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Automated analyses of non-ionic surfactants in terms of hydrophobic and polyoxyethylated chain lengths

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ABSTRACT

A novel automated system for the analysis of polyoxyethylated (POE) non-ionic surfactants is proposed, which is capable of providing information on both hydrophobic and POE chain lengths. A polystyrene–divinylbenzene copolymer gel is effective for the hydrophobic chain analysis because the separation is not influenced by the distribution of POE chains. On the other hand, a K^+-form cation-exchange resin is effective for elucidating the distribution of POE chains. An automated system was constructed by combining these two separation methods, and was applied to the analysis of the distributions of hydrophobic and POE chains in a commercial Brij 35.

INTRODUCTION

Polyoxyethylene (POE) chains play important roles in surface-active compounds, *e.g.*, POE chains are utilized to vary HLB (hydrophile–lipophile balance) values, wetting abilities, solubility in water, critical micelle concentration, Kraft points of ionic surfactants and cloud points of non-ionic surfactants [1]. According to statistics in the USA [2], the production of non-ionic surfactants comprised 24% of the total surfactant sector in 1989, and POE ethers represented more than 70% of the non-ionic surfactant production. The production and consumption of non-ionic surfactants appear to continue to increase because of the increasing variety of industries that require surfactants.

The analysis of POE surfactants has thus become increasingly important, and has been treated in a number of papers. Usually, non-ionic surfactants are polydisperse with regard to both the POE chain and the hydrophobic chain lengths [1]. It is obvious that methods which are capable of providing information on both POE and hydrophobic moieties are necessary. Chromatography is therefore a suitable choice, and has been extensively employed for such analyses. Among gas [1], liquid [1,3–16] and supercritical fluid chromatographic methods [17,18], high-performance liquid chromatography (HPLC) is preferred mode because of the simple instrumentation and easy handling, even though the separation performance is not necessarily better than with the other methods.

Although reversed-phase or normal-phase chromatography has been usually utilized for the separation, and proved to be efficient in some instances [3–14], there remain some problems especially in the separation in terms of POE chain lengths; it is difficult to separate POE chains having many (*e.g.* > 30) oxyethylene (OE) units from each other; the separation conditions are different for each sample, and the resolution is poor when the compound has a long hydrophobic chain. Therefore, many repeated trial and error experiments are necessary until an acceptable separation is achieved.

In previous work, a novel method for the separation in terms of POE chain lengths was devel-

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oped [15,16], wherein a cation-exchange resin was used in the alkali metal ion form. In this method, POE forms a complex with a counter cation in an ion-exchange resin, and is separated according to the complex formation ability; the longer the POE chain, the stronger is the complexation ability. Although hydrophobic chains also affect the retention, the effect is so marginal that the same separation conditions are applicable to different samples. If this method is efficiently combined with other methods capable of recognizing differences in the hydrophobic chain lengths, it will be useful in the analysis of non-ionic surfactants.

EXPERIMENTAL

The chromatographic system, illustrated in Fig. 1, was composed of Tosoh computer-controlled pumps CCPD (P1) and CCPM (P2), which were used for the separation in terms of hydrophobic chain lengths and POE chain lengths, respectively, an SPT-3-202U pump (Nippon Seimitsu Kagaku) in the concentration process, a CO-8000 column oven (Tosoh) and UV-8000 (Tosoh) and 875-UV (JASCO) UV detectors (D). A 150 mm × 4 mm I.D. stainless-steel column packed with MCI gel CHP-5C (Mitsubishi Kasei) and a 50 mm × 4.6 mm I.D. TSK-gel IC-Cation-SW column were used as separation columns. The former column (C1), which contains styrene–divinylbenzene copolymer gel, was utilized for the separation according to the hydrophobic chain lengths, whereas the latter (C2), which contained a cation-exchange resin in the potassium form, was used in POE chain analyses. A PTFE concentration column (C3) (5 mm × 2 mm I.D.) was also packed with MCI gel CHP-5C.

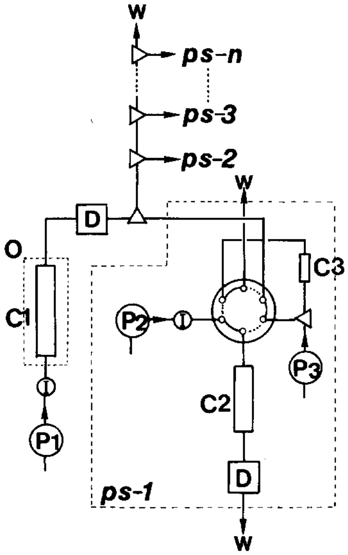

Fig. 1. Schematic diagram of the system for the analysis of POE surfactants. C1, C2 = Separation columns; C3 = concentration column; P1, P2, P3 = pumps; D = UV detector; I = injection valve; W = waste.

Methanol of analytical-reagent grade was used after distillation. Acetonitrile of HPLC grade was purchased from Wako. POE(9) dodecyl ether [POE(9)D, where the number in parentheses denotes the average number of oxyethylene units] and POE(20) hexadecyl ether [POE(20)H] were gifts from Nikko Chemicals. POE(10) octadecyl ether [POE(10)O] and POE(20)O were purchased from Sigma. Other reagents were of analytical-reagent grade and used as received, unless stated otherwise.

According to the literature [6], terminal hydroxyl groups in POE were esterified by reaction with 3,5-dinitrobenzoyl (DNB) chloride in dry benzene. This derivertization facilitated the gradient separation and enhanced the detection sensitivity.

RESULTS AND DISCUSSION

Separation in terms of hydrophobic chains

The separation of non-ionic POE surfactants in terms of the hydrophobic chain length will be of primary importance. This procedure should not be affected by the distribution of POE chains. Although one might think that this separation could be performed under the usual reversed-phase conditions, it was not easy because reversed-phase stationary phases can usually differentiate POE chain lengths to some extent; peak broadening due to the distribution of POE chains was observed. Most published work has been focused on the distribution of POE chains, and very little attention has been paid to hydrophobic chain analysis [3,4].

Kudoh [3] reported that acetone–water was a suitable mobile phase for separations in terms of hydrophobic chains, and that POE chain lengths did not affect the retention times when acetone–water (9:1) was used as a mobile phase. Although systematic studies were not shown, the balance between water and acetone concentrations seems to be important in eliminating the influence of the POE chain distribution. However, acetone is not in general a preferred solvent for UV detection.

Melander *et al.* [5] reported that the dependence of the retention on the number of OE units is reversed at a particular concentration of an organic solvent. They analysed this result with a two-state model; a POE chain exists as a zig-zag and a helix form in a mobile phase, and both the two have different retention abilities. Their results imply that a compound containing polydisperse POE chains can be eluted as a single peak regardless of the POE chain lengths, with a mobile phase of appropriate organic solvent content. However, as terminal groups and mobile phase compositions affect the equilibrium between the zig-zag and helix forms, their results are not directly applicable to the present case. Also, the best resolution is not necessarily obtained under the conditions, where all POE oligomers (or polymers) are simultaneously eluted.

In this study, C_8 and C_{18}-bonded silica gel and styrene–divinylbenzene copolymers were tested as stationary phases. DNB-POE was eluted at acceptable retention times when either C_8 or C_{18}-bonded phase was used with organic solvent (methanol, acetonitrile, tetrahydrofuran, etc.)–water (9:1) as mobile phases. However, in all instances, peak broadening according to the distribution of POE chains was observed. In contrast, MCI gel CHP-5C gave relatively narrow peaks and good separations when acetonitrile–methanol mixtures (1:5–1:4) were used as mobile phases. Table I gives the retention times of DNB-POE(10)O and DNB-POE(20)O as a function of temperature. The difference in the retention times becomes smaller with increase temperature, and is almost negligible at 43.8°C.

TABLE I

CHANGES IN THE RETENTION TIMES OF DNB-POE(10)O AND DNB-POE(20)O WITH TEMPERATURE

Retention times were measured on MCI gel CHP-5C with acetonitrile–methanol (1:4) mobile phase.

Temperature (°C)	Retention time (min)	
	POE(10)O	POE(20)O
14.0	40.5	37.0
23.0	25.6	25.0
33.6	16.8	16.0
43.8	11.3	11.2

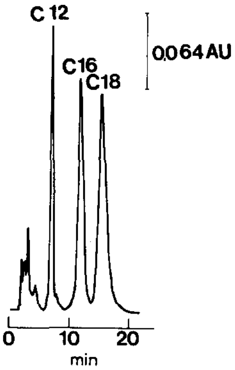

Fig. 2. Typical separation in terms of hydrophobic chain lengths. Column temperature, 43.8°C; mobile phase, acetonitrile–methanol (1:5); detection at 254 nm. Other conditions are given in the text.

Fig.2 shows the separation of DNB-POE adducts of dodecyl, hexadecyl and octadecyl alcohols under the condition mentioned above.

Separation in terms of POE chain lengths

Our previous work indicated that the separation according to POE chain lengths on a K^+-form cation-exchange resin is sensitive to the temperature because the complexation process is exothermic [16,19]. Although then use of a thermostated system is essential, shifts of peak position due to changes in the column temperature were negligible for the experiments at room temperature (*ca.* 15°C).

As the retention of POE increased exponentially with increasing number of OE units, gradient elution should be considered. The retention of POE can be reduced by adding a solvent unfavourable for the resin phase complexation or by adding a salt to the methanolic mobile phase. Both water and acetone, for example, are solvents unfavourable for the resin phase complexation of POE, because the strong donor ability of water towards alkali metal ions and the low dielectric constant of acetone interfere with the complexation in the resin phase. However, the solubility of DNB-POE was lowered considerably in a solvent containing water, and acetone interfered with the UV detection of DNB-POE. In the latter instance, addition of a salt was therefore selected.

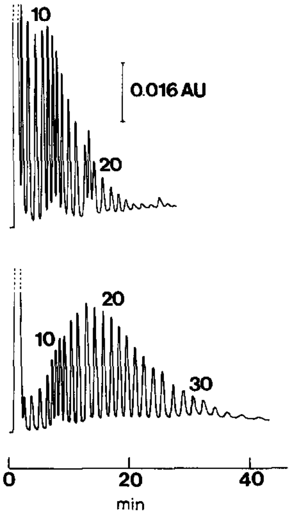

Fig. 3. Typical separation in terms of POE chain distribution of POE(10)O (top) and POE(20)O (bottom). Mobile phase, methanol (0–3 min) to 7.5 mM KCl in methanol (30 min). Other conditions are given in the text.

TABLE II

RECOVERIES (%) OF DODECYL ALCOHOL ADDUCTS OF DNB-POE ON A CONCENTRATION COLUMN

The organic solvent and water flow through the concentration column for 10 min after loading a sample.

n[a]	Flow-rate of water (ml/min)			
	1.63	2.28	3.42	5.7
7	51.0[b]	63.7	97.4	97.4
8	50.1	66.4	97.4	95.4
9	50.3	66.9	102	95.9
10	51.9	66.8	99.5	96.0
11	50.6	66.1	94.4	98.0
12	50.1	65.6	93.7	93.7
13	51.3	65.4	94.1	92.7
14	51.9	65.1	94.4	102
15	54.7	51.6	97.1	96.4

[a] Number of oxyethylene units.

[b] The flow-rate of acetonitrile–methanol (1:4) was kept at 1 ml/min.

POE forms a complex with a cation added to the mobile phase, and the retention is reduced as a function of the concentration of the cation. It was confirmed in previous work [20] that POE complexes were not retained on the ion-exchange resin because of the lack of effective complexation sites and energetically unfavourable conformational changes of POE chains [19]. As the complexation ability in solution phases is enhanced with an increasing number of OE units, the retention of longer POE is more effectively reduced by adding a salt. Fig.3 shows results of the analysis in terms of the distributions of POE chains in POE(10)O and POE(20)O. Peaks were identified by comparing the retention times with those of monodisperse compounds. More than 30 oligomers are separated within 1 h.

Preliminary study for constructing an automated system

To construct an automated system for the nonionic surfactant analysis, the above two methods should be effectively combined. For such a purpose, column switching will be useful. However, as peaks obtained from the separation in terms of the hydrophobic chain length are not sharp enough because of the effect of the distribution of POE chains, column switching will cause marked peak broadening or poor detectability and thus low reliability in the POE analysis step. A use of a concentration column was therefore considered.

The same stationary phase as used in the first separation step was packed in a concentration column. Effluents from the first separation column were mixed with water and passed through the concentrator. Table II lists the recoveries of DNB-POE (9)D eluted from the first separation column with acetonitrile–methanol (1:4) as the mobile phase. Flow-rates of water mixed with the effluents from the first separation column were varied under a constant flow (1 ml/min) of the effluents. When the ratio of the flow rates reaches 3.42, the recovery becomes almost 100% regardless of POE chain lengths.

Automated system

The proposed automated system is illustrated in Fig. 1. Hydrophobic chain analyses are performed with pump P1 and separation column C1, and POE analyses with P2 and C2. Pump P3 delivers water to the concentration column, C3. Effluents from C1 flow down to the concentrator through a three-way valve. After the concentration is completed, the POE analysis starts by rotating the centre six-way valve. To desorb analytes completely from the concentrator, the injection of 100 μl of acetonitrile was necessary; this can be done through an injection valve (I). As can be seen in Fig. 3, typical POE analysis takes 1 h. If we use only one POE analysis system (denoted ps-1 in Fig.1), this system should be repeatedly operated; it takes several hours until all analyses are completed. If we can prepare several POE analysis systems (ps-2, ps-3, ..., ps-*n*) such a time-consuming procedure can be avoided; that is, the peak eluted second from C1 is analysed with ps-2, that eluted third with ps-3, etc. Fig. 4 shows results of analysis of Brij 35, which is the tradename of POE(23)D, according to the present concept. The instrumentation available in our laboratory was insufficient to construct several POE analysis systems. The analysis by ps-1 was therefore repeated until all analyses were completed; four chromatograms in which POE chains were separated according to the difference in the chain lengths were obtained with the same system. The chromatogram on the left-hand side shows the separation in terms of hydrophobic chain length; injection peaks and peaks corresponding to the elution of C_{12}, C_{14}, C_{16}, and C_{18} appeared. Although the POE analysis could not be done for C_{18} because of the extremely low concentration, POE distributions of C_{12}, C_{14} and C_{16} components are analysed as shown on the right-hand side of Fig. 4. Also, injection peaks involved the elution of di-DNB-PEG and mono-DNB- PEG, which show different retention abilities on the cation-exchange resin and thus result in the peak splittings in the chromatogram.

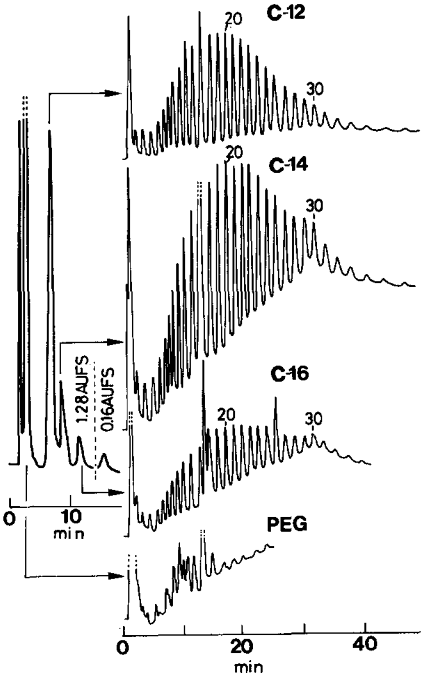

Fig. 4. Results of the analysis of Brij 35. Chromatographic conditions are given in the text and Figs. 2 and 3. Detection, 0.16 a.u.f.s. for DNB-POE(*n*)D and 0.04 a.u.f.s. for others in POE separation steps.

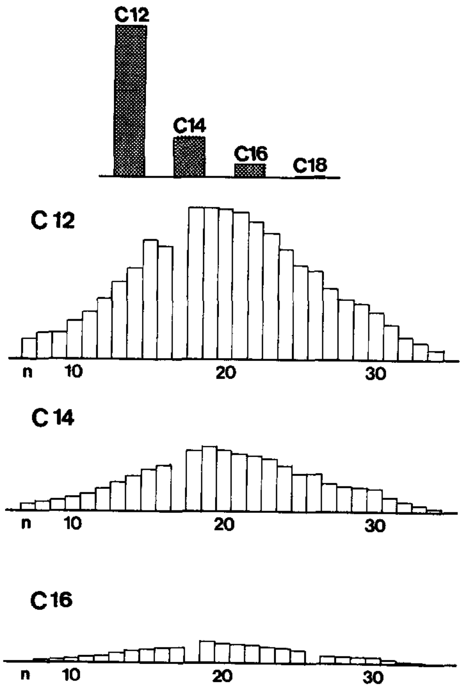

Fig. 5. Relative concentrations calculated from results in Fig. 4. The histogram at the top shows relative concentrations according to hydrophobic chains. The others are for POE chain lengths. The same absorption coefficient for all DNB-POE molecules was assumed.

The absorption coefficients may vary for different DNB-POE molecules. In such a case, the peak areas do not reflect the concentrations of the DNB-POE oligomers. However, Desbene *et al.* [6] stated that the absorption coefficient is the same for all DNB-POE molecules. Fig. 5 shows the relative concentrations obtained for Brij 35 by assuming the same absorption coefficient for all DNB-POE molecules.

The average number of OE units contained in this surfactant was estimated to be 21.3.

In conclusion, non-ionic surfactants containing POE have been effectively analysed by the proposed method, which provides information both on the hydrophobic chain and the POE chain lengths. This POE analysis method has the weak point that compounds having less than six OE units cannot be separated. However, the uses of such surfactants are limited owing to their low solubility in water. If it is necessary to analyse such short POE chains, a reversed-phase stationary phase can be used instead of the present cation-exchange resin.

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