Atmospheric Pressure Photoionization and Laser Desorption Ionization Coupled to Fourier Transform Ion Cyclotron Resonance Mass Spectrometry to Characterize Asphaltene Solubility Fractions: Studying the Link between Molecular Composition and Physical Behavior

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Introduction

Understanding the relationship between composition of asphaltenes and their behavior is of central importance in the development of predictive, preventive and remediation tools for asphaltene deposition. In the current work, a series of asphaltene solubility fractions extracted from a heavy crude oil have been analyzed using laser desorption ionization (LDI) and atmospheric pressure photoionization (APPI) coupled to Fourier transform ion cyclotron resonance mass spectrometry. The objective is to find how molecular compositional data compares and correlates with information found using other techniques.

FT-ICR MS Analysis

Fractions were analyzed using a solarIX XR FT-ICR mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 12 T refrigerated actively shielded superconducting magnet (Bruker Biospin, Wissembourg, France) and the Paracell™ analyzer cell. An Apollo II Dual ESI/MALDI ion source was used. Samples were analyzed using positive ion mode using APPI and LDI. Internal mass calibration, spectral interpretation and export of mass lists were performed using DataAnalysis 4.2 (Bruker Daltonics). The analysis of the data including calculation of molecular formulae and relative abundances of compound classes was performed using Composer 1.6.6 (Sierra Analytics). Double bond-equivalence (DBE) values were calculated using the following equation:

\[ \text{DBE} = \frac{c-h}{2} + \frac{n}{2} + 1 \]  \hspace{1cm} (1)

For the elemental formulae C_{\text{H}}\text{N}_{\text{O}}\text{S}_{\text{S}}

Experimental

Samples

A residue was separated by solubility. The fractionation was performed using an Accelerated Solvent Extractor Dionex 300. The PTFE supported residue was placed into a 100 mL stainless steel cell and extracted with a series of solvents/ solvent blends. This procedure yields 6 fractions: hydrocarbon solubles (Fraction 1), 15/85 CH\text{Cl}_{2}/n-heptane solubles (Fraction 2), 30/70 CH\text{Cl}_{2}/n-heptane solubles (Fraction 3), CH\text{Cl}_{2} solubles (Fraction 4) and 90/10 CH\text{Cl}_{2}/n-heptane solubles (Fraction 5) and Fraction 6 which is composed of the remaining material and is extracted using a 90/10 CH\text{Cl}_{2}/n-heptane blend at high temperature (120°C). A summary of properties of the fractions is shown in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Yield (wt%)</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
<th>S</th>
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<td>1.61</td>
<td>4.20</td>
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</tr>
<tr>
<td>3</td>
<td>19</td>
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<td>7.99</td>
<td>1.39</td>
<td>647</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>82.46</td>
<td>7.31</td>
<td>0.40</td>
<td>647</td>
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<td>82.46</td>
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</table>

Solubility Parameter Distributions

Solubility parameters were calculated using the third rule that correlates density with solubility parameter for hydrocarbon molecules:

\[ \delta = 17.347 \times 1.6793 + 2.904 \]  \hspace{1cm} (3)

Fig. 7 shows a comparison between solubility parameter distributions of the same class (class N) in different fractions. There is a significant overlap among classes from different fractions, but it can be seen that solubility parameters shift to larger values from fractions 2 to 4. Similar results were observed for other classes.

Results

Class Distributions of the Fractions.

Class distribution (radial column classes) plots are shown in Fig. 1 for both APPI and LDI. According to these figures, APPI results indicate that, for the more abundant fractions (fractions 2 to 4), the predominant classes are S and N containing classes. For fraction 1 (or ‘matteiros’), S and HC are the most abundant classes. In contrast, LDI shows a large relative abundance of N class followed by S and NS-classes in all the fractions. S and SNS-classes are clearly diminished in comparison with APPI. This is expected since LDI is very sensitive toward aromatic nitrogen-containing species. (Fig.1)

Aromaticity

Fig. 2 shows a comparison between average aromatics determined from APPI and LDI for the different classes: Fa(DBE)/(C+N) and Fa(N). C and N are weighted average carbon and nitrogen. DBE represents the weighted average double bond equivalent. Fig. 2 indicates that average aromatics obtained by LDI tend to be larger than those obtained by APPI. Interestingly, the results for nitrogen-containing classes are very close, while the larger differences found correspond to classes S and NS.

Average and Bulk Properties

Figs. 3 to 6 show the comparison of bulk properties determined by standard characterization, i.e. elemental analysis and molecular weight with results obtained using APPI. Average density for each molecule was calculated according to:

\[ \rho = 0.0647H + 1.6793 \]  \hspace{1cm} (2)

Where H represents the hydrogen content (wt%). The density for each class was obtained as the weighted average value based on intensity.

Fig. 5. Molecular Weight comparison

Fig. 6. Density comparison

Fig. 7. Solubility Parameter Distribution for N-class

Conclusions

There is a qualitative agreement between the compositional data provided by these MS techniques and the data obtained using more conventional analytical methods. According to the gathered data, both techniques preferentially ionized the most aromatic molecules in the sample and, as a consequence, H/C ratios and molecular weights were lower. Densities and solubility parameters were larger than those determined by more standard techniques.

Fig. 8. Solubility Parameter Distribution comparison

Fig. 1. Distribution of compound classes observed for the fractions using positive ion mode APPI and using positive ion mode LDI.

Fig. 2. APPI and LDI comparison

Fig. 3. H/C Molar Ratio comparison

Fig. 4. DBE/C-N content comparison

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Fig. 6. Density comparison

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Fig. 8. Solubility Parameter Distribution comparison

FT-ICR MS Analysis

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