Characterization of a complex ethoxylated propoxylated alcohol polymer mixture using LC-HRMS and Kendrick mass defect (KMD) analysis

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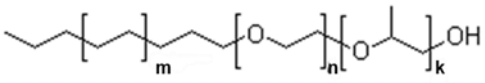
Polymers are used in a variety of applications, from biomedicine to the oil and gas industry. Because of their wide use, there has been a growing awareness and need for characterization. High resolution mass spectrometry (HRMS), coupled with soft-ionization techniques, specifically electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI), is an effective tool in polymer characterization and quantification.[1–3] The combination of these ionization methods has led to the detection of a large range of polymer systems.[1–3]

Ethoxylated propoxylated alcohols are frequently used as cleaning agents and emulsifiable agents; common uses include mechanical dishwash detergents, spray or recirculation cleaners, and floor cleaners.[4] These polymers are a class of nonionic surfactants that contain a hydrophobic alkyl chain [-CH_2-] attached to hydrophilic ethoxylate [-C_2H_4O-] chain and a propylene oxide group [-CH_3CHCH_2O-].[5] The alkyl chain can vary in length, but is typically between 6 and 16 carbons in length for detergent range surfactants.[4] The ethoxylate and propylene oxide chains also vary in length, and can range significantly from 1 to 40 units. Due to the large number of possible monomer combinations, characterization of these compounds is extremely complex. One of the most successful data prioritization approaches for polymer analysis is Kendrick mass defect (KMD) analysis. KMD transformation ensures all the related homologs in a series will have the same KMD, leading to the identification of known and unknown homologs.[1] In this study, a mixture of ethoxylated propoxylated alcohols were characterized using the X500B QTOF System and the calculated columns feature in SCIEX OS Software 2.0.1 was used to perform KMD analysis.



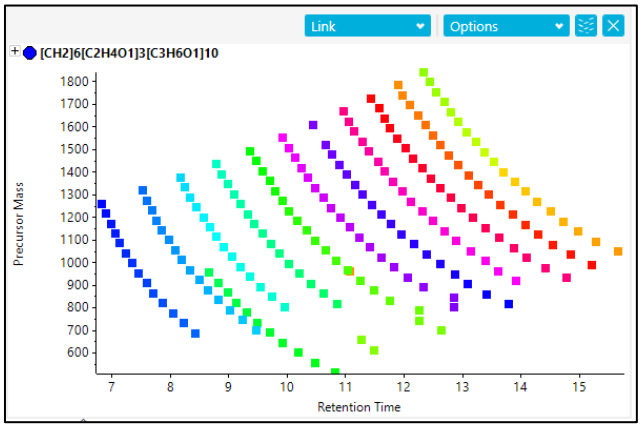


Figure 1. Analysis of ethoxylated propoxylated (C6-C10) alcohols. (Top) Example structure of an ethoxylated propoxylated (C6-C10) alcohol. (Bottom) Visualization of precursor masses using SCIEX OS Software 2.0.1.

Key features of the X500B QTOF System and SCIEX OS Software

- High-resolution MS and MS/MS at fast acquisition rates for polymer characterization using the X500B QTOF System
- Efficient data visualization and flexible data processing with SCIEX OS Software
  - The calculated columns feature allows for custom data manipulation without the need for third-party software
  - Calculating KMD *in situ* greatly simplifies this complex polymer analysis, allowing the user to focus on a few homologous series rather than thousands of individual features

Methods

Sample preparation: The sample analyzed was a mixture of ethoxylated propoxylated (C6-C10) alcohols (CAS Number 68987-81-5). Approximately 0.1 g of sample was placed in a 20 mL glass vial with 10 mL of 1:1 methanol/water. Samples were then vortexed for 10 min and stirred overnight at 25°C. The sample was then diluted 1:10 with 1:1 methanol/water.

Chromatography: A 5 µL aliquot of the samples was injected into an ExionLC™ AC System coupled to a X500B QTOF System. Separation was performed using a Phenomenex Kinetex 2.6 µm C8 100 mm x 3 mm analytical column. The LC mobile phases consisted of 0.1% formic acid and 5 mmol/L ammonium formate in water (A) 0.1% formic acid and 5 mmol/L ammonium formate in 98:2 acetonitrile/water (B) at a flowrate of 0.8 mL/min and column temperature of 40°C. Gradient conditions are listed in Table 1.

Table 1. Gradient conditions used for the LC separation of polymer homologs.

Step	Time (min)	B (%)
0	*0*	*50*
1	*3*	*50*
2	*16*	*95*
3	*23*	*95*
4	*23.1*	*50*
5	*25.5*	*50*

Mass spectrometry: The sample was analyzed in positive electrospray ion (ESI+) mode using the Turbo V™ Ion Source. The source temperature was set at 500°C, the ion source gas 1 at 50 psi, the ion source gas 2 at 40 psi, the curtain gas at 30 psi and the CAD gas at 8 psi. The spray voltage was set at 5500 V. The TOF experiment was performed at collision energy 10 V, a declustering potential of 80 V, and mass range 100-3000 m/z. The MS/MS experiment performed was an information dependent acquisition (IDA) method with a declustering potential of 80 V, collision energy of 35 V and a collision energy spread of +/- 15 V.

Data processing: Data were processed using the SCIEX OS-Q Software 2.0.1. A suspect screening approach was used to identify specific chain lengths. The suspect list was built in Microsoft Excel and contained the formulas of all theoretical combinations of monomers. The formulas were then pasted into SCIEX OS Software and assigned an exact mass. Additionally, calculated columns and custom flagging rules were used to perform the KMD analysis (Figure 2).

Figure 2. Data processing in SCIEX OS Software 2.0.1. Calculating the A) Kendrick mass based on ethoxylate repeating units and B) Kendrick mass defect (KMD) using calculated columns feature.

Results

Chromatographic separation is extremely important for polymers, as multiple isomers are possible. For example, when polyethylene glycols (PEGs) are polymerized, there is only one isomer of each PEG because the ethylene oxide (EO) monomer is symmetrical.[5,6] However, when polypropylene glycols are polymerized, several isomers exist, as the oxygen on each end of the propylene oxide (PO) monomer is not symmetrical.[5–7] These isomers then must be chromatographically separated. The use of the Phenomenex Kinetex C8 column resulted in excellent chromatographic separation (Figure 3a). As the propylene oxide group increased, an increase in retention time was observed. However, as the ethylene oxide group increased, a decrease in retention time was observed due to their hydrophilic properties (Figure 3b).

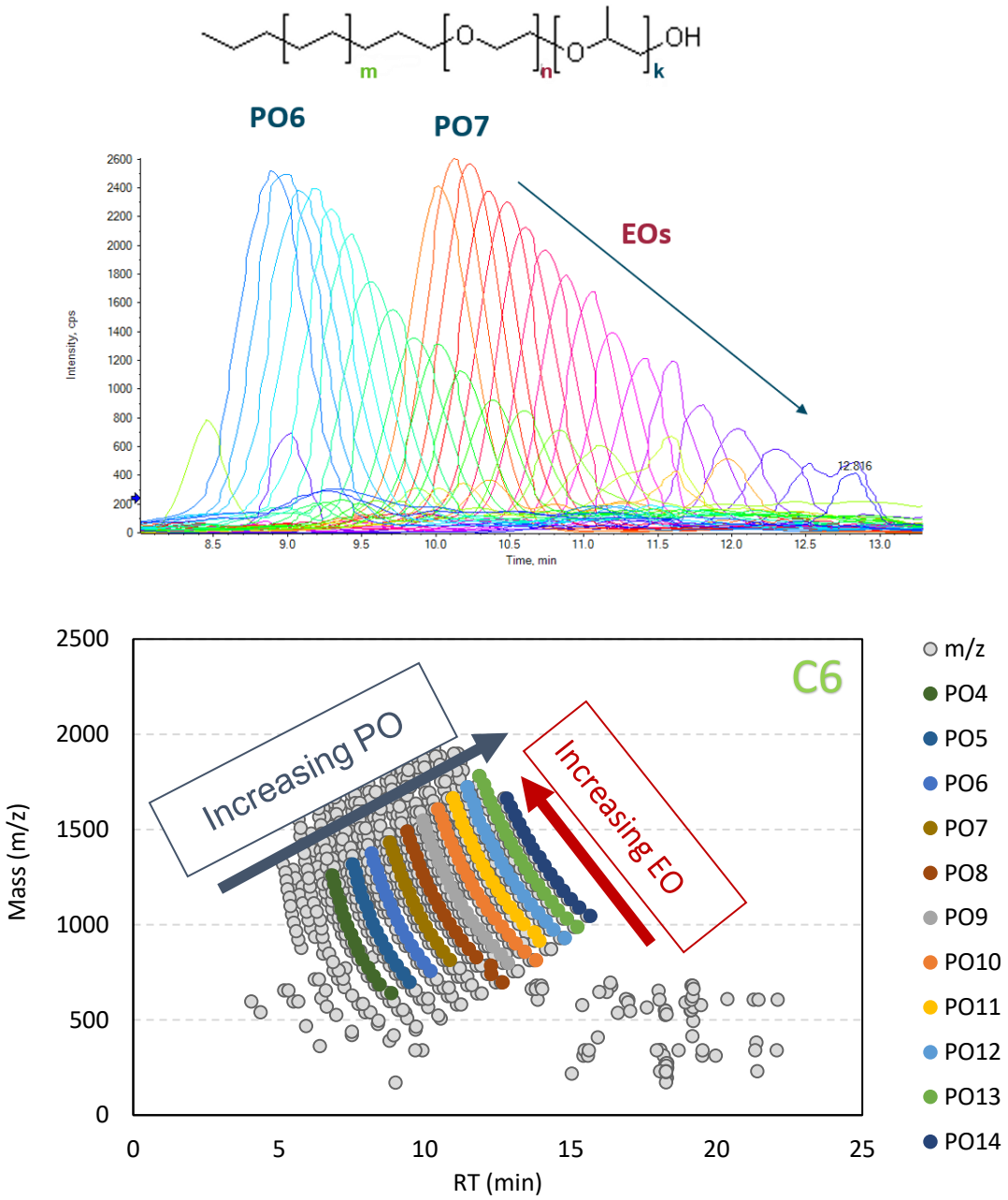


Figure 3. Chromatography of ethoxylated propoxylated alcohols. (Top) Extracted ion chromatograms (XICs) of the 6 and 7 propylene oxide (PO) monomers highlight the very good chromatography achieved with the Kinetix C8 column. (Bottom) Non-targeted peak finding identified numerous features and interesting patterns emerged. As the propylene oxide (PO) group increased, an increase in retention time was observed. However, as the ethylene oxide (EO) group increased, a decrease in retention time was observed.

The average molecular mass of this polymer sample was 1500 Da. The analyzed sample contained over 1000 combinations of alkyl, ethoxylate, and propylene oxide groups. Alkyl groups ranged from 6 to 10 units, with ethoxylate and propylene oxide groups ranging from 4 to 24 and 1 to 16 units, respectively. Both the proton adduct and the ammonium adduct were observed, but the ammonium adduct had a higher intensity.

Additionally, compounds existed in both single and double charge states. This created a relatively complex result (Figure 3b), as each individual polymer had multiple features associated with it. However, SCIEX OS Software 2.0.1 allows the user to group these charge states and adducts into a single component, which greatly reduced the complexity to only a few hundred compounds.

To further simplify the results, the calculated columns feature in SCIEX OS Software 2.0.1 was used to calculate the KMD (Figure 4). Once the KMD was calculated, the features with the same KMD were grouped using calculated columns. These grouped features could then be characterized based on alkyl, ethoxylate, and propylene oxide chain lengths. Thus, the data can be summarized as containing 12 unique sets of KMDs, differing by only the number of ethoxylate units.

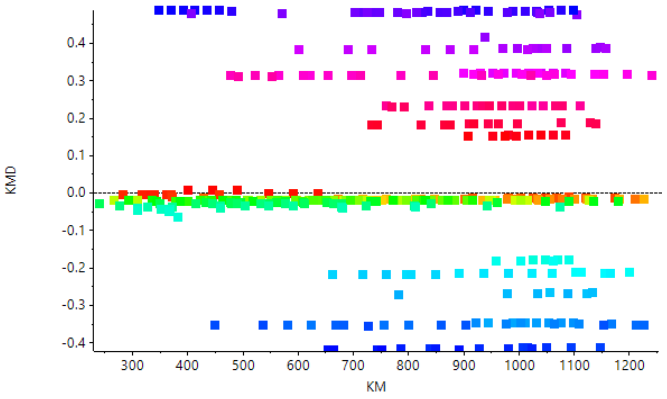


Figure 4. Custom columns in SCIEX OS Software. Computation of Kendrick mass defect (KMD) vs. Kendrick mass (KM) can be performed then plotted.

Summary

In this study, an LC-HRMS method for the analysis of polymers using the X500B QTOF System was presented. The ethoxylated propoxylated alcohol sample was chromatographically separated using a Phenomenex Kinetex C8 column. Over 1000 different combinations of alkyl, ethoxylate, and propylene oxide groups were identified using a suspect screening approach. SCIEX OS Software 2.0.1 was able to group adducts and charge states, greatly reducing the number of features. Additionally, using the calculated columns function, KMD analysis was able to further reduce the dataset complexity into several homologous series differing by only normalized repeating units.

References

1. Dimzon, I. K. Analytical and Statistical Approaches in the Characterization of Synthetic Polymers, Universiteit van Amsterdam, 2015.
2. Terrier, P., Desmazieres, B., Tortajada, J. and Buchmann, W. (2011) APCI/APPI for Synthetic Polymer Analysis. *Mass Spectrom. Rev.* **30**, 854–874.
3. Murgasova, R.; Hercules, D. M. (2002) Polymer Characterization by Combining Liquid Chromatography with MALDI and ESI Mass Spectrometry. *Anal. Bioanal. Chem.* **373 (6)**, 481–489.
4. U.S. EPA. Substance Registry Services (SRS) - Ethoxylated propoxylated C6-10 alcohols. (accessed Sep 10, 2019).
5. Herzberger, J.; Niederer, K.; Pohlit, H.; Seiwert, J.; Worm, M.; Wurm, F. R.; Frey, H. (2016) Polymerization of Ethylene Oxide , Propylene Oxide , and Other Alkylene Oxides : Synthesis , Novel Polymer Architectures , and Bioconjugation. *Chem. Rev.* **116**, 2170–2243.
6. Thurman, E. M.; Ferrer, I.; Rosenblum, J.; Linden, K.; Ryan, J. N. (2017) Identification of Polypropylene Glycols and Polyethylene Glycol Carboxylates in Flowback and Produced Water from Hydraulic Fracturing. *J. Hazard. Mater.* **323**, 11–17.
7. Andrzejewska, E. (2001) Photopolymerization Kinetics of Multifunctional Monomers. *Prog. Polym. Sci.* **26 (4),** 605–665.

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