LC column. For spike tests, the pre-determined amounts of the corresponding standards were added to the commercial products. After homogenizing the mixture of the commercial products and the standards, the sample solutions were prepared through the identical processes as above.

Table 1
Retention times, detection limits and linear ranges of the studied surfactants

Surfactant	Retention time (min)[a]	Detection limit (μg)[b,c]	Linear range (μg)[c,d]
SLS	7.46 ± 0.10	5	15–105
AOS	8.36 ± 0.10	6	14–40
APG (C8)	10.49 ± 0.04	Not measured	Not measured
AOT	10.85 ± 0.15	20	34–140
APG (C10)	16.94 ± 0.05	0.8	2–60
CDE (C12)	19.53 ± 0.06	0.2	0.4–60
CDE (C14)	22.31 ± 0.06	Not measured	Not measured
NPE7	22.55 ± 0.07	0.2	0.4–45
LAE7	24.39 ± 0.06	0.6	1–65
LAE9-cap	24.44 ± 0.07	1	3–110

The number of experiments for each surfactant was more than 5.
[a] The R.S.D. values of retention time were less than 1.5%.
[b] Detection limits in this works were determined based on experimentally detectable signals of 3 S/N level.
[c] Mass in the injected volume of 20 μL.
[d] Linear ranges were determined experimentally seven to nine point standard concentrations.

2.4. Peak identification

The surfactants separated with the LC column were identified using FAB-MS (JMS-AX 505H Mass Spectrometer, JEOL, Japan).

3. Results and discussion

The chromatographic results of each surfactant obtained with the given LC column are summarized in Table 1.

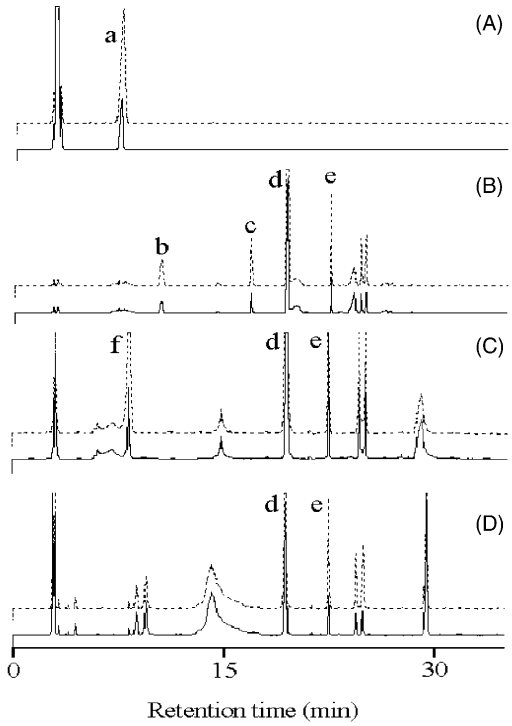

Fig. 1. The chromatograms of (A) tooth paste; (B) detergents for dishwashing (A); (C) detergent (B); and (D) liquid body cleanser: (a) SLS; (b) APG (C8); (c) APG (C10); (d) CDE (C12); (e) CDE (C14); and (f) AOS. The dashed chromatograms are those of the spiked samples.

Table 2
Surfactant concentrations of commercial and spiked samples

Commercial product	Surfactant	Sample concentration (%)	Added concentration (%)	Total concentration (%)
Tooth paste	SLS	3.2 ± 0.06	3.0	6.2 ± 0.07
Detergent A	APG	3.0 ± 0.06	3.0	6.0 ± 0.10
	CDE	4.5 ± 0.05	4.0	8.5 ± 0.08
Detergent B	AOS	2.1 ± 0.04	2.0	4.1 ± 0.05
	CDE	2.0 ± 0.05	2.0	4.0 ± 0.05
Body cleanser	CDE	1.9 ± 0.03	2.0	3.9 ± 0.05

The number of experiments for each commercial product was 4.

Although the chromatographic distribution of the oxyethylene glycol homologues of hydrophobic NPE7, LAE7 and LAE9-cap was not observed at all, the alkyl homologues of APG and CDE were resolved into two peaks, respectively. On the other hand, LAE7 and LAE9-cap showed an identical retention time.

The detection limit and linear range of the studied surfactants were summarized in Table 1. The calibration curves were obtained after injecting the standard solutions of several concentrations at least five times. Noting that all the studied surfactants except NPE7 show extremely poor responses to UV absorption, the results in Table 1 implies that ELSD was effective in the analysis of various surfactants in the studied concentration ranges. The detection limits observed in this work in nonionic surfactants (four species) were close to the previously reported values obtained with ELSD [1,2].

Fig. 1a–d shows the chromatograms of the surfactants contained in four commercial products. The stable base lines of the chromatograms and the clearly resolved peaks including homologues of APG were notable. For the validation of the analyses in this work, spike tests were performed (the dashed chromatograms in Fig. 1) and the results were summarized in Table 2. The observed results indicate that the entire analysis procedure, including sample preparation, was not associated with any matrix effect. The absence of matrix effect was confirmed by changing the composition of the eluent, as well.

The analytical procedure of the LC/ELSD combination used in this work has some limitations. For example, the chromatograms of linear alkylbenzene sulfonate (LAS) and sodium lauryl ethoxylated sulfate (SLES) were too broad to be analyzed even qualitatively. On the other hand, it was impossible to separate the homologues of surfactants, like NPE7, LAE7 and LAE9-cap studied in this work.

The chromatographic conditions in this works may be useful at least in screening various surfactants simultaneously and rapidly with one LC run. However, some limitations should be overcome to broaden the usefulness of the LC/ELSD combination as discussed previously.

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