Characterization of Asphaltenes precipitated at different solvent power conditions using Magnetic Resonance Mass Spectrometry

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Introduction

It is well known that asphaltene precipitation is affected by several factors, including temperature, precipitant/sample ratio, contact time, etc. In practical terms, this means that for the same crude oil, a different set of molecules would precipitate forming a distinct asphaltene depending on these factors. Although it is expected that the molecules more prone to precipitate are going to be those with the higher aromaticity, higher molecular weight and/or higher polar nature, significant variations in the amount and distribution of the molecules can occur as shown by previous studies.¹⁻² In the present work, the effect of solvent power on asphaltene properties (heptane to crude oil ratio) has been investigated using a combination of analytical techniques.

Elemental Analysis¹ **Heptane to Crude** Oil ratio (HCOR) H/C (wt%) (wt%) 82.86 11.01 1.59 83.58 10.41 1.49 1.5 84.08 10.00 1.43 2 80.94 8.72 1.29 5 81.35 8.41 1.24 10 100 80.33 8.04 1.20

Table1: Elemental analysis of asphaltenes as a function of the heptane to crude oil ratio (HCOR) APPI and LDI

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MRMS Analysis

Asphaltenes were analyzed using a solariX 2XR FT-ICR mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7 T refrigerated actively shielded superconducting magnet (Bruker Biospin, Wissembourg, France) and the Paracell™ analyzer cell. Apollo II Dual ESI/MALDI ion source was used. Samples were analyzed using APPI in positive ion mode with resolving power of 1.300.000 at m/z 400 using quadrupolar detection and absorption mode processing. Internal mass calibration, spectral interpretation, and export of mass lists were performed using DataAnalysis 5.0 (Bruker Daltonics). The analysis of the data including calculation of molecular formulas and relative abundances of compound classes was performed using PetroOrg 10.0 (Florida State University). Double bond equivalence (DBE) values were calculated using the following equation:

DBE = c - h/2 + n/2 + 1For the elemental formula $C_c H_h N_n O_o S_s$.





HCOR using APPI positive ion mode



positive ion mode data.



(1)

Fig. 2. Relative abundances for classes containing different numbers of heteroatoms obtained by APPI.



Fig. 4. C number distributions of different HCOR using APPI positive ion mode.



Fig. 7. H/C molar ratios. Calculation is based on APPI positive ion mode data.

Separation of Asphaltenes

Asphaltenes were separated from a medium crude oil (API of 30.4). Different heptane/oil ratios were used to induce precipitation. After blending, solutions were kept in static conditions for 24 h. Blends were filtered using a Teflon membrane filter (0.2 mm). The filtered cake was not washed with additional heptane after filtration.

FT-IR and NMR Analysis

FT-IR spectra were obtained on a Bruker ALPHA Eco with single reflection ATR module and ZnSe crystal.

¹H-NMR spectra were measured on a Bruker Advance III NMR 400 MHz system



Fig. 5. DBE vs C plots for class HC of different HCOR using LDI positive ion mode.



Fig. 8. FT-IR spectra of the asphaltenes as a function of HCOR



Fig. 9. Aromatic character measured by FT-IR and ¹H-NMR.



Results

Class distribution plots are shown in Fig.1 based on weighted average intensities considering radical cations as well as protonated species generated by positive LDI. In this plot, HC classes as well as classes containing one heteroatom become less abundant as the heptane to crude oil ratio increases. The opposite happens for most classes containing two or more heteroatoms. Similar results are found when positive APPI is used. Fig.2 shows relative abundances for classes containing different numbers of heteroatoms (APPI) as a function of the heptane to crude oil ratio (HCOR).

Based on weighted relative abundances, DBE distributions for the samples are shifted to the rights with higher solvent ratios indicating larger DBEs as shown in Fig. 3. In contrast, molecular size distribution do not show a clear tendency (Fig. 4). Additionally, calculations indicate that while differences in average DBE can be as large as 6 units between different HCOR, the maximum difference in molecular size is around 1.5 carbon atoms. These tendencies were also observed for individual classes as shown in Fig. 5 for the class HC (LDI).

The appearance of molecules with larger DBEs as the solvent power of the solvent decreases leads to an increase in the aromaticity. Fig. 6 compares the aromaticity distributions according to relative abundances. Aromaticity was calculated as DBE/(C+N). In general, average H/C molar ratios show the right tendencies. Fig. 7 compares experimental values obtained by elemental analysis (see Table 1) and values calculated as averages H/C molar ratios based on APPI data. Similar results are obtained when LDI data is used for the calculations of average H/C molar ratios.

Fig. 8 shows the corresponding IR spectra of the asphaltenes obtained at different HCORs. The comparison of the spectra indicates that the signals corresponding to aromatic moieties increase significantly as HCOR increases. Assuming that the extinction coefficients of the aromatic and aliphatic C-H groups do not vary much among the asphaltene samples, the ratio of the bands 1600 cm⁻¹ and 2920 cm⁻¹ can be considered a measure the aromaticity.

These ratios are shown in Fig. 9 for different samples. Aromaticity was also evaluated using ¹H-NMR based on the aromatic proton/aliphatic proton ratio. This data is also shown in Fig.9.

Both techniques yield similar tendencies: There is an increase in the aromaticity as the solvent power decreases. This is in agreement with enrichment of more aromatic molecules in the filtered cake based on mass spectrometric analysis.

References

3664-3674.

Conclusions

- MS.
- deposition.



¹ Andersen, S. I. *Fuel Sci. Technol. Int.* **1994**, *12*,51-74. ² Carbognani Ortega, L. et al. *Energy Fuels* **2015**, *29*,

> Composition of the asphaltenes changes dramatically depending on the solvent power of the heptane to crude oil ratio (HCOR).

Decreases in solvent power produce asphaltenes that are more aromatic. In particular, asphaltenes become enriched in molecules with larger DBEs and with more heteroatoms per molecule. In contrast, no significant changes in molecular size were observed as a function of the heptane to crude oil ratio.

FT-IR and ¹H-NMR measurements confirm the tendencies evaluated by

This study provides new information about the nature of molecules that precipitate under different conditions and can help to understand the mechanism that leads to asphaltene

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