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Increasing UV detection sensitivity in the supercritical fluid chromatographic analysis of alcohol polyethers

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Abstract

Alcohol ethoxylates (AEOs) that contain a wide distribution of oligomers pose a challenge for ultraviolet (UV) absorbance detection due to the fact that the AEOs absorb strongly only in the range of commercial UV detectors between 190 and 200 nm. Most mobile phase components, with the exceptions of water and carbon dioxide, also absorb in this region. Ethoxylated hexadecanol and octadecanol were derivatized with disilazane–chlorosilane mixtures for the formation of phenyl containing silylethers. Derivatized samples were analyzed by supercritical fluid chromatography (SFC) coupled with both electrospray ionization mass spectrometry and UV absorbance detection. An increase in the number of phenyl groups incorporated into the derivatives increased the number of oligomers observed by UV detection. An increase in the number of oligomers detected increased the calculated average molar ethoxylate values. The average molar oligomer values calculated by SFC–UV for these alcohols were consistent with the nominal reported values.

Keywords: Alcohol ethoxylates; Ultraviolet; Mass spectrometry; Derivatization

1. Introduction

Alcohol ethoxylates (AEOs) are non-ionic surfactants, which are traditionally characterized by their average molar oligomer values. Average molar oligomer value is controlled during surfactant synthesis by the ratio of ethylene oxide to fatty alcohol being ethoxylated and choice of catalyst [1]. The distribution of oligomers in a surfactant mixture in turn establishes commercially applicable uses. Traditionally, various chromatographic tools [2–10] and proton nuclear magnetic resonance spectrometry (^{1}H NMR) [11–13] have been used for analysis of AEOs. Since AEOs do not contain a functionality capable of strongly absorbing ultraviolet (UV) radiation above wavelength of 195 nm, they are commonly derivatized with UV absorbing groups for detection [4–6,9,10].

^{1}H NMR is capable of determining average molar oligomer value of non-derivatized AEOs by making a ratio between the integral of ethoxylate protons and the integral of the terminal methyl protons of the fatty alcohol. Although ^{1}H NMR is useful for calculation of average molar oligomer value, and does not require derivatization, it is not applicable for determination of oligomeric distribution. In fact, the presence of impurities, such as polyethylene glycol, may alter the calculated average oligomer value in ^{1}H NMR. On the other hand, chromatography of derivatized AEOs using UV detection has been useful for both calculation of average oligomer value and oligomeric distribution [9–11]. For example, it has been shown that in the high performance liquid chromatography (HPLC) separation of AEOs containing a benzene ring, equal UV molar response for all oligomers is afforded [11].

According to Beer's law, UV absorbance is linearly correlated with moderately low concentrations. Therefore, oligomers that are present at low concentration, close to the

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limit of detection, will be difficult to detect. Hoffman et al. [9,10] have formed a phenyldimethyl silylether (1Ph) derivative of alcohol polyethers for their analysis by supercritical fluid chromatography (SFC) with UV detection. Calculated average oligomer values were slightly below both the ^{1}H NMR calculated and reported nominal values.

The intent of the current research was to further increase the sensitivity of AEOs analyzed by SFC–UV in an effort to observe oligomers present at low concentrations. This has been accomplished by comparing the response of a methyldiphenyl silylether (2Ph) derivative to that of a 1Ph derivative. It was anticipated that an increase in the number of phenyl groups associated with derivatized oligomers would increase detection sensitivity. Derivatized samples were separated by SFC on a sulfonamide-embedded alkyl stationary phase using methanol-modified CO_2 as the mobile phase. Electrospray ionization mass spectrometry (ESI-MS) was used for identification of comparable analyte peaks in UV chromatograms.

2. Experimental

2.1. Surfactant samples and derivatizing reagents

An octadecanol polyoxyethylene ether with a reported average molar polyoxyethylene (EO) value of 10 ($C_{18}EO_{10}$) and a hexadecanol polyoxyethylene ether with a reported average EO value of 20 ($C_{16}EO_{20}$) were provided by Uniqema (New Castle, DE, USA). 1,3-Diphenyl-1,1,3,3-tetramethyldisilazane (DPTMDS) (96% pure), 1,3-dimethyl-1,1,3,3-tetraphenyl disilazane (DMTPDS) (97% pure), and chlorodiphenylmethylsilane (MDPCS) (97% pure) were obtained from Sigma–Aldrich (Milwaukee, WI, USA). Phenyldimethylchlorosilane (PDMCS) (98.9% pure) was purchased from Gelest (Tullytown, PA, USA). Acetonitrile (MeCN) and methanol (MeOH) were obtained from Burdick & Jackson (Muskegon, MI, USA).

2.2. Derivatization

Samples were initially derivatized at an equal surfactant concentration for both 1Ph and 2Ph derivatives. Then, the surfactant concentration was decreased in order to determine if 2Ph derivatives might require a lower concentration for achieving adequate sample characterization. The derivatization method used in this study was similar to the one employed by Hoffman et al. [9,10]. The method was as follows: approximately 45–90 mg of each sample was placed into a 2.0 mL GC vial. For the formation of 1Ph derivatives, 150 μL of DPTMDS, 1350 μL of acetonitrile, and 31 μL of PDMCS were added to the vial. For the formation of 2Ph derivatives, 150 mg of DMTPDS, 1350 μL of acetonitrile, and 31 μL of MDPCS were added to the vial. All vials were then capped, mechanically shaken for 30 s, and placed in a heating block at 80 °C for 1 h. After cooling, samples were filtered through a 0.45 μm PTFE syringe filter (Millipore, Bedford, MA, USA). A white precipitate formed during each reaction. The precipitate was washed five times with 5 mL of acetonitrile, dried, and analyzed by IR spectroscopy. The precipitates formed during both the 1Ph and 2Ph derivatization reactions were identified as ammonium chloride by comparison of each IR spectrum to the spectrum of a neat sample of ammonium chloride.

2.3. Packed-column SFC–UV system

An A5000 analytical SFC system (Mettler-Toledo Autochem Berger Instruments, Newark, DE, USA) was used in this study. The system consisted of an automatic liquid sampler (ALS) with a 10-μL loop used to make injections and a thermal control module (TCM) used to control column temperature. UV data were recorded at 215 nm by a model 1100 series UV detector (Agilent, Little Falls, DE, USA). SFC-grade carbon dioxide (Air Products and Chemicals, Allentown, PA, USA) was used as the primary mobile phase. Acclaim PA C_{16} (Dionex, Sunnyvale, CA, USA) packed columns were used for SFC separations. The dimensions of the Acclaim PA C_{16} columns were 150 or 250 mm × 4.6 mm with an average particle size of 5 μm. The mobile phase flow rate (liquid) was 2.4 mL/min. The oven temperature was 40 °C, and the outlet pressure was held at 120 bar. Mobile phase modifier programming with methanol was used for elution. Each mobile phase method started with a 5-min hold at 1% modifier to elute excess derivatizing materials. All methods then contained a linear gradient at 1% modifier per minute to a set concentration depending on the sample composition. A 2-min hold at the upper modifier concentration was then followed by a return to 1% modifier at 25%/min. A 5-min post-run was used for system equilibration.

2.4. SFC–ESI-MS system

The SFC system for SFC–ESI-MS was a Model G1205A (Hewlett-Packard, now Agilent, Wilmington, DE, USA). This instrument was upgraded with a Model FCM-1200 fluid control module, a Model 719 autosampler, and Berger Instruments SFC ChemStation control software, version 3.3.9 (all from Mettler-Toledo Autochem Berger Instruments, Newark, DE, USA). Column, mobile phase, and oven temperature were the same as described in the packed-column SFC–UV system. An Isco Model 260D syringe pump (Lincoln, NE, USA) delivered make-up flow of methanol containing 1 mM ammonium acetate downstream of the UV detector. Make-up flow was supplied at 200 μL/min. The SFC effluent was diverted to the mass spectrometer via a Valco zero-dead-volume tee (Houston, TX, USA) positioned downstream of the back-pressure regulator. The remaining flow was sent to waste. Pneumatically assisted electrospray ionization mass spectra were obtained with an API 365 mass spectrometer (Perkin-Elmer Sciex, Thornhill, Canada) in the positive ion mode. Q1 was scanned from *m*/*z* 150 to *m*/*z* 2000, while Q2 and Q3

were operated in radiofrequency (rf)-only mode. The dwell time was 0.2 ms with a 5.0-ms interscan pause. The ion spray capillary, the orifice, and the multiplier potentials were held at +4.5 kV, +40 V, and −2 kV, respectively. The nebulizer gas pressure was 60 psi (nitrogen). Turbo gas was supplied at approximately 8 L/min at a nominal temperature of 450 °C.

2.5. Spectrometry of derivatized samples

UV absorbance spectroscopy of samples, to determine appropriate detection wavelength, was performed with an Agilent 8453 diode array spectrophotometer (Little Falls, DE, USA). IR absorbance spectroscopy was performed with a Perkin-Elmer Spectrum One FT-IR (Perkin-Elmer, Shelton, CT, USA). IR spectra were recorded from 450 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

3. Results and discussion

Alcohol ethoxylate samples with a wide molar-mass and concentration-by-weight distribution pose an analytical challenge for UV detection due to some components being present close to the limit of detection, while other components represent a substantial portion of the mixture. The goal of this study was to increase UV detection sensitivity of alcohol ethoxylate oligomers. $C_{18}EO_{10}$ and $C_{16}EO_{20}$ surfactant samples were derivatized with disilazane–chlorosilane mixtures for formation of silylethers that contained either one or two phenyl groups. SFC–ESI-MS was used to identify the peaks in SFC–UV chromatograms, as well as to identify oligomers present below the limit of UV detection. Data from SFC–UV chromatograms were then used to calculate average molar oligomer values.

3.1. Calculation of average molar oligomer value

Previous research regarding the chromatographic separation of ethoxylated compounds that contain a benzene group has shown that each oligomer produces an equal molar UV response [11]. Thus, average molar oligomer values can be calculated in a straightforward fashion from UV chromatographic data. SFC combined with mass spectrometry detection (discussed later) provided identification of oligomer peaks in the SFC–UV chromatograms. The sum of the products obtained by multiplying the mole fraction of each oligomer and its assigned EO value produced the average molar oligomer value. Calculation of average molar oligomer value, in this manner, is dependent on the number of oligomers detected and included in the calculation. Detection of increasingly higher EO oligomers in theory should increase the calculated average molar oligomer value. Previously, the $C_{18}EO_{10}$ and $C_{16}EO_{20}$ samples that are examined in the current study were analyzed by ^1H NMR and were found to yield average molar oligomer values of 10.7 and 21.4, respectively [10].

3.2. SFC–ESI-MS analysis

ESI-MS in the positive ion detection mode was used tandemly with UV detection for identification of oligomers in UV chromatograms. ESI-MS, as practiced in this work, is far more sensitive than UV detection. The relatively high concentration of the samples was necessary to insure UV detection of the low-abundance, high EO oligomers. But these high concentrations made it possible to observe very low concentration of impurities produced during ethoxylation by ESI-MS. Although the samples were supposed to be primarily ethoxylated octadecanol or ethoxylated hexadecanol, derivatized C_{12}, C_{14}, C_{16}, C_{18}, and C_{20} ethoxylated alcohols were also detected in both samples. The concentrations of these impurities were not significant and detection of the impurities was only due to the relatively high concentration of the samples.

Review of contour plots aided in the analysis of SFC–ESI-MS data. As shown here, retention time is located along the *x*-axis, mass-to-charge ratio (*m*/*z*) is found on the *y*-axis, and relative ion abundance is described as colored contours in the graph. Fig. 1 shows an enlarged region of the contour plot created from SFC–ESI-MS data of the 1Ph derivatized $C_{16}EO_{20}$ sample. A series of peaks can be seen in the contour plots of the analyzed surfactants in which ethoxylate and alkyl chain lengths increase moving diagonally from the lower left corner of the plot to the upper right corner of the plot. It can be seen that the Acclaim PA C_{16} sulfonamide-embedded alkyl phase efficiently separated homologs with the same degree of ethoxylation as well as oligomers of the same alkyl chain.

Methanol containing ammonium acetate was added post-UV detector to aid in detection through formation of adduct ions. Analytes were detected as the protonated molecule ($[M + H]^+$), and $[M + NH_4]^+$ and $[M + Na]^+$ adduct ions, but $[M + NH_4]^+$ ions were primarily used for identification in this work

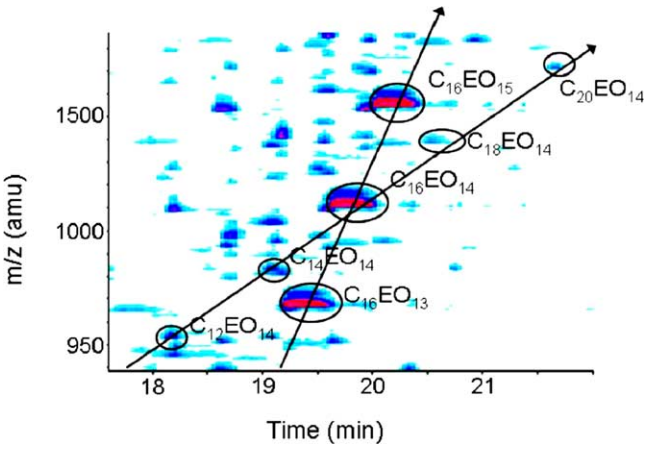

Fig. 1. Enlarged SFC–ESI-MS contour plot of 1Ph derivatived $C_{16}EO_{20}$. Acclaim PA C_{16}, (2) 150 mm × 4.6 mm, 5 μm. Oven: 40 °C, outlet pressure: 120 bar, flow rate: 2.4 mL/min, modifier: methanol, modifier gradient: 1% for 5 min, linear increase 1%/min to 25%, hold 2 min, linear decrease to 1% at 25%/min, 5 min post-run.

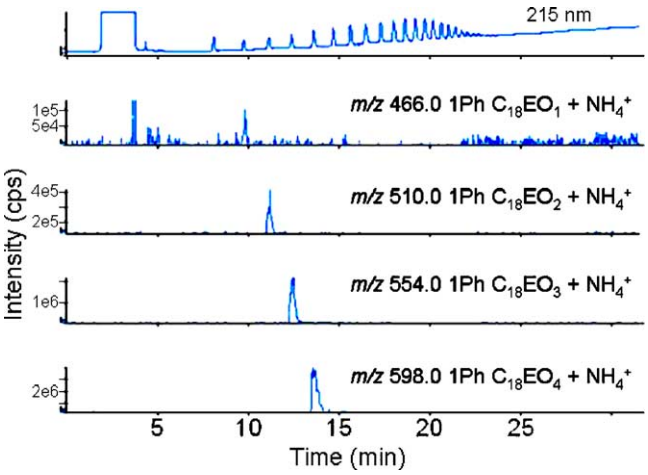

Fig. 2. Extracted ion and UV chromatograms of 1Ph derivatized $C_{18}EO_{10}$. Acclaim PA C_{16}, 250 mm × 4.6 mm. See Fig. 1 for conditions. UV detector wavelength 215 nm.

because they appeared to be associated with more oligomers than the other adduct ions. Extracted ion chromatograms were used to identify peaks in UV traces (Fig. 2). It should be noted that the mass spectrometric detector response for the first few oligomers increases greatly as EO chain length increases. This is not a new observation, and is thought to be a function of how well the ethoxylate chain can chealate the ammonium ion. Research by Okada [12] and Crescenzi et al. [13] support this notion as each laboratory has demonstrated that ethoxylated compounds are increasingly able to form adduct ions as the EO chain length increases. Multiply charged species are also seen in the contour plots at the appropriate *m/z* value where $z = 2$. Furthermore, separation between oligomers was 22 *m/z* units as compared to singly charged oligomers that were separated by 44 *m/z* units. By scanning the region between *m/z* 150 and *m/z* 2000, it was possible to identify the 1Ph derivatized $C_{18}EO_{10}$ sample oligomers with up to 35 EO units as $[M + NH_4]^+$ adduct ions. Oligomers with 30–44 EO units were observed as $[M + 2NH_4]^{2+}$ adduct ions. The mass spectral data of the 1Ph $C_{16}EO_{20}$ derivatized sample showed oligomers containing 2–36 EO units as $[M + NH_4]^+$ adduct ions and oligomers containing 19–58 EO groups as $[M + 2NH_4]^{2+}$ adduct ions. The single EO oligomer of the 1Ph derivatized $C_{16}EO_{20}$ sample was only detected as its $[M + Na]^+$ adduct ion.

3.3. Effect of derivative

Ideally absorbance is linearly related to concentration and molar absorptivity. Increasing the number of UV active groups per molecule should increase its absorptivity. Therefore, following this reasoning, a derivative that incorporated two phenyl groups was investigated and compared to derivatized AEOs containing a single phenyl group. It should be noted that the commercially produced derivatizing reagents were 94–99% pure and therefore contained extraneous compounds. An amide-embedded alkyl stationary phase and a sulfonamide-embedded alkyl phase (Acclaim PA C_{16}) were evaluated for the separation of the derivatized samples. The amide-embedded alkyl phase produced co-elution between the oligomeric series and excess 2Ph derivatizing materials and was therefore not used in this study. Using the Acclaim PA C_{16} phase, the residual reagents used to form 1Ph derivatives co-eluted in a tight band significantly resolved from the derivatized oligomers. The reagents employed in the 2Ph derivatization, on the other hand, contained compounds that have a greater interaction with the same stationary phase and are more strongly retained on the column. The excess 2Ph derivatizing reagents are well resolved by Acclaim PA C_{16} unlike the materials used in the 1Ph derivatization, but also elute prior to the oligomeric series. Without MS detection it would be difficult to differentiate between derivatized oligomers and extraneous peaks in the UV chromatograms. Analysis of reagent blanks confirmed that extraneous peaks were due to impurities in the reagents, not derivatized impurities in the surfactant samples.

A $C_{18}EO_{10}$ sample was derivatized to form 1Ph and 2Ph derivatives employing the same concentration of surfactant (60 mg/mL). Since the concentration of each sample was identical the difference in detection between derivatives should be due to the number of phenyl groups incorporated into the oligomers. An average of 25 oligomer peaks were detected in the chromatogram of the 1Ph derivative, while the chromatogram of the 2Ph derivative produced an average of 31 oligomers detected by UV absorbance. The average molar oligomer values calculated from data for the 1Ph and 2Ph derivatives were 9.6 and 10.1, respectively. A comparison between the two derivatives revealed that the 2Ph derivative produced 246% of the cumulative oligomer peak area of the 1Ph derivative. Fig. 3 contains the UV chromatograms of the 1Ph and 2Ph derivatives of the $C_{18}EO_{10}$ sample. It illustrates both the presence of excess derivatizing material and the increased detector response of the 2Ph derivative versus the 1Ph derivative. The calculated relative molar concentrations of individual oligomers ranged from 7.8% to 0.04% (calculated

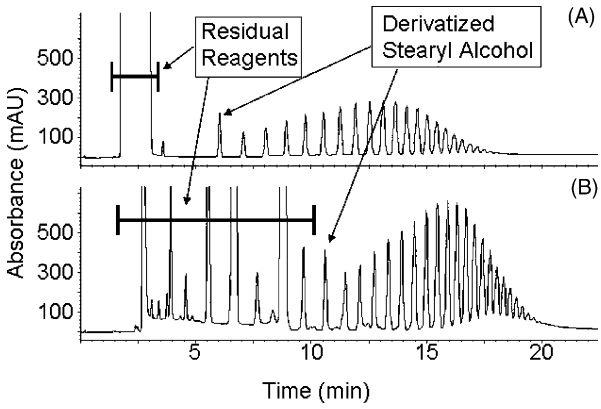

Fig. 3. SFC–UV chromatograms of 1Ph and 2Ph derivatized $C_{18}EO_{10}$. Acclaim PA C_{16}, 250 mm × 4.6 mm. See Fig. 1 for conditions. UV detector wavelength 215 nm. (A) 1Ph $C_{18}EO_{10}$ (60 mg/mL); (B) 2Ph $C_{18}EO_{10}$ (60 mg/mL).

Table 1
$C_{18}EO_{10}$ 2Ph oligomer distribution

EO no.	Composition (%)
1	3.05
2	3.22
3	3.78
4	4.47
5	5.30
6	5.94
7	6.81
8	7.43
9	7.64
10	7.80
11	7.58
12	6.91
13	6.16
14	5.26
15	4.36
16	3.51
17	2.75
18	2.11
19	1.66
20	1.19
21	0.87
22	0.61
23	0.43
24	0.29
25	0.19
26	0.18
27	0.16
28	0.12
29	0.11
30	0.08
31	0.04

from 2Ph peak area data). Derivatized octadecanol alcohol was also detected in the $C_{18}EO_{10}$ sample. The derivatization and chromatographic methods developed in this work may be useful for quantitation of residual fatty alcohols present in AEOs.

Table 1 shows the average distribution of oligomers of the 2Ph $C_{18}EO_{10}$ sample produced from a single SFC–UV chromatogram. The ability to provide both oligomeric distribution and average molar oligomer value is an advantage over ^{1}H NMR, which only provides average molar oligomer information. This can be especially important in products, which contain blends of ethoxylated or propoxylated alcohols. The increase in molar absorptivity of the 2Ph derivative allowed an average of seven additional oligomers to be detected as compared to the 1Ph derivative.

The $C_{18}EO_{10}$ sample was also derivatized as the 2Ph analog at approximately 30 mg/mL, half the concentration of the previous samples, to determine if a lower concentration of surfactant could be used for adequate calculation of average molar oligomer values. The less concentrated sample produced a similar number of detected oligomer peaks as did the more concentrated sample and an average molar oligomer value of 10.1 EO.

The ability of the 2Ph derivative to reduce the amount of sample necessary for analysis was also demonstrated with a $C_{16}EO_{20}$ sample. The sample was derivatized at two concentrations: (a) a higher concentration (70 mg/mL) 1Ph derivative and (b) a lower concentration (30 mg/mL) 2Ph derivative. Both derivatives produced approximately 38 detectable oligomer peaks. The calculated average molar EO values for the 1Ph and 2Ph derivatives were 19.2 and 20.1, respectively. The relative molar concentration of individual oligomers in the $C_{16}EO_{20}$ sample was between 6.2% and 0.35% (calculated from 2Ph peak area data). Compared to the 2Ph derivatized $C_{18}EO_{10}$ sample, which had an individual oligomer molar concentration range between 7.8% and 0.04%, the 2Ph derivatized $C_{16}EO_{20}$ sample had an oligomer distribution in which its less abundant oligomers were present at a higher concentration than the less abundant oligomers in the $C_{18}EO_{10}$ sample. Due to higher concentrations of individual oligomers in $C_{16}EO_{20}$, the oligomers were not present below the limit of detection and therefore may explain the similar number of oligomers detected in each $C_{16}EO_{20}$ sample regardless of sample concentration or derivative type.

Due to the increased sensitivity of the 2Ph derivative, highly ethoxylated oligomers were more clearly seen than those in 1Ph derivatives for both surfactants. The higher sensitivity increased the calculated average molar EO value of the $C_{16}EO_{20}$ sample by 0.9 EO unit bringing the calculated value within 0.1 EO unit of the nominal value. A comparison of the cumulative oligomer peak area of each derivative, divided by the sample's respective concentration, revealed that the 2Ph derivative produced 288% of the cumulative oligomer peak area of the 1Ph derivatized sample. In each case, it would be expected that the 2Ph derivative would produce approximately 200% of the cumulative oligomer peak area of a 1Ph derivative of the same surfactant sample. We do not fully understand the departure of the cumulative response from the expected value. An increase greater than 200% may be due to co-elution of other derivatized species (such as polyethylene glycol, for example) in the separation of 2Ph derivatives. Alternatively, one might expect that the molar absorptivity of two adjacent (i.e., vicinal) phenyl groups would be greater than double the absorptivity of two isolated phenyl groups. Regardless, for each surfactant type analyzed the 2Ph derivative was capable of producing higher average molar oligomer values. A noticeable difference between the two types of derivatives was that the 2Ph derivative exhibited a longer retention time compared to the 1Ph derivative.

3.4. Method repeatability

Two $C_{18}EO_{20}$ samples were derivatized with DMTPDS–MDPCS to form the 2Ph derivative. Each derivative mixture was separated three times. The average molar EO value calculated was 10.1 with an R.S.D. of 0.8%. Since "average molar oligomer value" is a relative measure of distribution it was important to compare peak areas of several chromatograms. As long as all (or a large majority) of the peaks were detectable, and they were equally derivatized, then the correct

oligomer value should be obtained. In other words, it would be possible to have chromatograms that vary greatly in total peak area but give equal average molar oligomer values as long as the peak ratios were consistent. For this purpose, the peak area of an individual oligomer from the reproducibility study was compared to determine reproducibility of raw peak area. The peak areas of the 4 EO oligomer of each $C_{18}EO_{20}$ chromatogram were compared. This oligomer was picked because it was well resolved in each of the chromatograms. The peak area of the four EO oligomer was divided by the mass of sample used for each derivatization. This produced an adjusted peak area that was normalized to the mass used for the individual derivatizations, which accounted for slight differences in the mass of sample used. The R.S.D. of peak areas was 7.6%. This level of reproducibility for the raw peak area of the oligomer was deemed acceptable for the purposes of this work.

4. Conclusions

The molar absorptivity of derivatized alcohol ethoxylates was increased in this study by increasing the number of phenyl groups associated with each oligomer. This was an improvement over the previously reported 1Ph derivative. Due to the impurities present in the derivatizing material, interpretation of chromatograms became more complicated for 2Ph derivatives than 1Ph derivatives due to extraneous peaks. Use of reagents of high purity would alleviate the problems associated with extraneous reagent peaks. The derivative containing two phenyl groups provided higher sensitivity than derivatives containing a single phenyl group and therefore lower concentration of 2Ph derivatives were required to provide accurate analysis for distribution of oligomers and average molar oligomer value. The high sensitivity of ESI-MS detection was demonstrated since none of the SFC–UV methods were capable of detecting all of the oligomers detected by ESI-MS. The derivatization and chromatographic methods were capable of producing average molar oligomer values consistent with nominal reported values. Thus, the 2Ph derivatization and separation methods described here could be employed for quality control applications of neat alcohol ethoxylates for the determination of average molar oligomer values and oligomeric distributions. Derivatized fatty alcohols, present due to incomplete ethoxylation, were detected in surfactant samples. The methods described here could also be used for the quantitation of excess fatty alcohols present in AEOs.

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