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

Matthias Wiltz, Markus Godejohann, Sven Ollmanns, Estrella Rogel
Bruker Daltonik GmbH, 28359 Bremen, Germany
Bruker Biospin GmbH, 28277 Rheinstetten, Germany
O&G L. Ortega, L. et al.

Introduction
It is well known that asphaltene precipitation is affected by several factors, including temperature, precipitation/solvent/sample 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. 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.

MRMS Analysis
Asphaltenenes were analyzed using a Bruker 384 FT-JIT-IC mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7 Tesla actively shielded superconducting magnet (Bruker Biospin, Wissembourg, France) and the Panalytical AXS UltraH. A self-developed solvent evaporation system was used. Samples were analyzed using APPI in positive ion mode with resolving power of 1 300 000 at m/z 400 using quadrupoles to select the desired daughter ion. Spectra were acquired in positive ionization mode using Panalytical G2 scan parameters. The analysis included the calculation of molecular formulas and relative abundances of compound classes using NanoLog 1.0 (Florida State University). Double bond equivalence (DBE) values were calculated using the following approach:

DBE=C-H n/(n+1)

For the elemental formula CnHmOg

Separation of Asphaltenenes
Asphaltenenes were separated from a medium crude oil (API of 30.4) by precipitation at different solvent power conditions using a fractionator (McGill University, Montreal, Canada). The precipitate was washed with heptane and the combined washings were concentrated. The asphaltene cake was not washed with additional heptane after filtration. The precipitate under different conditions (heptane to crude oil ratio) was obtained at different HCORs. The solvent power (HCOR) was varied from 1:25 to 1:100.

Table 1: Elemental analysis of asphaltene as a function of the heptane to crude oil ratio (HCOR) API and LDI

<table>
<thead>
<tr>
<th>Heptane to Crude Oil Ratio (HCOR)</th>
<th>Elemental Analysis</th>
<th>H/C</th>
<th>C/H</th>
<th>O/H</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:25</td>
<td>0.82  11.01  1.59</td>
<td>1.5</td>
<td>3.55</td>
<td>10.41</td>
</tr>
<tr>
<td>1:10</td>
<td>0.68  11.01  1.59</td>
<td>1.5</td>
<td>2.48</td>
<td>10.00</td>
</tr>
<tr>
<td>1:5</td>
<td>0.64  11.01  1.59</td>
<td>1.5</td>
<td>1.80</td>
<td>6.72  1.29</td>
</tr>
<tr>
<td>1:3</td>
<td>0.64  11.01  1.59</td>
<td>1.5</td>
<td>1.80</td>
<td>6.72  1.29</td>
</tr>
<tr>
<td>1:2</td>
<td>0.64  11.01  1.59</td>
<td>1.5</td>
<td>1.80</td>
<td>6.72  1.29</td>
</tr>
<tr>
<td>1:1</td>
<td>0.64  11.01  1.59</td>
<td>1.5</td>
<td>1.80</td>
<td>6.72  1.29</td>
</tr>
<tr>
<td>1:0.5</td>
<td>0.64  11.01  1.59</td>
<td>1.5</td>
<td>1.80</td>
<td>6.72  1.29</td>
</tr>
</tbody>
</table>

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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 are taken as a measure of aromaticity. The opposite happens for 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).

Fig. 1. FT-IR spectra of the asphaltene fraction obtained at different HCOR.

Based on weighted relative abundances, DBE distributions for the samples are shifted to the right with higher solvency indicating larger DBE as shown in Fig. 3. In contrast, molecular size distributions 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 (LDS).

FT-IR and NMR Analysis
FT-IR spectra were obtained on a Bruker Alpha II Dual ESI/MALDI ion source. Apollo II Dual ESI/MALDI ion source was used. The analysis included the calculation of molecular formulas and relative abundances of compound classes using NanoLog 1.0 (Florida State University). Double bond equivalence (DBE) values were calculated using the following approach:

DBE=C-H n/(n+1)

For the elemental formula CnHmOg

Conclusions
Composition of the asphaltenes changes dramatically depending on the solvent power of the heptane to crude oil ratio. 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 MALDI imaging MS. 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 deposition.

References

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