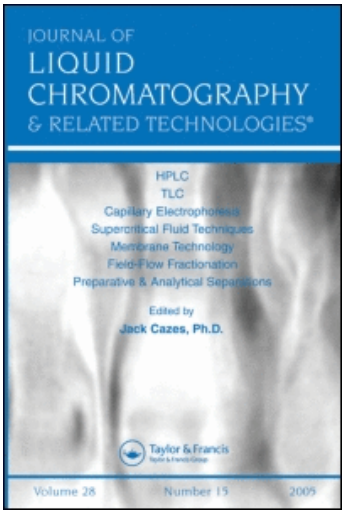

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SEPARATION OF OCTYLPHENOL POLYETHER ALCOHOLS SURFACTANTS BY CAPILLARY COLUMN SFC AND HPLC

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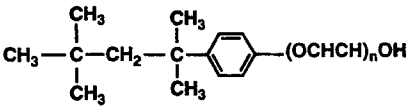
ABSTRACT

Separation of nonionic octylphenol polyether alcohols (OPA) by supercritical fluid chromatography (SFC) and HPLC is described. Using a density programming and a 50-μm i.d. capillary column, a total of 18 group oligomers was separated. The effects of the operating parameters, such as temperatures of mobile phase, flame ionization detector (FID) and injector, on SFC analysis were investigated. The results demonstrated that the separation efficiency is better when mobile phase temperature is above 100 °C, which must be due to the higher volatility of the oligomers. The results also demonstrated that the change of FID temperature from 300 °C to 420 °C has no effect on the total peak response. The study shows that injector cooling is not necessary when the analyte is in methanol. The total peak response was lower when the injector temperature was changed from 21 °C to 10 °C. A group of polar oligomers was found in OPA in HPLC analysis, not found in SFC. The result indicates that the polar oligomers present in OPA were not soluble in supercritical fluid carbon dioxide and, therefore, not observed in SFC.

INTRODUCTION

There has been considerable interest in using surfactants to enhancesubsurface remediation. [1, 2, 3] Because surfactants increase the solubility of hydrocarbon contaminants in ground-water systems, they could potentially greatly



$\overline{n} = 9 - 10$

Figure 1 The molecular structural formula of octylphenol polyether alcohols (OPA)

reduce the number of pore volumes to be pumped in a cleanup effort. [3] Nonionic octylphenol polyether alcohols (OPA) is under consideration for this application. OPA, as other alkylphenol polyethoxylates such as nonylphenol and linear alkylbenzenesulphonates, is used as a detergent ingredient, [4] which may be discharged into municipal and industrial wastewater, eventually entering natural waters. [5, 6] These surfactants have been studied with respect to their behavior in wastewater treatment and their environmental impact. [7]

OPA, similar to other commercial surfactants such as T-MAZ, [8, 9] CS-330 [10] and Dowfax, [11] is a complex mixture of many isomers, homologues and oligomers. OPA is an aromatic nonionic surfactant and prepared by the reaction of octylphenol with ethylene oxide. The structural formula is shown in Figure 1. The complexity of this chemical is mainly due to the various lengths of ethylene oxide units $(OCHCH)_n$. According to the manufacturer, the average number of ethylene oxide units is 9 to 10, which corresponds to an average molecular mass of 584 to 626.

Because of the low volatility and high molecular weight, OPA is difficult to analyze by gas chromatography (GC). High temperature GC was used to analyze sucrose fatty acid ester fractions, [12] however, a derivatization procedure has to be performed prior to analysis.

Capillary supercritical fluid chromatography has been demonstrated as a very effective technique for the separation of nonionic surfactant polymers. [8, 13, 14, 15] Capillary supercritical fluid chromatography (SFC) performance is very much dependent on operating parameters, such as temperatures of mobile phase, injector and flame ionization detector. It is important to choose the proper operating parameters to optimize SFC performance. Although capillary SFC has been used to analyze nonionic surfactants such as alcohol ethoxylates, T-MAZ and Triton surfactants previously, [8, 13, 14, 15, 16] there are relatively few publications on the detailed investigations of the effects of the operating parameters on SFC analysis of nonionic surfactants. This work provides a detailed study of the effects of these operating parameters on SFC separation of OPA. The results have significance not only to the analysis of OPA, but also to optimization of SFC conditions for other nonionic polymers.

Reverse phase chromatography has been used to separate polymers previously. [9, 17] There are several advantages using HPLC for the polymer analysis: aqueous samples can be directly injected into an HPLC system, eliminating the need for sample extraction procedures; sample injection for HPLC system in our lab is automated, therefore more samples can be analyzed per 24 hour period. The separation was performed using reverse phase chromatography to see how the SFC separation of the oligomers differs from HPLC.

MATERIALS AND METHODS

Supercritical carbon dioxide (Scott Specialty Gases, Inc., Plumsteadville, PA, USA) was used as the mobile phase. OPA was purchased from Union Carbide

Chemicals and Plastics Company Inc. (Danbury, CT, IL, USA). Polyethylene glycol standards with molecular masses of 440, 600 and 960 were from Polymer Laboratories Ltd (Foster City, CA, USA). All solutions were made with methanol (Burdick and Jackson, Baxter Healthcare Corporation, Muskegon, MI, USA).

SFC

SFC analysis was performed on a Dionex (Dionex Corporation, Sunnyvale, CA, USA) 600-D Supercritical Fluid/Gas Chromatography system which includes a syringe pump to generate the high-pressure fluid flow, a chromatograph oven for temperature control, flame ionization detector (FID), and a data acquisition and processing system. All chromatographic conditions, including density programming, are computer-controlled. To obtain maximum sensitivity, the hydrogen/air ratio (1/10) was optimized and the detector operated in the most sensitive range. The flow rates were H_2: 30 ml/min, air: 300 ml/min and N_2: 25 ml/min. The detector body was heated to 390 °C. Samples were introduced into the chromatographic system using a Valco injector (Valco, Houston, TX, USA). The injection mode used was time split with the injection duration of 0.1 second. 1 µl of the sample was loaded to the injector loop which has a volume of 0.5 µl. With 0.1 second time split injection, 0.3 µl (60% of 0.5 µl) sample was loaded to the SFC column. The injector was cooled at 10 °C with a NesLab constant temperature circulator (NesLab, Portsmouth, NH, USA).

Separations were accomplished using a 10 meter SB-Biphenyl-30 capillary column from Dionex which has a 50-µm i.d. coated with approximately 0.25-µm film thickness. Prior to detection the supercritical fluid was decompressed, and the mobile phase linear velocity was controlled to approximately 1.5 cm/sec by connecting the

terminal end of the capillary column to a frit restrictor attached through a fused butt connector.

HPLC

Instrumentation was from Waters (Waters Associates, Milford, MA, U.S.A.), which included a 484 tunable absorbance detector, a 600E multisolvent delivery system and a 717 autosampler. Separations were accomplished using a Waters NovaPak C18 stainless steel column (3.9 x 150 mm). The mobile phase was 25% acetonitrile. The injection volume was 100 µl at an eluent flow rate of 1.0 ml/min. Data acquisition and processing was accomplished with a Waters Maxima 820 chromatography workstation, which included a system interface module and a NEC PowerMate SX/16 computer.

RESULTS AND DISCUSSION

SFC Separation

The density of the mobile phase is the primary factor involved in the partitioning of a solute between the stationary and mobile phase in SFC, and density is not directly proportional to pressure near the critical point. [18] Therefore linear density programming is preferred over pressure programming for resolving components of mixtures with a wide molecular mass range.

The chromatogram of OPA, Figure 2a, was obtained under the following conditions: (1) 0.3392 g/ml (150 atm, at 100 °C), held for 6 minutes and ramped to

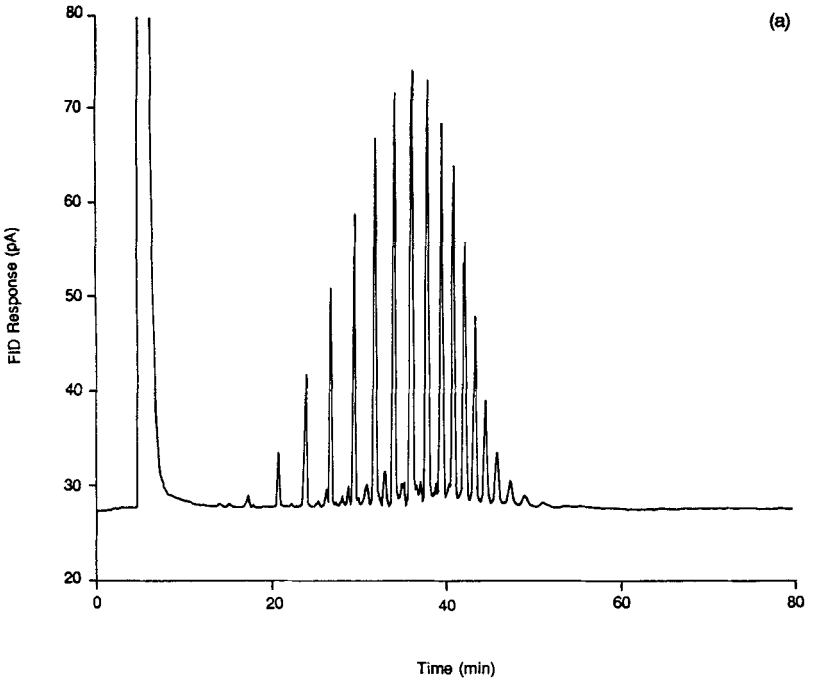


Figure 2 SFC chromatograms of OPA and PEG standards

Conditions: CO_2 mobile phase at 100 °C; FID at 390 °C; injector temperature: 21 °C. Linear isothermal density program: (1) 0.3392 g/ml (150 atm, at 100 °C), held for 6 minutes and ramped to 0.7100 g/ml (340 atm, at 100 °C) at 0.01 g/ml/min and held for 20 minutes; (2) from 0.7100 g/ml to 0.7430 g/ml (380 atm, at 100 °C) at 0.01 g/ml/min and then held for 10 minutes. Samples: (a) OPA, 43 µg/µl; (b) PEG 600, 70 µg/µl.

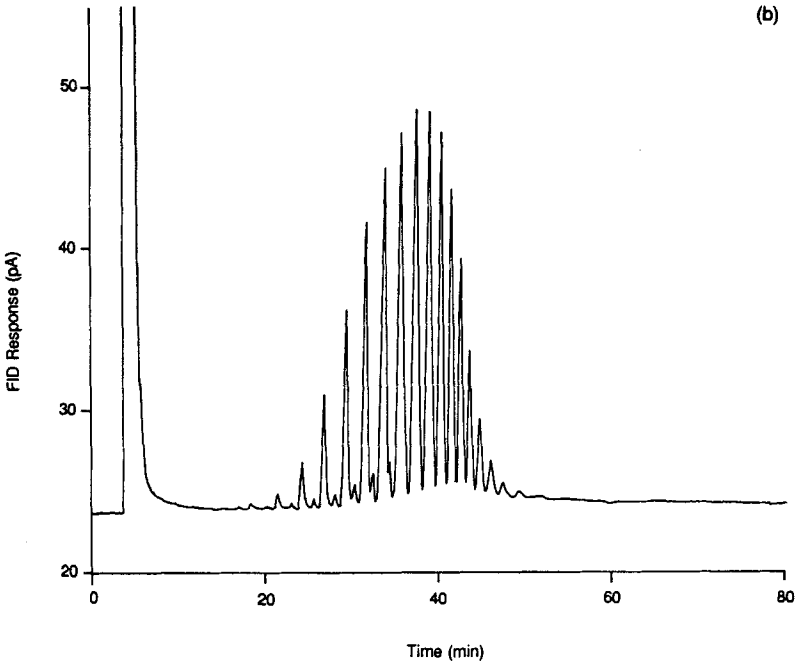


Figure 2 (continued)

0.7100 g/ml (340 atm, at 100 °C) at the rate of 0.01 g/ml/min and held for 20 minutes; (2) 0.7100 g/ml to 0.7430 g/ml (380 atm, at 100 °C) at 0.01 g/ml/min and held for 10 minutes.

Polyethylene glycol standards were used to estimate the average molecular mass of OPA as was done previously for T-MAZ. [8] The chromatogram shown in Figure 2b is a PEG standard with an average molecular mass of 600 using identical SFC conditions as in Figure 2a. Two chromatograms (Figures 2a and 2b) showed significant similarity in retention times and peak distribution, which demonstrated that the average molecular mass of OPA is about 600, confirming that of the range of 584

to 626 from the manufacturer. In addition, it also demonstrated that the oligomers of OPA and PEG have very similar solubilities at the same density of the mobile phase and the SB-Biphenyl-30 capillary column has almost no selectivity in polarity difference between molecules of OPA and PEG.

Two other PEG standards with average molecular mass of 440 and 960 were also analyzed. As expected, oligomers in PEG 440 elutes earlier than OPA and PEG 600, because of their smaller molecular mass than OPA and PEG 600. Oligomers in PEG 960 elutes later than OPA and PEG 600, which is due to the higher molecular mass.

Effect of Mobile Phase Temperature

The effect of mobile phase temperature on the separation was examined by changing column oven temperature. The isothermal separation was performed at 80 °C, 100 °C, 120 °C and 150 °C with density programming started at 150 atm and ended at 380 atm. Resolution between the oligomers is much higher at 100 °C, 120 °C and 150 °C than that at 80 °C. Integrated from 12 to 60 minutes, the total peak response of the injection of 52 μg/μl standard is essentially constant at 80 °C, 100 °C, 120 °C and 150 °C (Table 1), however, the heights of the major peaks at 150 °C are 10% to 92% higher than at 80 °C. This indicates that the efficiency is better at higher temperatures which is due to the change in the volatility of the oligomers. [19]

There are several additional advantages of operating the column at higher temperature, when possible. First, it will prevent condensation in FID restrictor of

TABLE 1 Average Peak Area and Relative Standard Deviation at Various Mobile Phase Temperatures of 52 µg/µl OPA

Mobile Phase Temperature (°C)	Peak Area [a] (%RSD)
80	8923836 (4.4)
100	8833640 (3.2)
120	9053170 (4.3)
150	8873713 (3.9)

[a] Averaged from 3 experiments

RSD: Relative Standard Deviation = 100 x (Standard Deviation / Average Peak Area)

compounds with high molecular mass as indicated in the previous studies. [8, 14] Second, when operating at higher column temperature, [16] it is expected to result in an increase in the solute diffusion coefficients and an improvement in the linearity of the mobile phase density-pressure isotherm. This results in faster optimum velocities, and more even peak spacing in density-programmed chromatograms of oligomers.

Effect of FID Temperature

Analysis was performed at various FID temperatures: 300 °C, 350 °C, 390 °C and 420 °C. As shown in Table 2, the total peak response remained basically unchanged. The indication is that OPA, with an averaged molecular mass of 584 to 626, does not condense in the restrictor at FID temperature as low as 300 °C. The condensation in the restrictor was significant when polymers with high molecular masses, such as T-MAZ (MW, 1300) and alkyl ethoxylated alcohols were analyzed at FID temperature of 350 °C. [8, 14]

TABLE 2 Average Peak Area and Relative Standard Deviation at Various FID Temperatures of 43 µg/µl OPA

FID Temperature (°C)	Peak Area [a] (%RSD)
300	7610953 (3.8)
350	7349170 (4.1)
390	7448399 (2.9)
420	7782887 (4.7)

[a] Averaged from 3 experiments.

RSD: Relative Standard Deviation = 100 x (Standard Deviation / Average Peak Area)

TABLE 3 Peak Area and Peak Area Ratio at Injector Temperatures of 10 °C and 21 °C

Concentration (µg/µl)	Injector Temperature (°C)	Peak Area [a]	Area (10 °C) / Area (21 °C) [b]
25	10	4339909	0.91
52	10	7448399	0.84
25	21	4787291	
52	21	8833640	

[a] Averaged from 3 experiments.

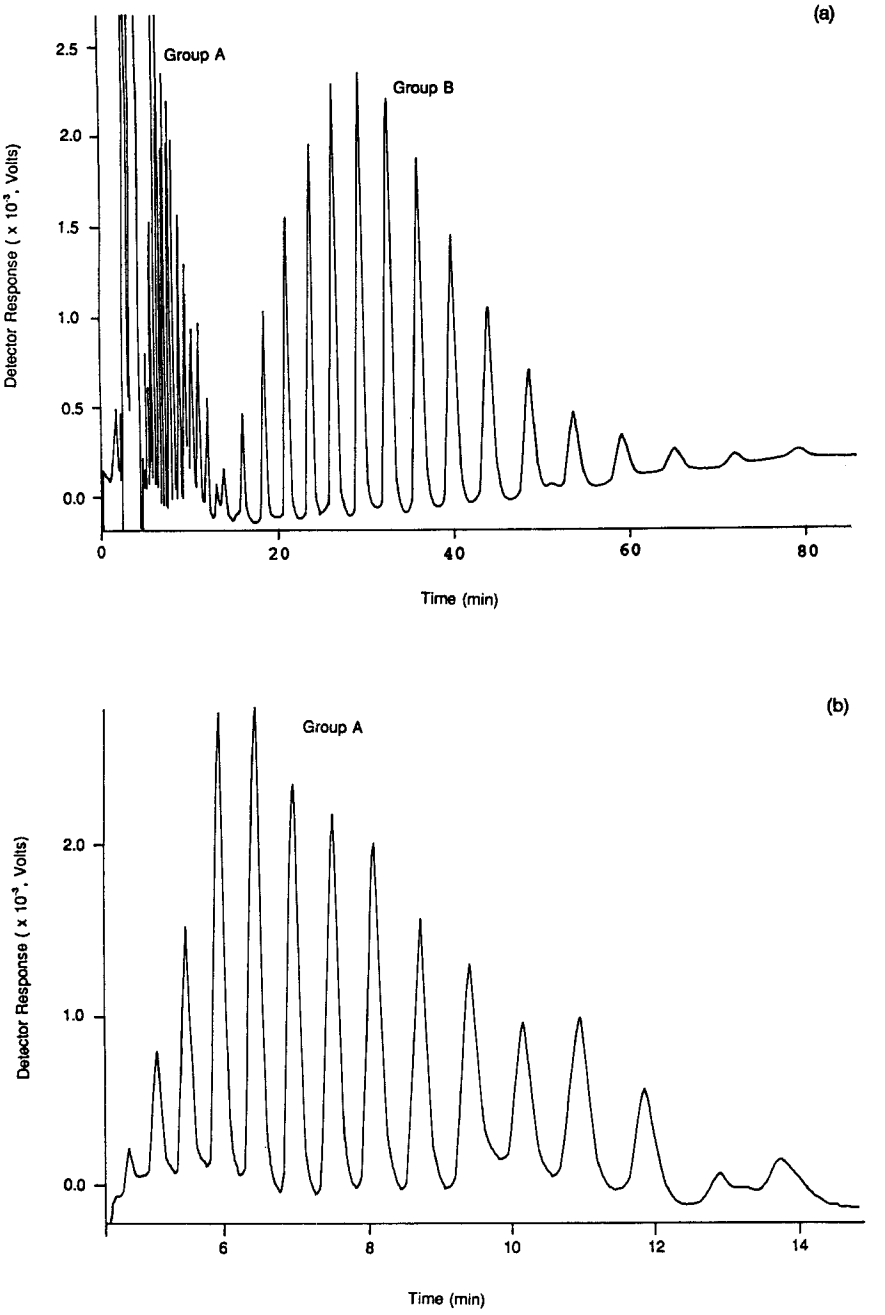
[b] Area (10 °C) / Area (21°C) : The ratio of peak areas at injector temperature 10 °C vs. that at 25 °C.

Effect of Injector Temperature

Experiments were carried out with the injector at 10 °C (cooled by a water bath) and at room temperature (21 °C). OPA standards of 25 and 52 μg/μl were loaded into the sample loop and immediately injected. Integrated as one peak group from 12 to 50 minutes, the responses were 9% and 16% lower for the 25 and 52 μg/μl standards when the injector temperature was at 10 °C than that at 21 °C (Table 3). This can be attributed to the precipitation of OPA in the sample loop, which became significant at high concentration. The result indicates that injector cooling is not needed when the analyte is in methanol. However, if methylene chloride is used as a solvent, vapor bubbles can enter into the sample loop when the injector is not cooled, due to the high volatility of methylene chloride. [8, 14]

HPLC Separation

As shown in Figure 1, since molecules in OPA have a benzene ring, a hydrocarbon chain, oxyethylene groups, and hydroxyl group, a C_{18} column offers desirable interactions between the stationary phase, OPA molecules and the mobile phase. Figures 3 show the HPLC separation of 1000 ppm OPA. Figure 3b shows the peak group A in Figure 3a. These chromatograms again demonstrate the complicity of this industrial chemical as it was shown in the SFC analysis. The peak group A was not found in the SFC separation (Figure 2a). The oligomers in peak group A must be more polar and smaller than oligomers in peak group B, because polar and small molecules elute faster than less polar and larger ones in the reverse phase chromatography. Polar oligomers may not soluble in supercritical fluid carbon dioxide,



Figures 3 HPLC chromatograms of OPA

(a) 1000 ppm OPA standard; (b) group A in Figure 3(a).

which explains peak group A was not observed in SFC separation. A total of 15 oligomers was found in the peak group A and 16 in the peak group B as found in SFC separation (Figure 2a). We also used a Waters NovaPak C_8 column and the separation of peak group A was not as good as using a C_{18} column. The study demonstrate HPLC is a very valuable technique for polymer analysis as we previously indicated, [9] especially for polar polymers. [10]

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DISCLAIMER

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QA/QC REQUIREMENTS

All QA/QC aspects of this work were performed in accordance with the requirements of the ManTech Environmental Research Services Corporation Quality Assurance Program Plan.

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