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Separation and characterization of octylphenol ethoxylate surfactants used by reversed-phase high-performance liquid chromatography on branched fluorinated silica gel columns

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Abstract

The separation and characterization of octylphenol ethoxylate surfactants were carried out by reversed-phase high-performance liquid chromatography on branched fluorinated silica gel columns. For Triton X-100, simultaneous separation of octylphenol ethoxylate oligomers, positional isomers of octylphenyl group and butylphenol ethoxylate oligomers was achieved. These oligomers were completely separated and identified by means of MS spectra. Ethoxylated oligomers are eluted in the sequence from small to large oligomers. Fifty-five oligomers of Triton X-405 could be separated by using gradient elution. To separate octylphenol ethoxylate surfactant, non-end-capped branched fluorinated silica gel columns were superior to end-capped columns. The relationship between ln k' and methanol concentration was linear, indicating that branched fluorinated silica gel columns were operating in the reversed-phase mode. As Van 't Hoff plots of capacity factor for all oligomers gave straight lines, the equilibrium of conformation for the ethylene oxide chain might lay to one side of either zigzag or meander conformers.

Keywords: Fluorinated silica gel columns; Stationary phases, LC; Octylphenol ethoxylates; Ethoxylates; Surfactants

1. Introduction

Non-ionic surfactants of the alkylphenol polyethoxylate type are widely used in both domestic and industrial detergent formulations. Commercial ethoxylated alkylphenol surfactants usually contain complex mixtures of compounds that have isomerism in the alkyl chain and in the position of substitution, oligomers with widely different ethylene oxide numbers and free polyethylene glycol (PEG). It is important to identify and quantify the respective oligomers and isomerism of ethoxylated surfactants for study of the reaction mechanism or application.

Various chromatographic procedures such as thin-layer chromatography [1,2], gas chromatography [3,4], supercritical fluid chromatography [5] and

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high-performance liquid chromatography (HPLC) have been developed for the separation of the non-ionic surfactants into their different oligomers. HPLC is the most ideal technique for the evaluation of the product composition of non-ionic surfactants [6], because information about the distribution of ethoxymers, the average degrees of ethoxylation [7], the hydrophobic moiety [8] and the PEG content [9] of the sample can be readily obtained.

Separations of ethoxylated non-ionic surfactants have been attempted by HPLC with both normal-phase [10–16] and reversed-phase systems [17–25]. In normal-phase HPLC, the ethoxylated oligomers are separated according to increasing number of ethylene oxide units. The columns used for separation of ethoxylated oligomers have packings as bare silica gel [10–12] and bonded stationary phases of amino [14], diol [15] or cyano types [16]. However, normal-phase HPLC has the drawback that alkyl chain homologues with common degrees of ethoxylation cannot be separated. Reversed-phase HPLC on octyl or octadecyl silica gel (ODS) columns allows the hydrophobic moiety of the surfactant to be investigated [22,23]. Porous graphitic carbon column [24] and trimethylsilane coated silica gel column [25] partially separated ethoxylated oligomers. Kudoh et al. [26] reported the separation of *n*-alkylphenol ethoxylate used with fluorescent derivatization on ODS columns, but baseline separation of alkylphenol ethoxylate without derivatization was not achieved.

We have reported the syntheses and characterization of the branched polyfluoroalkylsilane (BFS) coated silica gel columns under the trade name of Fluofix [27,28]. The structure of the silylation reagent of BFS is shown in Fig. 1. BFS column is operating in the reversed-phase mode [29] and shows superior separations for diastereomers, geometrical isomers, polyphenol, and structural isomers of including fluorine atom. The separation of non-ionic surfactants on the fluorinated columns has not been reported. We have attempted to analyze non-ionic surfactants such as octylphenol ethoxylate surfactants.

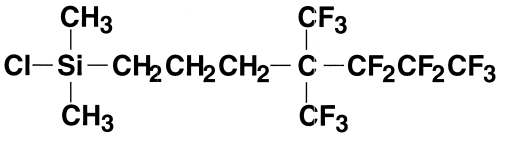

Fig. 1. Molecular structure of the silylation agent on branched polyfluoroalkylsilane coated silica gel.

In this paper we describe the separation and characterization of branched octylphenol ethoxylates in accordance with the distribution of their ethoxymer by reversed-phase HPLC on BFS columns.

2. Experimental

2.1. Chemicals

HPLC-grade methanol and water were purchased from Kanto (Tokyo, Japan). Uracil was purchased from Wako (Osaka, Japan). Octylphenol ethoxylate with two different molecular size distributions were purchased from Pierce (IL, USA) under the trade names of Triton X-100 and 405. According to the manufacturer, the average ethoxylation numbers are 9.6 and 40, respectively. These purchased samples were 10% aqueous solution. The solution of 0.020 g/ml of octylphenol ethoxylate in methanol was prepared.

2.2. Column

Two commercially available BFS columns, Fluofix 120N and 120E (NEOS, Kobe, Japan) which were synthesized according to a previously reported method using high-purity silica gels (average particle diameter 5 μm and average pore diameter 12 nm) were used [27]. Fluofix 120E (250×4.6 mm I.D.) was end-capped with trimethylsilane while Fluofix 120N (250×4.6 mm I.D.) was not end-capped.

2.3. HPLC measurements

2.3.1. LC–UV

The LC–UV system consisted of a Waters Module-1 plus (Milford, MA, USA) with a high-

performance pump, a variable-wavelength UV detector, an auto-sampler and a column temperature controller, combined with a microcomputer controlled with a Waters millennium chromatographic processing software. The flow-rate was fixed at 1 ml/min and the UV detector was set at 280 nm. The injection volume was 10 μl. The retention time of each sample was determined by three consecutive injections. Uracil was used for estimation of the column void time t_0 in minutes. The capacity factors (k') were obtained from $(t_r - t_0)/t_0$, where t_r is the retention time of the solute in minutes. Numbers of theoretical plate (N) were calculated by the 4σ method and asymmetry factors (A_s) were calculated at 10% of peak height with the following calculation method.

$$A_s = a/b$$

where a is the front width of the peak at 10% of peak height and b is the back width of the peak at 10% of peak height.

2.3.2. LC–MS

The liquid chromatograph was a Hewlett-Packard 1090L (Palo Alto, CA, USA). Mass spectra were obtained by a JMS-LX2000 double focussing mass spectrometer (JEOL, Tokyo, Japan) with a JEOL JMA-DA7000 data system connected to an LC system by a frit-fast atom bombardment (FAB) interface. A block diagram of the frit-FAB interface is shown in Fig. 2. The xenon particle energy was 4 keV, the emission current 5 mA, the accelerating voltage 3 kV and the magnetic field scanning range m/z 50–1500 in 3 s per scan. The flow-rate was 1 ml/min and the injection volume was 20 μl. After passing through the UV detector, the eluent from the column was mixed with a 1% glycerol in methanol

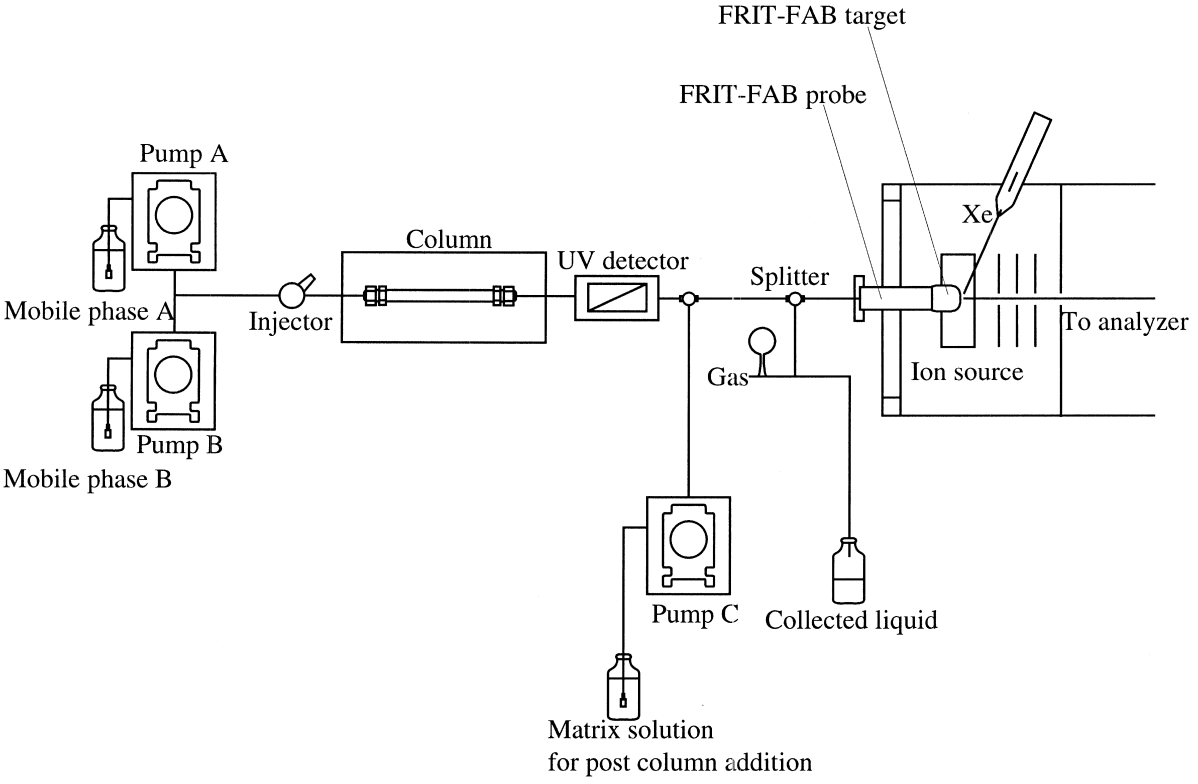

Fig. 2. Schematic diagram of the liquid chromatograph and frit-FAB interface.

solution at 0.3 ml/min by the post-column method [30].

3. Results and discussion

3.1. Separation of octylphenol ethoxylated oligomers

For Triton X-100, the best overall separation was achieved with a methanol–water (50:50) mobile phase, the resulting chromatogram is shown in Fig. 3. Triton X-100 is completely separated in the ethoxylated oligomers by use of the non-end-capped BFS column. On this separation, three types of ethoxymer's distribution are detected. The first type of the distribution appeared from 15 to 30 min (B5–B14) and the second one from 60 to 200 min (M3–M16). The third one (I7–I11) overlapped with the second distribution region.

Fig. 4 shows the chromatogram of Triton X-100 using end-capped BFS under the same analytical conditions as non-end-capped BFS. The retention times on the end-capped BFS is longer than that on the non-end-capped BFS. The chromatogram has so large tailing peaks that large-size oligomers separate incompletely. Fig. 5 shows the relationship between N or asymmetry factor A_s and ethoxylate number. N decreases with increasing ethoxylate number on both end-capped and non-end-capped BFS. N on non-end-capped BFS is larger than that on end-capped BFS. A_s increases with increasing ethoxylate number on end-capped columns, but on non-end-capped column A_s of the ethoxylate having over 8 EO units is small, about 2. Obviously, non-end-capped BFS can separate non-ionic surfactants such as octylphenol ethoxylate better than end-capped BFS.

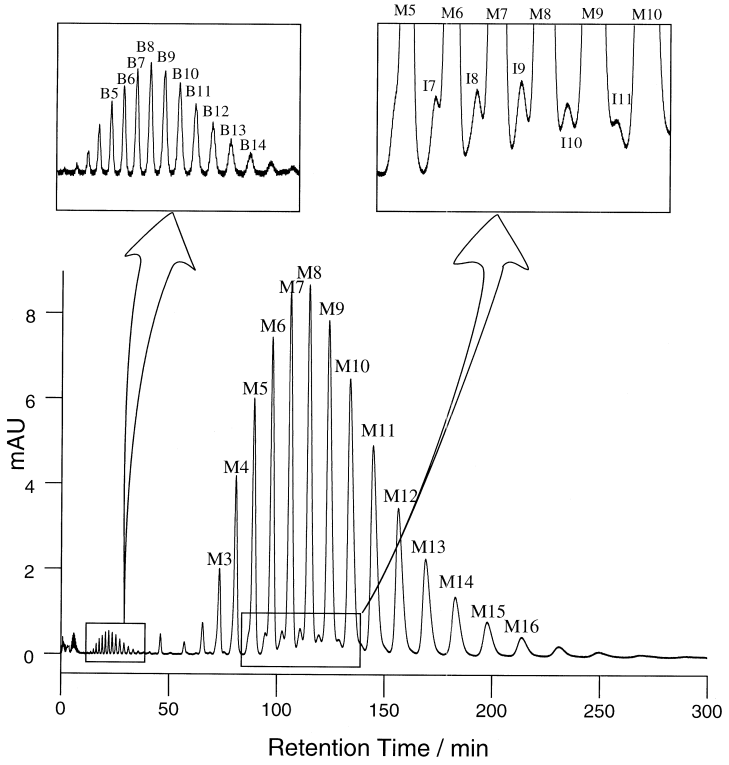

Fig. 3. Separation of Triton X-100 commercial surfactant. Chromatographic conditions: non-end-capped BFS (250×4.6 mm I.D.); flow-rate, 1 ml/min; mobile phase, methanol–water (50:50); detection, UV at 280 nm; temperature, 40°C; sample, 0.020 g/ml of Triton X-100 in methanol; injection volume, 10 μl.

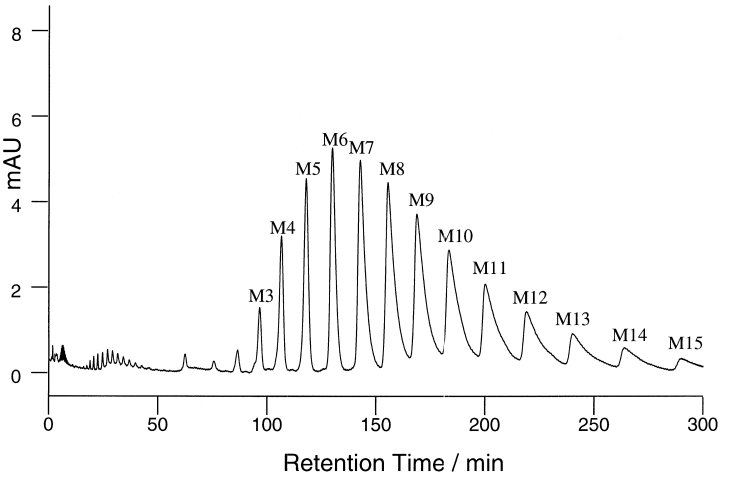

Fig. 4. Separation of Triton X-100 commercial surfactant. Chromatographic conditions: end-capped BFS (250×4.6 mm I.D.); flow-rate, 1 ml/min; mobile phase, methanol–water (50:50); detection, UV at 280 nm; temperature, 40°C; sample, 0.020 g/ml of Triton X-100 in methanol; injection volume, 10 μl.

On non-end-capped BFS, octylphenol ethoxylated oligomers elute in the order of increasing size of oligomers. We have attempted to separate higher ethoxylated non-ionic surfactants such as Triton X-405. Fig. 6 shows the chromatogram of Triton X-405 and the gradient profile. Fifty-five oligomers of Triton X-405 are detected at 280 nm. Each ethoxylate number is assigned by the result of simultaneous analysis of the mixture of Triton X-100 and 405. It is indicated that the large size oligomers can be clearly separated by using reversed-phase HPLC on BFS. This method can be applied to control the

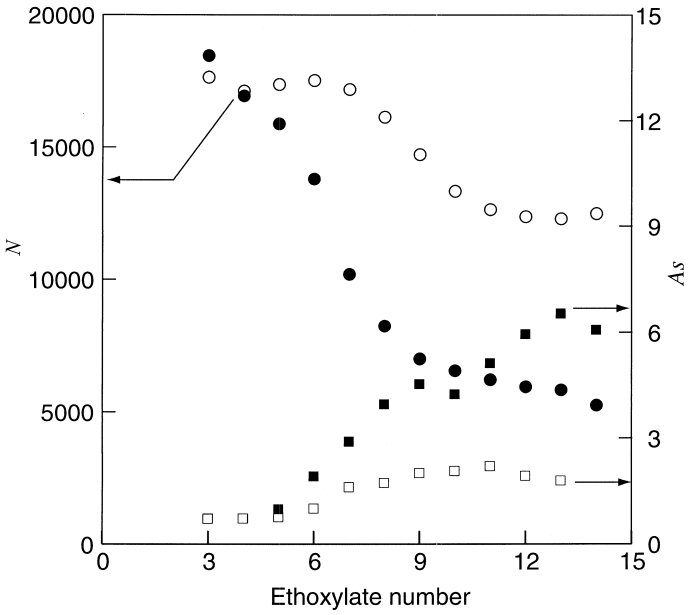

Fig. 5. Plots of (N) and (A_s) against ethoxylate number. Symbols: (○) N on non-end-capped BFS, (●) N on end-capped BFS (□) A_s on non-end-capped BFS, (■) A_s on end-capped BFS.

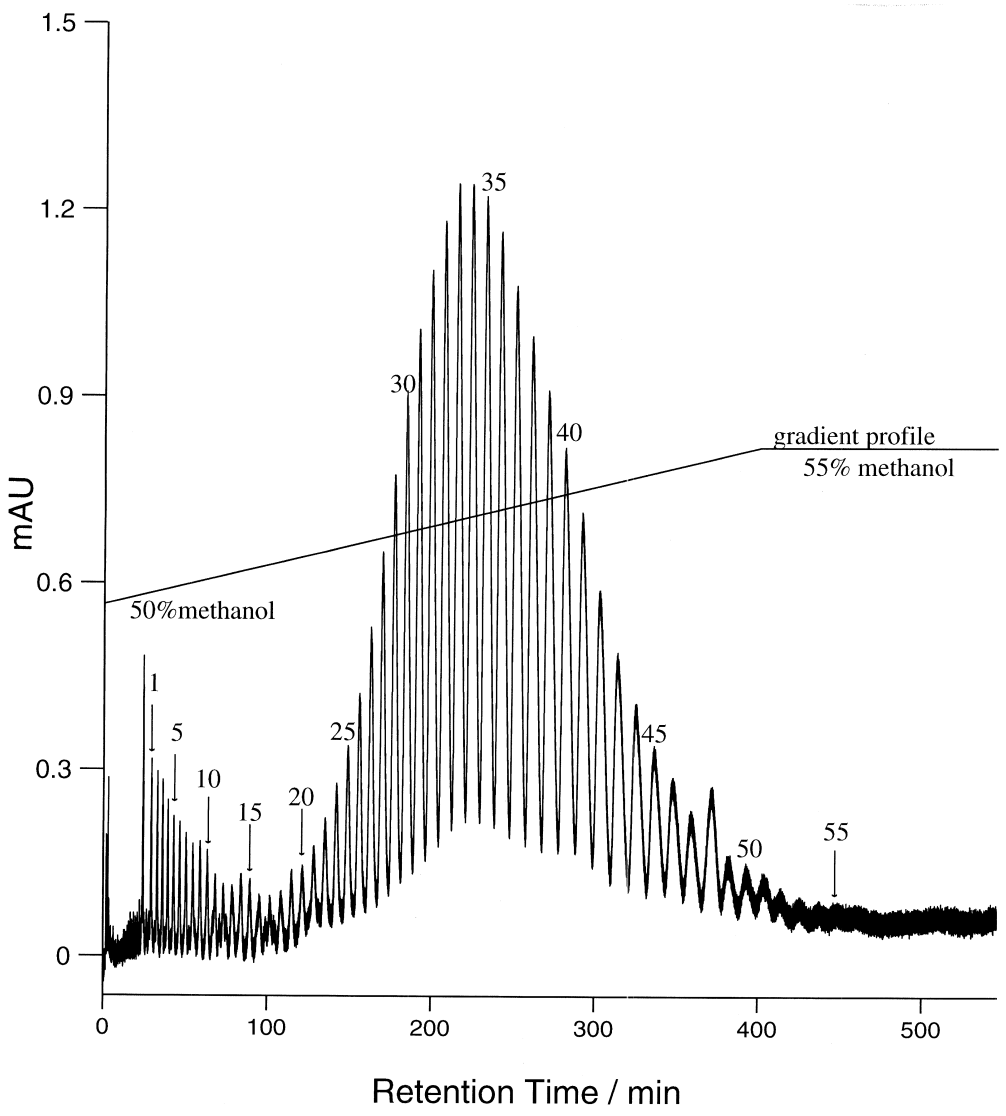

Fig. 6. Separation of Triton X-405 commercial surfactant. Chromatographic conditions: non-end-capped BFS (250×4.6 mm I.D.); flow-rate, 1 ml/min; mobile phase, linear gradient from methanol–water (50:50) to methanol–water (55:45) in 400 min; detection, UV at 280 nm; temperature, 40°C; sample, 0.020 g/ml of Triton X-405 in methanol; injection volume, 10 μl.

quality of industrially produced non-ionic surfactants.

We have examined fast separation of Triton X-100. Generally retention time is decreasing with increasing temperature and concentration of organic solvent in the mobile phase in reversed-phase HPLC. A short column length also helps in reducing the retention time. Fig. 7 shows the chromatogram of Triton X-100 at 70°C on BFS of which the column length is 150 mm. Octylphenol ethoxylated oligomers are separated within 65 min. It is necessary to adjust suitable water content in the mobile phase for rapid separation. When the water content is under about 40%, clearly separation cannot be accom-

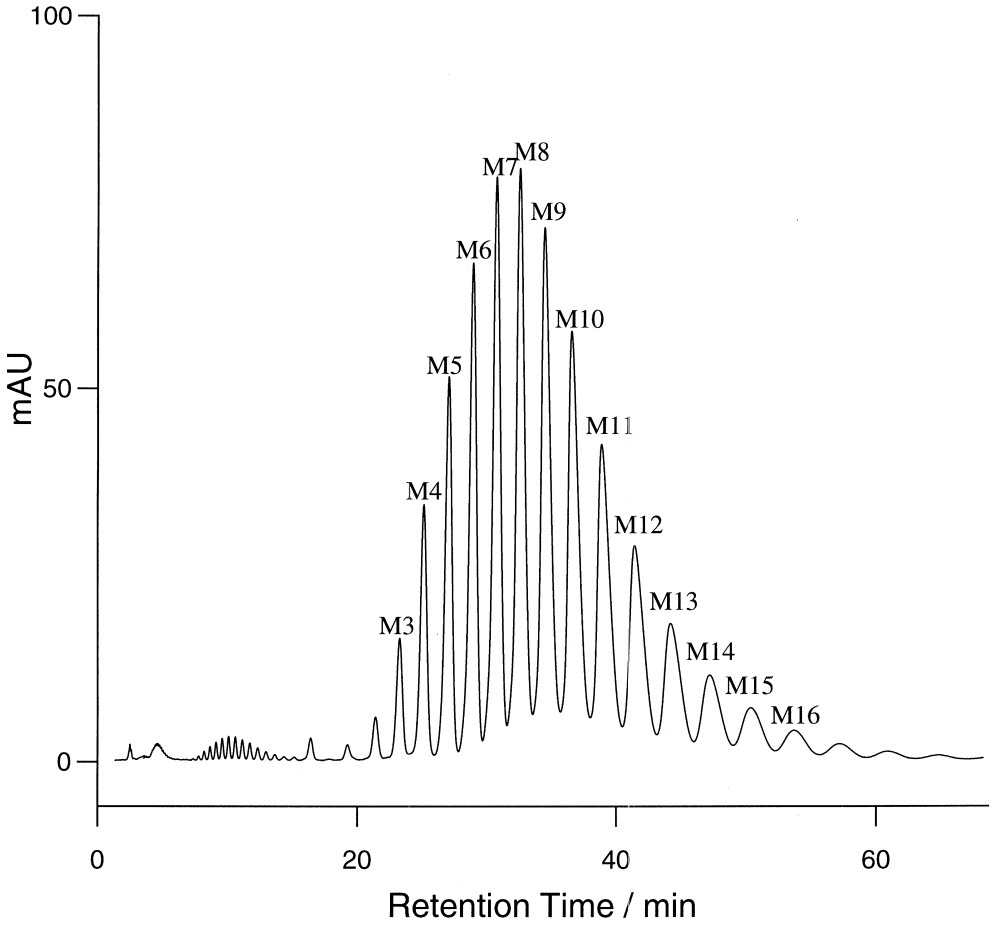

Fig. 7. Separation of Triton X-100 commercial surfactant. Chromatographic conditions: non-end-capped BFS (150×4.6 mm I.D.); flow-rate, 1 ml/min; mobile phase, methanol–water (50:50); detection, UV at 280 nm; temperature, 70°C; sample, 0.020 g/ml of Triton X-100 in methanol; injection volume, 10 μl.

plished. The rapid separation of the main components was attained by a short column length and any increasing temperature.

3.2. Influence of water contents in mobile phase and temperature

The dependence of ln k' of octylphenol ethoxylated oligomer (M3~14) on the methanol concentration (v/v) at 40°C is shown in Fig. 8. The ln k' linearly decreases with increasing concentration of methanol in the mobile phase. That is the typical tendency in reversed-phase HPLC [31]. It is indicated that BFS is operating in the reversed-phase mode during analyses of octylphenol ethoxylated oligomers. As these linear lines are not parallel, the resolution of each oligomer increases with increasing water content.

In reversed-phase HPLC, the capacity factor usually decreases with increasing temperature; then the Van 't Hoff plot is linear [32,33]. Fig. 9 shows Van 't Hoff plots of the capacity factor of octylphenol ethoxylate on BFS. The plots of all oligomers give straight lines. There are a few reports about Van 't Hoff plots for alkylphenol ethoxylated oligomers on reversed-phase HPLC. Melander et al. [34] have

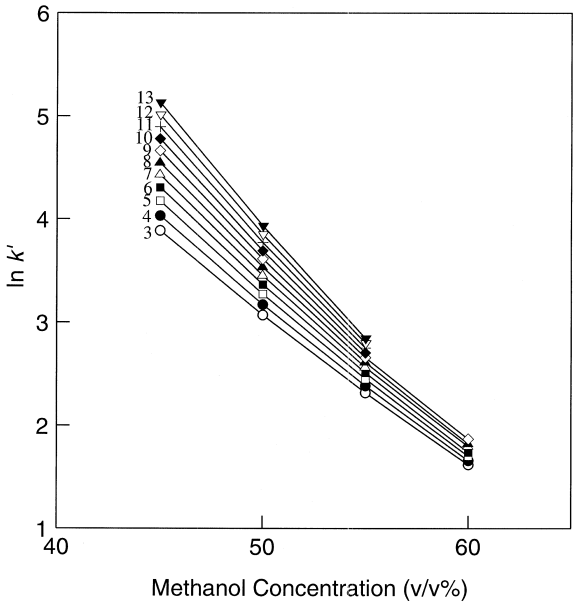

Fig. 8. Plots of the logarithm of the capacity factor against methanol content of water–methanol solvent mixture. Digits in the graph are ethoxylate number of Triton X-100.

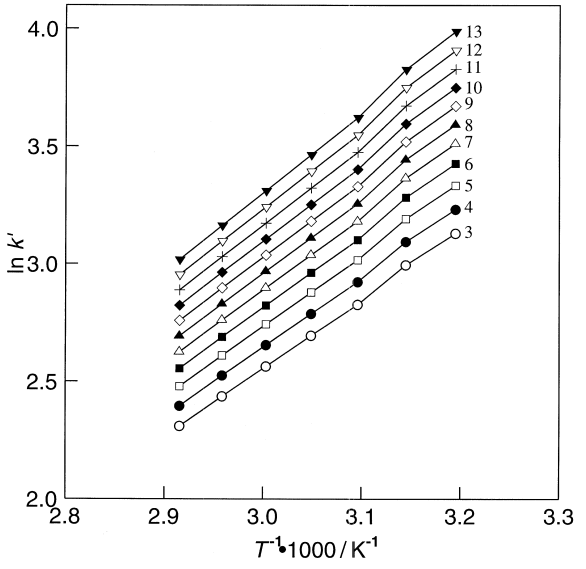

Fig. 9. Van 't Hoff plots of the capacity factors corresponding with each ethoxylated number in Triton X-100. Chromatographic conditions: non-end-capped BFS (250×4.6 mm I.D.); flow-rate, 1 ml/min; mobile phase, methanol–water (50:50); detection, UV at 280 nm. Digits in the graph are ethoxylate number of Triton X-100.

reported on phenyl ethoxylated oligomers in an acetonitrile–water system. In this case the plots are curved because of two conformers. For PEG the existence of two conformers called zigzag and meander is well known [35]. At high and low degrees of polymerization of the PEG the chain assumes the compact dihedral helical structure (called meandering form) and an extended open coil (called zigzag form), respectively. It may be considered that the linearity of Van 't Hoff plots is attributed to the existence of a single conformation.

3.3. Identification of separated peaks used by MS detection

The surfactants of octylphenol ethoxylate are prepared according to Fig. 10 [36]. Diisobutylene is obtained by treating *tert.*-butanol with 50% sulfuric acid (step 1) and is purified by distillation from mixture of isobutylene, diisobutylene and triisobutylene. Although diisobutylene has two types of isomeric structure, there is only one structure of the product for alkyl group made by condensation of diisobutylene with phenol (step 2). Diisobutylphenol has positional isomers such as the *ortho* and *para* derivatives. According to the manufacturer, the major compound of Triton X-100 is the *para* derivative. The surfactants of the Triton X series are obtained by reaction with ethylene oxide (step 3).

Separated peaks of three distributions, as shown in Fig. 3, can be identified by means of FAB-MS. For the mass spectrum of M9, the following quasi-molecular ions as well as fragment ions are observed; m/z 89, 133, 531 and 603 which correspond to $[\text{diethylene oxide}+\text{H}]^+$, $[\text{triethylene oxide}+\text{H}]^+$, $[\text{M-C}_5\text{H}_{11}]^+$, $[\text{M}+\text{H}]^+$, where M represents the molecular species. Each m/z value corresponds to the protonated molecule. The peak of M9 is identified to be *para*-octylphenol nona-ethylene glycol. Other peaks from M3 to M16 are identified in the same manner as summerized in Table 1. The fragment ion peak of m/z 89 and 133 are observed for all peaks of distribution M and I. The distribution I (I7–I11) is overlapped with the region of distribution M (M3–M16). The molecular ion peak of I9 is the same as M9 of 603. The octyl group isomer does not exist as shown in Fig. 10. *para*-Octylphenol containing a small amount of *ortho*-isomer is produced

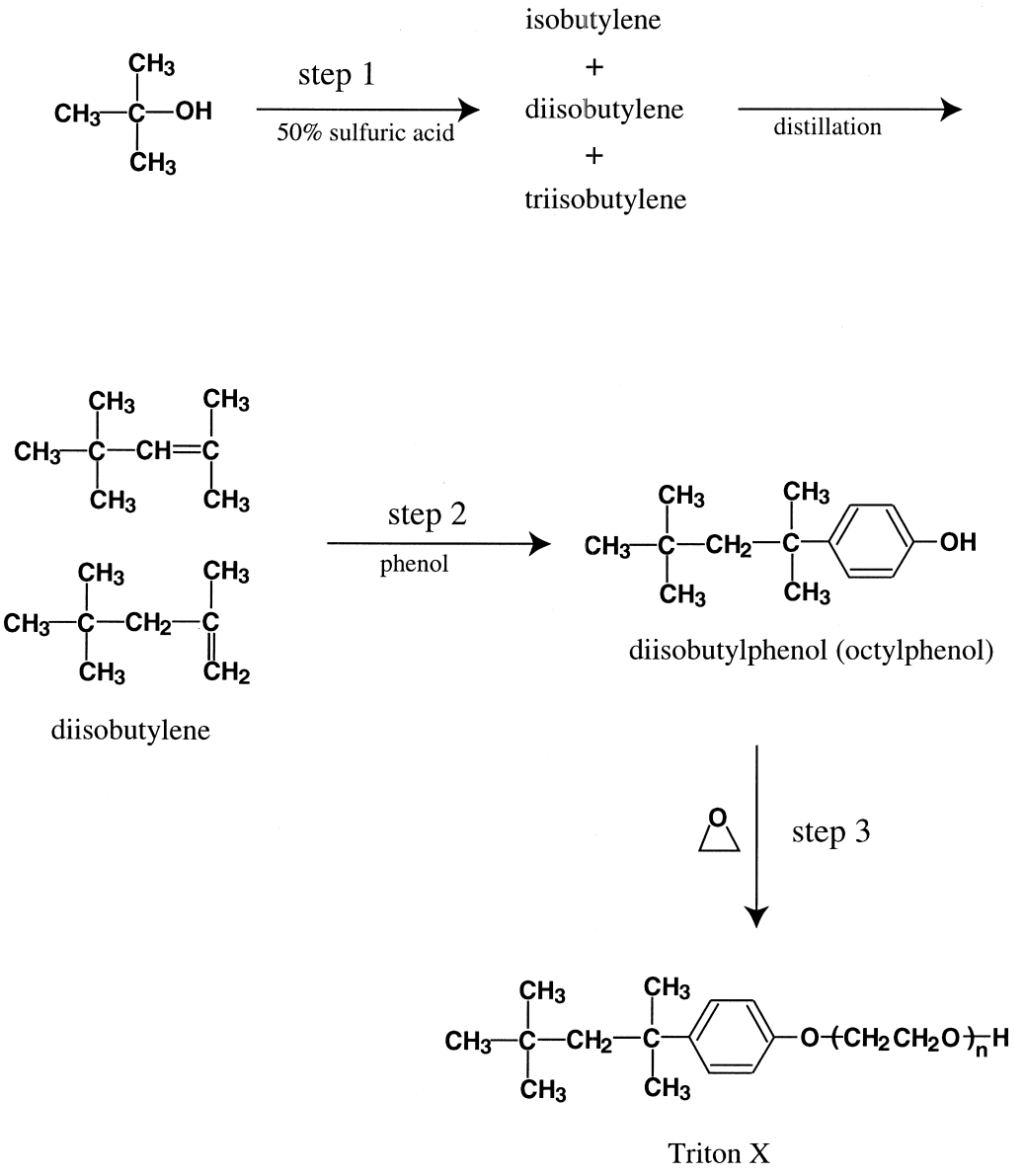

Fig. 10. Synthetic procedure of Triton X.

with that synthetic procedure. At the next step a small amount of *ortho*-isomer is also ethoxylated. Therefore, the small peaks in Fig. 3 are presumably *ortho*-octylphenyl ethoxylate. The peak of I9 can be identified as *ortho*-octylphenol nona-ethylene glycol. Each of the peaks from I7 to I11 is identified in the same manner.

The distribution B (B5–B14) in Fig. 3 is detected by UV detection at 280 nm. Saturated hydrocarbon, double bond and polyethylene glycol part without an aromatic ring, as shown in Fig. 10, do not absorb light at about 280 nm. Each component of distribution B must include an aromatic ring showing absorption at 280 nm. The molecular ion peak of B9 is observed at m/z 547. Diisobutylene may contain contaminated isobutylene despite the distillation in

Table 1
The m/z value and isolated molecule for three distributions[a]

Peak name	Fragment ion peaks	Molecular ion peak
M3	$89[(EO)_2+H]^+$, $133[(EO)_3+H]^+$, $267[C_3H_6\text{-}C_6H_4\text{-}O\text{-}(EO)_3H]^+$	$339[p\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(EO)_3H+H]^+$
M4	$89[(EO)_2+H]^+$, $133[(EO)_3+H]^+$, $311[C_3H_6\text{-}C_6H_4\text{-}O\text{-}(EO)_4H]^+$	$383[p\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(EO)_4H+H]^+$
M5	$89[(EO)_2+H]^+$, $133[(EO)_3+H]^+$, $355[C_3H_6\text{-}C_6H_4\text{-}O\text{-}(EO)_5H]^+$	$427[p\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(EO)_5H+H]^+$
M6	$89[(EO)_2+H]^+$, $133[(EO)_3+H]^+$, $399[C_3H_6\text{-}C_6H_4\text{-}O\text{-}(EO)_6H]^+$	$471[p\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(EO)_6H+H]^+$
M7	$89[(EO)_2+H]^+$, $133[(EO)_3+H]^+$, $443[C_3H_6\text{-}C_6H_4\text{-}O\text{-}(EO)_7H]^+$	$515[p\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(EO)_7H+H]^+$
M8	$89[(EO)_2+H]^+$, $133[(EO)_3+H]^+$, $487[C_3H_6\text{-}C_6H_4\text{-}O\text{-}(EO)_8H]^+$	$559[p\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(EO)_8H+H]^+$
M9	$89[(EO)_2+H]^+$, $133[(EO)_3+H]^+$, $531[C_3H_6\text{-}C_6H_4\text{-}O\text{-}(EO)_9H]^+$	$603[p\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(EO)_9H+H]^+$
M10	$89[(EO)_2+H]^+$, $133[(EO)_3+H]^+$, $575[C_3H_6\text{-}C_6H_4\text{-}O\text{-}(EO)_{10}H]^+$	$647[p\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(EO)_{10}H+H]^+$
M11	$89[(EO)_2+H]^+$, $133[(EO)_3+H]^+$, $619[C_3H_6\text{-}C_6H_4\text{-}O\text{-}(EO)_{11}H]^+$	$691[p\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(EO)_{11}H+H]^+$
M12	$89[(EO)_2+H]^+$, $133[(EO)_3+H]^+$, $663[C_3H_6\text{-}C_6H_4\text{-}O\text{-}(EO)_{12}H]^+$	$735[p\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(EO)_{12}H+H]^+$
M13	$89[(EO)_2+H]^+$, $133[(EO)_3+H]^+$, $707[C_3H_6\text{-}C_6H_4\text{-}O\text{-}(EO)_{13}H]^+$	$779[p\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(EO)_{13}H+H]^+$
M14	$89[(EO)_2+H]^+$, $133[(EO)_3+H]^+$, $751[C_3H_6\text{-}C_6H_4\text{-}O\text{-}(EO)_{14}H]^+$	$823[p\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(EO)_{14}H+H]^+$
M15	$89[(EO)_2+H]^+$, $133[(EO)_3+H]^+$, $795[C_3H_6\text{-}C_6H_4\text{-}O\text{-}(EO)_{15}H]^+$	$867[p\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(EO)_{15}H+H]^+$
M16	$89[(EO)_2+H]^+$, $133[(EO)_3+H]^+$, $839[C_3H_6\text{-}C_6H_4\text{-}O\text{-}(EO)_{16}H]^+$	$911[p\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(EO)_{16}H+H]^+$
I7	$89[(EO)_2+H]^+$, $133[(EO)_3+H]^+$	$515[o\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(EO)_7H+H]^+$
I8	$89[(EO)_2+H]^+$, $133[(EO)_3+H]^+$, $487[C_3H_6\text{-}C_6H_4\text{-}O\text{-}(EO)_8H]^+$	$559[o\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(EO)_8H+H]^+$
I9	$89[(EO)_2+H]^+$, $133[(EO)_3+H]^+$, $531[C_3H_6\text{-}C_6H_4\text{-}O\text{-}(EO)_9H]^+$	$603[o\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(EO)_9H+H]^+$
I10	$89[(EO)_2+H]^+$, $133[(EO)_3+H]^+$, $575[C_3H_6\text{-}C_6H_4\text{-}O\text{-}(EO)_{10}H]^+$	$647[o\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(EO)_{10}H+H]^+$
I11	$89[(EO)_2+H]^+$, $133[(EO)_3+H]^+$	$691[o\text{-}C_8H_{17}\text{-}C_6H_4\text{-}O\text{-}(EO)_{11}H+H]^+$
B5	$89[(EO)_2+H]^+$	$371[C_4H_9\text{-}C_6H_4\text{-}O\text{-}(EO)_5H+H]^+$
B6	$89[(EO)_2+H]^+$	$415[C_4H_9\text{-}C_6H_4\text{-}O\text{-}(EO)_6H+H]^+$
B7	$89[(EO)_2+H]^+$	$459[C_4H_9\text{-}C_6H_4\text{-}O\text{-}(EO)_7H+H]^+$
B8	$89[(EO)_2+H]^+$	$503[C_4H_9\text{-}C_6H_4\text{-}O\text{-}(EO)_8H+H]^+$
B9	$89[(EO)_2+H]^+$	$547[C_4H_9\text{-}C_6H_4\text{-}O\text{-}(EO)_9H+H]^+$
B10	$89[(EO)_2+H]^+$	$591[C_4H_9\text{-}C_6H_4\text{-}O\text{-}(EO)_{10}H+H]^+$
B11	$89[(EO)_2+H]^+$	$635[C_4H_9\text{-}C_6H_4\text{-}O\text{-}(EO)_{11}H+H]^+$
B12	$89[(EO)_2+H]^+$	$679[C_4H_9\text{-}C_6H_4\text{-}O\text{-}(EO)_{12}H+H]^+$
B13	$89[(EO)_2+H]^+$	$723[C_4H_9\text{-}C_6H_4\text{-}O\text{-}(EO)_{13}H+H]^+$
B14	$89[(EO)_2+H]^+$	$767[C_4H_9\text{-}C_6H_4\text{-}O\text{-}(EO)_{14}H+H]^+$

[a] Chromatographic condition: non-end-capped BFS (250×4.6 mm I.D.); flow-rate, 1ml/min; mobile phase, methanol–water (50:50); temperature, 40°C; sample, 0.020 g/ml of Triton X-100 in methanol; injection volume, 20 μl.
EO: Ethylene oxide.

Fig. 10. A small amount of butylphenol may be there. From these results the peak of B9 can be identified as butylphenol nona-ethylene glycol. Normal-phase chromatography separates ethoxylated oligomers, but cannot resolve alkyl chain homologues. BFS is capable of separating simultaneously not only ethoxylated oligomers but also alkyl homologues such as butylphenol, *para*-octylphenol and *ortho*-octylphenol ethoxylate.

4. Conclusions

This paper describes attempts to separate and characterize octylphenol ethoxylated oligomers by reversed-phase HPLC and LC–MS on BFS. The elution systems allowed baseline separation, and identification of the structures of octylphenol ethoxylate surfactants. BFS simultaneously could separate by means of recognition of alkyl homologues such as butylphenol, *para*-octylphenol and *ortho*-octylphenol ethoxylate. Octylphenol ethoxylated oligomers were eluted in the sequence from small to large oligomers, which was the same elution order as normal-phase HPLC. Surfactants having average ethoxylation numbers as high as 40 could be separated under gradient conditions. The peaks on end-capped BFS had very large tailing and the separation was incomplete. Obviously non-end-capped BFS was more appropriate to separate non-ionic surfactants than end-capped BFS. As ln k' linearly decreased with increasing concentration of methanol in the

mobile phase, it was clear that BFS operated in the reversed-phase mode. From linear Van 't Hoff plots the existence of a single conformation for the ethylene oxide chain was suggested.

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