Molecular weight fractionating of phenolic compound by SPE in waxy crude oil samples and their characterization by ESI FT-MS

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Abstract

A method for the simultaneous isolation and separation phenolic compounds into different molecular weight ranges fractions using solid phase extraction SPE is presented and applied in seven waxy crude oil samples. The ESI FT-MS analysis of these fractions employing the Orbitrap Q-Exactive reveals the presence of phenolic compounds with carbon number >100. This findings corroborate previously results[1] indicating that alkylated monoaromatic phenols (DBE 4) aligns with paraffin molecules to form stable emulsions.

Introduction

Recently, Vaz et al[1] prepared and characterized emulsions of several waxy crude oils exhibiting similar properties to understand better the nature of their polar components. They demonstrate that the alignment of paraffin and the alkyl side chains of phenolic-like compounds contribute to the emulsion stability and affect the rheological behavior of the highly paraffinic crude oil. Due the different ionization efficiency of acidic on crude oil, low molecular weight acids dominate the electrospray ionization (ESI) process and suppress ionization of the higher mass (less efficiently ionized) acids. ESI analysis of these waxy crude oils not detected high molecular weight phenolic compounds due the ionization suppression. Recently, Rowland and co-authors[2] developed a new method for the simultaneous isolation of acids and separation into distinct molecular weight ranges using solid phase extraction SPE. The separation by molecular weight isolates acids into fractions with more similar ionization efficiency, enabling the detection of high molecular weight acids. With the aim of detect high molecular weight phenolic compounds to prove the evidence of paraffin alignment with the alkyl side chains of phenolic-like compounds, we performed the fractionation by SPE developed by Rowland and co-authors[2] to seven waxy crude oils and subsequent characterization of such fraction by ESI(-)-Orbitrap-MS.

Results and Discussions

The samples were analyzed using ESI(-)-Orbitrap. Briefly, all samples were diluted to ~1 mg mL^{-1} in 50:50 (v/v) toluene/methanol, which contained 0.1% w/v of NH_4OH. The obtained solution was directly infused at a flow rate of 3 µl min^{-1} into the ESI source. The fractionation of phenolic was carried out using a (strong anion exchanger – SAX) SPE phase. The sample (500 mg) was eluted at a rate of 1 drop/second and then fractionated using eight different solvent gradients. Fractions 1, 2 e 3 were extracted with DCM (100%), MeOH:DCM (50/50) and MeOH (100%) respectively. Formic acid (FA) was added to the extractor solvent from fraction 4 to fraction 8 and the sequence of elution was: MeOH:DCM:FA(90/10/5), MeOH:DCM:FA (80/20/5), MeOH:DCM:FA(70/30/5), MeOH:DCM:FA (60/40/5), and MeOH:DCM:FA(50/50/5). Molecular weight fractionation reduces the complexity of each sample, thereby increasing dynamic range, and also separates easily ionized low-molecular-weight acids from the less efficiently ionized high-molecular-weight acids. Alkylated monoaromatic phenols (DBE 4) were the most prevalent molecules in all fractions, followed by mono- and dicyclic monoaromatic phenols (DBE 5 and 6, respectively). Di- and tri-aromatic phenols (DBE 7 and 10, respectively) were also present in all of the crudes. At F7 and F8 were detected phenolic compounds (DBE 4) with up to 100 carbons. The alkyl chain of these phenolic compounds aligns with paraffin molecules to form stable emulsions.

Conclusions

The simultaneous isolation of phenolic and acids separation into distinct fractions based on molecular weight seven waxy crude oil samples enable the detection by ESI(-)-Orbitrap-MS of phenolic compounds with up to 100 carbons. The allignment of such phenols with paraffin molecules explain the rheological properties of crude oil samples.

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