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Separation of derivatized alcohol ethoxylates and propoxylates by low temperature packed column supercritical fluid chromatography using ultraviolet absorbance detection

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Abstract

Supercritical fluid chromatography (SFC) is capable of separating oligomers of alcohol ethoxylates (AEOs) and propoxylates (APOs) samples with pure carbon dioxide. The instrumental conditions, however, needed for separation necessitate both high temperature and high pressure. Derivatization of alcohol polyether samples with an UV absorbing agent has been achieved with a phenylated disilazane in hopes of employing a solvent-modified CO_2 mobile phase in conjunction with both lower CO_2 pressure and lower temperature for oligomer separation. A silylether containing a single phenyl group was formed via the derivatization of the hydroxyl termini of AEO and APO samples. The derivatized polyethers were detected at 215 nm with little or no interference from the mobile phase. Octadecylsilica (ODS) and a polar embedded alkyl bonded silica stationary phase were studied with the organic solvent-modified CO_2 mobile phase. The combination of an ODS phase and the polar embedded phase, tandemly stacked, produced the best chromatographic separation of oligomeric species. Data from SFC-UV separations combined with peak assignments from SFC with electrospray ionization–mass spectrometric (ESI–MS) detection produced average molar oligomer values for each surfactant sample.

Keywords: Derivatization, SFC; Surfactants; Alcohol ethoxylates; Alcohol propoxylates

1. Introduction

Alcohol ethoxylates (AEOs) and propoxylates (APOs) are non-ionic surfactants. AEOs and APOs contain two main molecular regions: (1) the hydroxyl-terminated oligoether region, which is either a polyethoxylate (EO) or polypropoxylate (PO) hydrophilic chain and (2) the alkyl chain region which is hydrophobic. The industrial synthesis of these compounds yields a complex oligomeric mixture of fatty ethers that contain a distribution of either EOs or POs of varying chain length. It is possible to also have various alkyl chain distributions if the starting materials contain fatty alcohols of different chain lengths. If water is present during the synthesis, polyethylene or polypropylene glycol distributions (PEGs or PPGs) are also produced.

Since the molecular size and structure of these surfactants determine their particular properties and hence application, therefore, it is necessary that they are well characterized. The average oligomer size and general oligomer distribution can be determined via chromatographic separation. Many techniques have, therefore, been used such as high temperature gas chromatography (HTGC) coupled with flame ionization detection (FID) [1] or atomic emission detection (AED) [2] for the quantitative characterization of relatively low molecular weight silyl and acetyl derivatized AEO samples. Both reversed- and normal-phase liquid chromatographic (HPLC) separations have been performed on samples containing AEOs. Evaporative light scattering detection (ELSD) has also been used with HPLC separation of non-derivatized AEOs [3–7]. In another study, capillary electrophoresis (CE)

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was employed [8] for the separation of ionic and non-ionic polymers containing polyethoxylate chains.

Supercritical fluid chromatography (SFC) is another option for separation of ethoxylated surfactants and has been performed on non-derivatized polyethers with both wall coated open tubular columns [5,9–14] and packed columns [15,16]. SFC can operate at lower temperatures than GC, thus allowing samples that are thermally labile to be analyzed. Also, supercritical fluids have densities similar to liquids and diffusivities similar to gases thus large molecular-weight molecules can be separated by SFC with shorter retention times relative to HPLC. Density programming of the CO_2 mobile phase has been used to control elution of the oligomeric analytes and can elute higher molecular-weight oligomers than high temperature GC [1]. Flame ionization detection (FID) has been the detector of choice with open tubular SFC for analysis of AEOs [5,9,11,14]. In a few reports SFC has also been combined with chemical ionization (CI) [10–12], low energy collisionally induced dissociation (CID) [10], and atmospheric pressure chemical ionization (APCI) [13] mass spectrometry for detection and identification of AEOs.

Alcohol ethoxylates and propoxylates lack either a strong ultraviolet (UV) or a fluorescent active component. Several surfactant derivatization methods have been developed for the addition of an UV chromophore in association with HPLC [17–22]. Naphthyl-isocyanate [20], 1-naphthoyl chloride [21], and 1-anthroylnitrile [22] have each been used to incorporate a fluorescent functional group into surfactants for detection with HPLC. Fatty alcohols in wastewater samples were derivatized by Dunphy et al. [23] with 2-fluoro-*N*-methylpyridinium *p*-toluenesulfonate for subsequent mass spectrometric detection. Silver and Kalinoski [1] and Asmussen and Stan [2] both used bis(trimethylsilyl)trifluoroacetamide (BSTFA) for the silylation of hydroxyl-terminated ethoxylated samples wherein GC analysis of the resulting homologous trimethyl silyl (TMS) ethers was performed. Berger and Todd [24] and Rumbelow et al. and Pinkston [25] took advantage of the UV transparency of pure CO_2. They formed the TMS derivatives of oligomeric alcohol ethoxylates and propoxylates and separated them by packed column SFC at relatively high temperature and pressure with UV absorbance detection at 191 and 195 nm.

Derivatization reactions, however, can produce by-products that interfere with analyte separation and identification. Katayama et al. [26], for example, used an ODS Sep-Pak cartridge to extract the esters formed via derivatization of fatty alcohols with 2-(4-carboxyphenyl)-5,6-dimethylbenzimidazole (CDB) in order to achieve the addition of a fluorescent tag. Meisnner and Engelhart [27] developed both an off-line solid phase extraction (SPE) cleanup method and an on-line cleanup method for derivatization of alcohols using carbazole-9-carbonyl chloride or 9-fluorenylmethyl chloroformate. They found that the off-line method produced better results for the analysis of AEO samples.

The separation methods noted above for analysis of alcohol polyethers have benefits and weaknesses. HTGC produces high resolution of low molecular weight oligomers but it is unable to elute the highest molecular weight ones (EO of ~20 or above). HPLC is able to elute high molecular weight non-derivatized oligomers but UV detection is precluded above 210 nm due to UV absorbance by the mobile phase. Tremendous advances have been made in HPLC–ELSD. The ELSD has the advantage of universality for non-volatile species but the UV detector still surpass the ELSD in dynamic range, operational simplicity, and reliability. SFC separation using pure CO_2 is able to elute high molecular weight TMS-derivatized oligomers but high temperature and high CO_2 pressure are necessary for the best separations.

In the present study, an ethoxylated and a propoxylated alcohol were separated via packed column supercritical fluid chromatography. Acetonitrile-modified CO_2 was used as the mobile phase such that the temperature and CO_2 pressure required for elution was less compared with SFC separations that used pure CO_2 as the mobile phase. Ultraviolet detection of the oligomers was attempted by derivatization of the surfactant samples with a phenyl-containing disilazane–chlorosilane mixture. SFC, using pure CO_2 as the mobile phase, was used to determine if absorbance of derivatized species was partially due to the polyether chain or was the absorbance unique to the silylether tag. Electrospray ionization–mass spectrometry (ESI–MS) detection was used for making peak assignments in the acetonitrile-modified CO_2 SFC packed column separations.

2. Experimental

2.1. Packed-column SFC

Three Berger Analytical SFC systems (Berger Instruments, Newark, DE), each from the authors laboratories, were used in this study. SFC-grade carbon dioxide (Air Products and Chemicals, Inc., Allentown, PA) was used as the primary mobile phase for each system.

2.1.1. Pure carbon dioxide system

A Deltabond methyl "SFC" packed column (Thermo-Hypersil-Keystone, Bellefonte, PA) was used for separation. The column dimensions were 2 mm × 250 mm with an average particle size of 5 μm and pore size of 300 Å. A 2 μl loop was used for injections. The mobile phase flow rate (liquid) was 0.5 ml/min (calculated 14.4 cm/s average linear velocity). The oven temperature was 200 °C and UV detection was at either 195 or 215 nm. CO_2 pressure programming up to a maximum of 370 bar was used for elution.

2.1.2. Acetonitrile-modified carbon dioxide system

Discovery C_{18} and Discovery RP-AmideC_{16} stationary phases (SUPELCO, Bellefonte, PA) were used for separation. The column dimensions were 4.6 mm × 250 mm with an

average particle size of 5μm and pore size of 180 Å. A 10 μl loop was used for injections. The mobile phase flow rate (liquid) was 2.4 ml/min (calculated 14.4 cm/s average linear velocity). The oven temperature was 40 °C, outlet pressure was held at 120 bar, and absorbance detection was recorded as described above. Modifier programming with acetonitrile up to 25% was used for elution.

2.1.3. SFC–ESI–MS system

Column, mobile phase, and oven conditions were the same as the acetonitrile modified carbon dioxide system. An Isco Model 260D syringe pump (Lincoln, NE) was used to add a make-up flow post UV detector of methanol containing 1 mM ammonium acetate. Make up flow was supplied at a constant flow of 100 μl/min. Electrospray ionization mass spectra were obtained with a Perkin-Elmer Sciex API 365 triple quadrupole mass spectrometer (Perkin-Elmer, Inc., Boston, MA) in the positive ion mode. Turbo gas temperature was 450 °C and the (mass-to-charge ratio) *m/z* scan range was 150–1500. The scan stepsize and dwell time were 0.2 *m/z* and 5 ms, respectively.

2.2. Surfactant samples and derivatizing reagents

Alcohol polyether samples were provided by Uniqema (New Castle, DE). A stearyl alcohol polyoxypropylene ether with an average nominal PO length of 15 ($C_{18}PO_{15}$) and a stearyl alcohol polyoxyethylene ether with an average nominal EO length of 10 ($C_{18}EO_{10}$) were analyzed in this study. 1,3-Diphenyl-1,1,3,3-tetramethyldisilazane (DPTMDS) and bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS) were obtained from Sigma–Aldrich, Inc. (Milwaukee, WI). Phenyldimethylchlorosilane (PDMCS) was purchased from Gelest, Inc. (Tullytown, PA). Sodium hydroxide was obtained from Mallinckrodt, Inc. (Paris, KY). Acetonitrile and dichloromethane (DCM) were obtained from Burdick & Jackson (Muskegon, MI).

2.3. Spectroscopy of derivatized samples

UV absorbance spectroscopy of derivatized and non-derivatized samples was performed with an Agilent 8453 diode array spectrophotometer (Little Falls, DE).

3. Results and discussion

The goals of this study were to develop a chromatographic method that used mild chromatographic operating conditions and UV detection for analysis of alcohol polyether samples. Previous reported separations of TMS derivatives of alcohol polyethers, which used pure CO_2 as a mobile phase, necessitated the use of high CO_2 pressure (in excess of 300 bar outlet) and relatively high oven temperature (above 150 °C). These conditions, which, over the long term, can lead to stationary phase decomposition, approach the maximum operating parameters of commercial analytical SFC instruments. Previous studies of polar and non-polar solutes have shown that use of an organic solvent-modified CO_2 mobile phase can significantly increase column efficiency [28]. Pure CO_2 allows detection of polyether surfactants at 195 nm, unfortunately use of an organic solvent to modify CO_2 may interfere with UV detection of alcohol polyethers at this wavelength. Therefore, in the work conducted here, silylether derivatives were formed that contained a phenyl moiety, which allowed UV detection outside the absorbance region of liquid solvents commonly used to modify CO_2 for SFC separations.

3.1. Derivatization

Alcohol polyethers were derivatized as their TMS ethers to increase their solubility in pure supercritical CO_2 and reduce undesirable interactions with the stationary phase. BSTFA with 1% TMCS was used for TMS ether formation. Approximately 45 mg of surfactant was dissolved in 1.5 ml of BSTFA–TMCS solution and heated for 60 min in an 80 °C oven. Due to the success of TMS ether derivative separations with pure CO_2, it was our intention to form an analogous silylether that contained a phenyl moiety, to use as an UV chromophore. DPTMDS was investigated for the formation of a phenyldimethyl silylether (1Ph) derivative. Protic solvents had to be avoided for the derivatization reaction to discourage the possibility of derivative hydrolysis, therefore, acetonitrile was used as the solvent. It was found that PDMCS was necessary in order to catalyze the reaction just as TMCS is used to catalyze silylation reactions with hexamethyldisilazane [29].

A brief study was performed with $C_{18}PO_{15}$ to determine the optimal reagent concentration for quantitative 1Ph ether formation. The ratio of moles of DPTMDS to moles of $C_{18}PO_{15}$ was varied by adding 50, 100, and 200 μl of DPTMDS to 45 mg samples of $C_{18}PO_{15}$ dissolved in 1350 μl of acetonitrile. A single drop of PDMCS was added to catalyze the reaction. DPTMDS–PDMCS derivatized samples were heated in an 80 °C oven for 60 min. Derivatized $C_{18}PO_{15}$ samples were then transferred to a separate collection vial with 2.0 ml of DCM. In an effort to quench the reaction the samples were next washed with 1 M sodium hydroxide and vortexed. The DCM layer, which contained the analytes of interest, was removed and placed in a separate vial. Sodium sulfate was added to the DCM layer to remove any water that may have been transferred. Dehydrated samples were filtered through a PTFE syringe filter (Millipore Corp., Bedford, MA). The samples were first evaporated to dryness under a stream of nitrogen while being gently heated and then re-dissolved in 1.5 ml of acetonitrile for SFC separation. The optimal ratio of DPTMDS to surfactant sample was determined by the number of oligomer peaks detected for each derivative. Final derivatization conditions were: 45 mg of $C_{18}PO_{15}$ with 150 μl of DPTMDS plus one drop of PDMCS

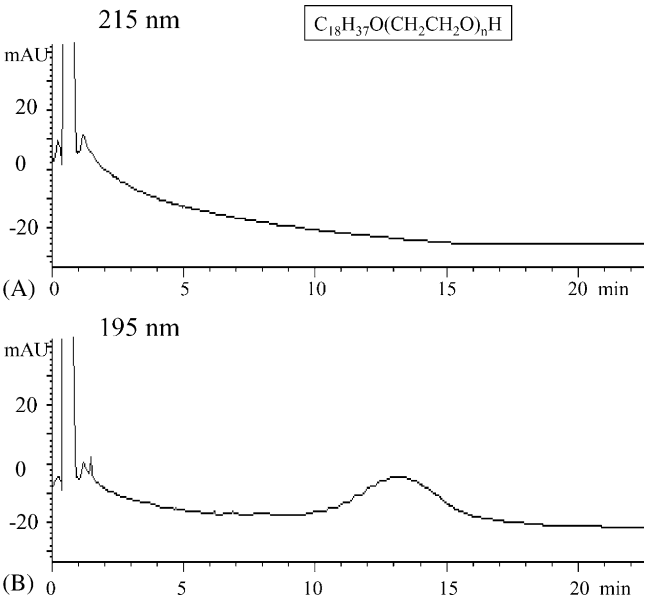

Fig. 1. SFC of non-derivatized $C_{18}EO_{10}$. Deltabond methyl column (2.0 mm × 250 mm); oven temperature: 200 °C; CO_2 flow rate: 0.5 ml/min. Linear pressure gradient: 100 bar held for 1 min, increased to 370 bar at 20 bar/min, hold at 370 bar for 8 min. Absorbance at: (A) 215 nm and (B) 195 nm.

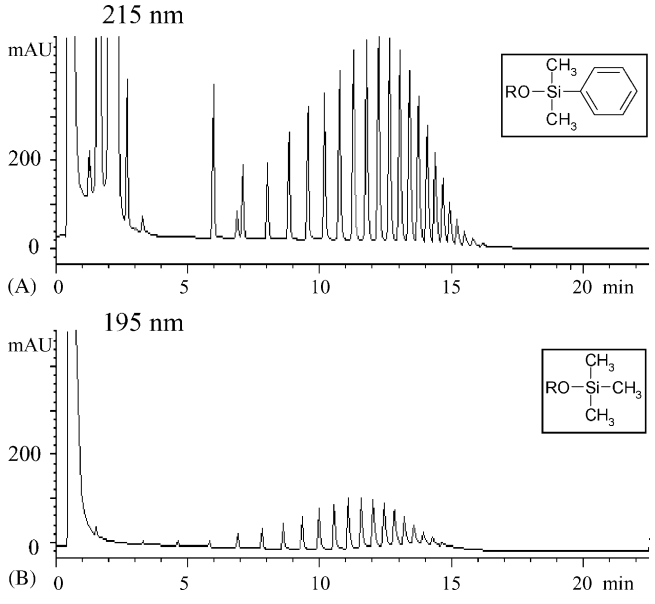

Fig. 2. SFC of derivatized $C_{18}EO_{10}$. $C_{18}EO_{10}$ derivatized with: (A) DPT-MDS and PDMCS, detection at 215 nm and (B) BSTFA with 1% TMCS, detection at 195 nm. See Fig. 1 for conditions.

dissolved in 1350 μl of acetonitrile. A similar method was used for derivatization of $C_{18}EO_{10}$. Samples separated with modified CO_2 were not subjected to liquid–liquid extraction. UV spectra of the derivatized samples exhibited significant absorbance around 215 nm.

3.2. Preliminary study with pure carbon dioxide

A Deltabond Methyl packed column was used for the SFC separation of both TMS- and 1Ph-derivatized surfactants using pure carbon dioxide. SFC separation with pure CO_2 was initially used as a means to determine if absorbance at 215 nm was unique to 1Ph derivatives. It was necessary to use both high temperature (200 °C) to provide high resolution separation and high CO_2 pressure (up to 370 bar outlet) for efficient elution of high molecular weight oligomers. Lower pressure and temperature separations were investigated but were unsatisfactory. Previous research by Berger and Todd [24] and Rumbelow et al. and Pinkston [25] used a similar separation scheme for TMS derivatives of ethoxylates and propoxylates. The chromatogram of non-derivatized $C_{18}EO_{10}$ (Fig. 1), with detection at both 195 and 215 nm, demonstrated the poor solubility and or undesirable column interactions of alcohol polyethers in pure CO_2, even at extreme instrument operating conditions. Minuscule absorbance was detected at 215 nm for non-derivatized surfactants.

Chromatographic separation was improved with the formation of TMS and 1Ph ether, which exhibited better interaction with the stationary phase (Fig. 2). Separations that used pure CO_2 confirmed the absorbance of the 1Ph derivatives was solely due to the phenyl group incorporated into the oligomers. This was done by comparing UV traces of TMS ether derivative separations at 195 and 215 nm. No absorbance was detected at 215 nm for TMS ether derivatives, therefore absorbance at 215 nm of 1Ph ether derivatives was solely due to the added phenyl group. The absorbance of the $C_{18}EO_{10}$ 1Ph ether derivative oligomers at 215 nm was greater than the absorbance of the TMS ether oligomers at 195 nm due to the apparent larger molar absorptivity of the 1Ph ether derivative.

We have found no reference to the use of phenylated disilazanes to derivatize alcohol polyethers for chromatographic purposes in the literature. Traditional uses for DPTMDS have included: (a) modification of glass surfaces [30]; and (b) the derivatization of PEGs for photometric determination of hydroxyl groups [31]. White et al. [32] have used PDMCS for the formation of monosaccharide phenyldimethyl silyl derivatives for analysis by HPLC.

3.3. Acetonitrile modified carbon dioxide

Use of acetonitrile-modified carbon dioxide allowed the use of lower temperature and CO_2 pressure due to its increased solvating strength relative to pure CO_2 at the same temperature and pressure. The lower temperature and pressure conditions also allowed for the use of bonded silica phases with greater alkyl chain length. Several silica-bonded phases were evaluated for separation of the surfactant samples including: bare silica, aminopropyl, cyanopropyl, polyethylene glycol, C_{18}, and amide-embedded alkyl phases. Discovery C_{18} and Discovery RP-AmideC_{16} provided the most satisfactory separations in preliminary investigations and were thus used as stationary phases with modified car-

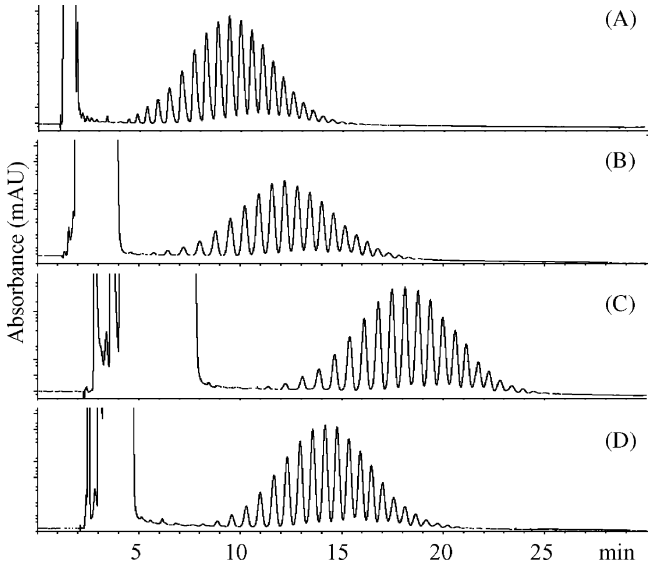

Fig. 3. SFC of $C_{18}PO_{15}$ derivatized with DPTMDS: CO_2 modified with acetonitrile. Oven temperature: 40 °C, CO_2 flow rate: 2.4 ml/min, outlet pressure: 120 bar, detection at: 215 nm. Linear modifier gradient: 1% modifier held for 5 min increased to 25% at 1%/min, hold at 25% for 5 min. (A) Discovery C_{18} column; (B) Discovery RP-AmideC_{16} column; (C) Two Discovery RP-AmideC_{16} columns; (D) Discovery C_{18} column+Discovery RP-AmideC_{16} column. All columns were 4.6 mm × 250 mm, 5 μm.

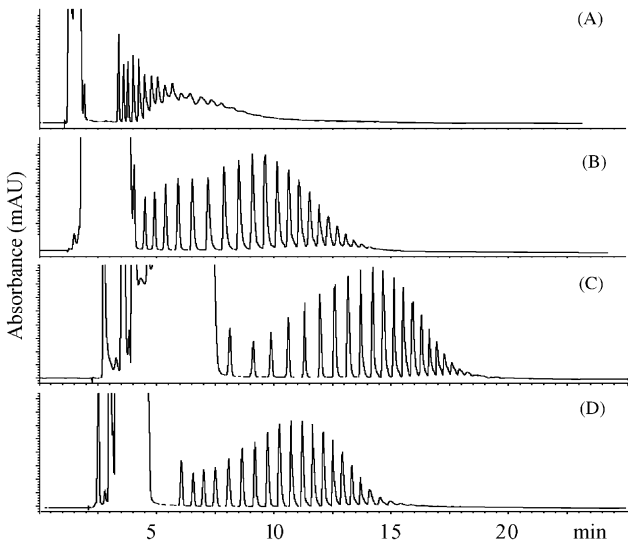

Fig. 4. SFC of $C_{18}EO_{10}$ derivatized with DPTMDS: CO_2 modified with acetonitrile. Oven temperature: 40 °C; CO_2 flow rate: 2.4 ml/min; outlet pressure: 120 bar; detection at: 215 nm. Linear modifier gradient: 1% modifier held for 5 min increased to 20% at 1%/min, hold at 20% for 5 min. (A) Discovery C_{18} column; (B) Discovery RP-AmideC_{16} column; (C) Two Discovery RP-AmideC_{16} columns; (D) Discovery C_{18} column+Discovery RP-AmideC_{16} column. All columns were 4.6 mm × 250 mm, 5 μm.

bon dioxide. Both the Discovery phases contained the same base silica, but the RP-AmideC_{16} phase differs in that it contained an amide group embedded in the C_{18} alkyl chain close to the silica surface. Acetonitrile was picked as the modifying solvent due to its low wavelength UV cutoff and its moderate polarity. Each sample was separated individually employing four column configurations: (a) a single Discovery C_{18} column; (b) a single Discovery RP-AmideC_{16} column; (c) a Discovery C_{18} column followed by a Discovery RP-AmideC_{16} column; and (d) two RP-AmideC_{16} columns (Figs. 3 and 4). The single C_{18} column yielded good resolution between the initial peaks which where made up of excess derivatizing agent and by-products of the reaction, and the derivatized analytes of interest. The RP-AmideC_{16} column produced good resolution between the oligomers in both samples, but it did not give a good separation of by-products of the derivatizing agent and the derivatized analytes of interest. A combination of a Discovery C_{18} column followed by a Discovery RP-AmideC_{16} column produced both good resolution between the oligomers themselves and between the initial residuals and oligomer peaks. Two RP-AmideC_{16} columns were tested in series but they gave a similar result to the one obtained with a single column but with longer retention times. In all of the separations, $C_{18}EO_{10}$ produced chromatograms with more narrow peaks than $C_{18}PO_{15}$ derivatives. The propylene groups of the $C_{18}PO_{15}$ repeat units are branched which creates the probability of different oligomeric combinations such as "tail" to "head" and "head" to "head". The greater isomer distribution of $C_{18}PO_{15}$ oligomers, thus, may account for wider chromatographic peaks compared to $C_{18}EO_{10}$, which contains unbranched chain ethylene groups.

As previously mentioned, the surfactants in this study contained a hydrophobic non-polar region and a hydrophilic slightly polar region. It is possible that the reason the Discovery RP-AmideC_{16} phase was able to produce better resolution of the oligomers compared to Discovery C_{18} was because it provided two modes of stationary phase–analyte interaction. The Discovery C_{18} phase separates the surfactant sample via a partition mechanism, while the addition of a polar amide group in the Discovery RP-AmideC_{16} phase makes available interactions with the polyether region of the surfactant thus producing increased retention and resolution. It is also possible that hydrogen bonding between the adjacent chains of amide groups in the Discovery RP-AmideC_{16} phase more effectively shields active sites on the base silica. This could account for the improved resolution of $C_{18}EO_{10}$ on Discovery RP-AmideC_{16} seen in Fig. 4 compared to the Discovery C_{18} phase. Research on similar phases containing polar embedded groups has been conducted for HPLC (but not SFC) applications. Polar embedded phases have shown improved peak shape for acidic, basic, and zwitterionic analytes [33] compared to conventional C_{18} phases. It is possible that some of the phenomenon associated with polar embedded phases used for HPLC can accrue with SFC applications as well.

3.4. Average molar oligomer values

Work by Wang and Fingas [34] demonstrated that oligomers of surfactants containing a phenyl group produce an

equal molar UV response and that oligomer repeating unit is not involved in UV detection. They were able to calculate an average molar oligomer value by the summation of the products of oligomer mole fraction (from peak area (%)) and number of repeating units of each oligomer. Molecular identification of oligomer peaks is, however, necessary for this calculation. SFC–ESI–MS of 1Ph ether derivatives using the acetonitrile-modified CO_2 system was used for peak identification in this study. The SFC–ESI–MS setup was similar to that used by Pinkston et al. [35]. A make-up flow of methanol containing 1 mM ammonium acetate was added to the chromatographic eluent post UV detector to aid in adduct ion formation. Oligomers were subsequently detected as their $[M+NH_4]^+$ adducts. Using the peak identifications it was possible to calculate average molar oligomer values for each analyzed sample. SFC separation of the 1Ph ether derivatives using the tandem stacked Discovery C_{18}–Discovery RP-AmideC_{16} configuration yielded an average polyoxyethylene (EO) value of 9.7 for $C_{18}EO_{10}$ and an average PO value of 12.6 for $C_{18}PO_{15}$. Deviation from the nominal value is not uncommon and may be due to variation between manufactured surfactant batches.

4. Conclusion

The goal of this research, the addition of an UV absorbing group to AEO and APO samples, was successfully met. Samples derivatized with DPTMDS–PDMCS produced favorable separations and afforded detection at 215 nm. The ability to detect analytes at 215 nm allowed the use of acetonitrile modified CO_2, which made it possible to separate a wide molecular weight distribution of derivatized oligomeric surfactants using relatively low temperature and pressure with UV detection. The use of lower temperature and CO_2 pressure for SFC allows a wide variety of stationary phases to be used for separations compared to conditions needed for pure CO_2 separations. Tandem stacking of an ODS stationary phase and a polar-embedded alkyl phase provided enhanced separations. When combined with mass spectrometric detection, it was possible to calculate average oligomer values for the samples analyzed. Further research is planned to increase chromatographic resolution and sensitivity of detection via investigation of other derivatives and optimization of stationary–mobile phase conditions.

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