Molecular Weight Distributions of Asphaltenes and Deasphalted Oils Studied by Laser Desorption Ionization and Ion Mobility Mass Spectrometry

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Laser desorption ionization (LDI) and ion mobility mass spectrometry (IM-MS) are applied to study molecular weight distribution and cross sections of petroleum asphaltene (ASPH) and deasphaltened oils (DAO). Ion mobility data confirmed the presence of gas-phase aggregation in LDI experiments. Most of the molecules with MW > 3000 g/mol in LDI result from gas-phase aggregation. Two-dimensional (2D) IM-MS trend lines are compared with model polymer systems to confirm the order of cross sections (polywax > polystyrene > DAO > ASPH > fullerene), and these data illustrate that ASPH has a more condensed average structure than DAO.

Determining chemical compositions of heavy petroleum has received growing attention in the research community, owing to the depletion of light crude oil supplies and increasing demand for hydrocarbon-based energy. Petroleum vacuum residue (PVR) is one type of heavy petroleum derived from vacuum distillation of crude oils. Nominally, all molecules in PVR boil above 540 °C. These heavy petroleum resources have a low H/C ratio and high S, N, O, and metal contents.1–4 PVR also contains a high level of asphaltenes (typically defined as n-heptane insolubles). Effective production and utilization of these heavy hydrocarbon resources requires better understanding of their chemical properties, including molecular weight distribution, functional groups, compositions, structures (e.g., condensed aromatic core versus two or three alkyl-bridged, small cores), etc.;5,6 however, even the determination of molecular weight distributions of heavy petroleum samples, in particular that of asphaltene, is still problematic as reflected in the large number of publications in this area.7–13 The difficulty arises as a result of the chemical nature of asphaltene samples (~50% boils above 700 °C and high polar content). Condensed phase aggregation of these molecules is well-known to have a direct impact on traditional MW measurement techniques, such asgel permeation chromatography14 and vapor pressure osmometry.13,16 Although gas-phase aggregation of asphaltenes has been reported for various ionization techniques including laser desorption,17,18 electrospray,17,18 and field desorption ionization,12 uniquely establishing the occurrence of aggregation is not straightforward when dealing with crude petroleum samples.

Ion mobility spectrometry (IMS) is a gas-phase, postionization separation method that adds new dimensions to mass spectrometry (MS).19–22 IMS separates gas-phase ions based on their collision cross section and, when coupled with mass (m/z) separation, has shown unique strength in differentiation of peptide mixtures,21,22 carbon clusters,26 and polymeric molecules22 that have significant overlaps in mass chromatograms. IM-MS is often used in conjunction with advanced ionization tools such as matrix-
assisted laser desorption ionization (MALDI)\textsuperscript{19,22,30} and electrospray ionization (ESI)\textsuperscript{24} to analyze high molecular weight and high-polarity materials. In this work, we explore IM-MS coupled with laser desorption ionization (LDI) for heavy petroleum characterization. Our primary interest is to differentiate aggregates with laser desorption ionization (LDI) for heavy petroleum high-polarity materials. In this work, we explore IM-MS coupled with laser desorption ionization (LDI) for heavy petroleum high-polarity materials.

EXPERIMENTAL SECTION

The asphaltene and deasphaltened oils (DAO) used in these studies were obtained from Exxon Mobil Research and Engineering Company. Asphaltene and DAO are separated by dissolving PVR in \textit{n}-heptane with a sample to solvent ratio of 1:10. Asphaltene is collected as \textit{n}-heptane insolubles (28\%). Elemental analyses were obtained by Exxon Mobil laboratories via standard assay, and aromatic carbon content was determined by \textit{13}C NMR. Polystyrene 1400 samples were purchased from Polymer Science Laboratory, and the polywax 650 was obtained from Aldrich. Samples were prepared for LDI by dissolving a specific portion of the sample in either benzene or toluene and spotting on an analysis plate using a dried droplet technique.

LDI-MS spectra were acquired on an Applied Biosystems time-of-flight (TOF) STR mass spectrometer using a 337 nm nitrogen laser (Spectra-Physics) at a firing rate of 20 Hz. Calibration of the nitrogen laser energy was performed using an Ophir Nova power/energy meter coupled to a PE-10 Ophir pyroelectric head. Calibration of the nitrogen laser energy was performed using an Ophir Nova power/energy meter coupled to a PE-10 Ophir pyroelectric head. All LDI-MS experiments were performed using the same instrument settings. Analysis of petroleum samples by field desorption mass spectrometry was conducted on a VG-ZAB mass spectrometer as described previously.\textsuperscript{12}

The LDI-IM-MS used in these studies was constructed in collaboration with Ionwerks, Inc. (Houston, TX) and is similar to instrumentation described previously.\textsuperscript{21,22,23} LDI was performed using a frequency-tripled solid-state Nd:YAG laser (355 nm, Power Chip) operated at a frequency of 300 Hz. After LDI, ions are extracted into the drift cell under the influence of a weak electrostatic field (10–20 V cm\textsuperscript{-1} Torr\textsuperscript{-1}), and IMS separations are carried out in a 15 cm long drift cell (periodic high-field/low-field regions) maintained at 1–10 Torr with He gas (measured with an Inficon capacitance manometer). In all IM-MS experiments, the LDI source is maintained at the same pressure as the drift cell. Typical IMS field strengths were 10–20 V cm\textsuperscript{-1} Torr\textsuperscript{-1}, and all measurements were performed at ambient temperature (ca. 23 °C). Ions eluting the drift cell were extracted into an orthogonal reflectron-TOF for mass analysis. The mass spectrometer was externally calibrated using C\textsubscript{60}, C\textsubscript{70} (Sigma), and insulin (Sigma). Unless otherwise noted, all spectra were acquired at a laser intensity equivalent to the observed signal threshold. High laser power (16 \textmu J/pulse) in these experiments corresponds to an intensity where the multichannel-plate detector was near saturation, and moderate laser power (8 \textmu J/pulse) was roughly between high and threshold intensities.

In many instances, it was necessary to compare IM-MS spectra of petroleum to that of other model compounds. Although codepositions of these samples provide the most direct method to accomplish this comparison, it is disadvantageous to allow the formation of coaggregates in the gas phase while conducting studies of gas-phase aggregation. Where necessary, comparisons were made through subsequent acquisitions for samples deposited adjacent to one another on a sample plate, followed by graphically overlaying the resulting spectra using Ionwerks custom software. In these experiments, the arrival time distributions (ATD) of ions at the detector are directly proportional to the ion-neutral collision cross sections (CCS), as described by McDaniel and Mason.\textsuperscript{34}

Molecular modeling was used to generate theoretical trend lines using polynuclear aromatic hydrocarbons (PAHs) as analogues for asphaltene molecules. Theoretical calculations were performed to optimize the structures of PAHs and their multimers. The energy of the structures was minimized using molecular mechanics calculations employing the cif02 force field in the Cerius\textsuperscript{2} (Accelrys Software Inc.) modeling environment. Theoretical CCS values were determined using the trajectory Monte Carlo method in MOBCAL.\textsuperscript{35,36}

RESULTS AND DISCUSSION

The determined bulk composition of the two samples is summarized in Table 1. Asphaltene shows increased S, N, metal, and aromatic carbon content and reduced H/C ratio as expected. Figure 1 contains the LDI mass spectra for asphaltene and DAO at three different laser intensities. These spectra were obtained using a standard high-resolution TOF mass spectrometer operated at high vacuum. Spectra acquired at 3 \textmu J/pulse (Figure 1, parts A and D) correspond to data acquired near the ionization threshold. In general, LDIMS data shows a lower MW distribution at threshold for these samples when compared to values by field desorption mass spectrometry (FD-MS). For example, analysis of the asphaltene sample by FD-MS reveals a MW distribution peaked around m/z 900 ranging from 300 to 3000 m/z.\textsuperscript{12} The results from FD-MS shows a higher MW distribution than data for LDIMS at threshold, which shows a MW distribution peaked

| Table 1. Sample Properties for the Petroleum Vacuum Residue Components: Asphaltene (ASPH) and Deasphaltenated Oils (DAO), 28 and 72 wt % of PVR, Respectively |
|---------------------------------|----------|----------|
| samples                         | ASPH     | DAO      |
| S (wt %)                        | 7.8      | 5.0      |
| N (wt %)                        | 1.2      | 0.5      |
| Ni, ppm                        | 341      | 72       |
| V, ppm                         | 841      | 166      |
| H/C                            | 1.2      | 1.5      |
| % aromatic carbon              | 46.5     | 29.5     |
at m/z 600 ranging from m/z 350 to 2500 (Figure 1A). These differences in MW distribution are similar to LDI analysis by other research groups, which report lower MW distributions by LDI-MS, and may arise from the differences in response factor for molecular weight and compound type between the two techniques. Increasing the laser energy reveals additional spectral features in both the low and high end of the MW distribution, e.g., compare the moderate (8 µJ/pulse) and high (16 µJ/pulse) laser-intensity spectra of Figure 1, parts B and C, and parts E and F, respectively). The change in MW distribution is most notable for asphaltene samples where increasing the laser intensity extended the MW distribution to about ∼7000 m/z at 18 µJ/pulse instead of ∼2500 m/z, as observed at threshold intensities. A correlation between MW distribution and laser intensity was also observed for the DAO sample. Herod and co-workers have previously described a bimodal, high MW component (>50 000 m/z) present in petroleum samples using size exclusion chromatography. This high MW distribution was also observed by the same group using LDI-MS under certain instrumental conditions (i.e., linear mode and reduced detector gain); however, we did not observe the ultrahigh MW distribution in the current study for our petroleum samples with conditions similar to that described in the literature.

We attribute the observed change in MW distribution to gas-phase phenomenon rather than preexisting species that become ionized only at the higher laser intensity. That is, the increase in signal for low molecular weight species arises from fragmentation caused by the higher laser energies (i.e., higher laser energy results in ions having higher internal energies which are released through fragmentation). Furthermore, the increase in high-mass signal may arise from the presence of gas-phase aggregates. High-mass ion signal is more pronounced in LDI spectra of asphaltenes than DAO (Figure 1), and asphaltenes are known to have a higher tendency for aggregation (i.e., higher aromaticity and more polar functionalities than DAO). The regularly spaced peaks present on the tailing edge of the MW distributions observed at higher laser power (Figure 1C) correspond to intervals of 24 m/z (carbon clusters) which have been previously observed.

In an effort to address the issue of gas-phase aggregation directly, vacuum residue samples were analyzed by LDI-IM-MS. Figure 2 contains the IM-MS spectra of an asphaltene sample overlaid with the spectra acquired from deposited fullerenes. Most notable in this data is the MW distribution of the asphaltene sample, which extends up to m/z greater than 15 000. This result was surprising considering there is no signal in this region for analogous LDI-MS experiments that do not incorporate mobility. We attribute this appearance of high MW signal to the higher pressure of the IMS experiment. In high-vacuum LDI-MS, ions are formed and transferred to the TOF mass spectrometer without experiencing collisions with a neutral gas molecule. When a bath gas is present, as in the LDI-IM-MS experiments, desorbed ions will experience numerous cooling collisions as they are extracted into the drift cell. With these cooling collisions, energy that would otherwise be released through declustering processes is transferred to the bath gas, thereby stabilizing aggregates that are present in the gas phase.

On close inspection of Figure 2, the drift-time distribution broadens around m/z 2500, then returns to typical peak widths

![Figure 1](https://example.com/figure1.png)

**Figure 1.** LDI of asphaltene and deasphalted oil (DAO) at various laser energies: (A and D) 3 µJ/pulse, (B and E) 8 µJ/pulse, and (C and F) 16 µJ/pulse (threshold, moderate, and high laser intensities, respectively).

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for petroleum samples at higher values of \(m/z\). The change in drift-time distributions (\(\sim m/z 2500\)) also corresponds to a change in trend-line slope, exhibiting a steeper slope for ion signal below 2500 \(m/z\) than at higher \(m/z\) values. A probable explanation is that this broadening and slope change arises from the superimposition of more than one trend line at this mass-mobility range, one trend line resulting from monomers, and a second resulting from higher-order aggregates. The slope of higher MW species is lower, indicative of tighter packing for "sheets" of low molecular weight monomers. This interpretation is consistent with previous reports\(^{(41,42)}\) which demonstrated that aggregation of asphaltenes occurs via \(π\)-stacking interactions, which can lead to a blocklike formation, with significantly higher mobility than a corresponding quasi-planar structure of the same molecular weight.

Analysis of the trend-line width and slope, as well as the absence of signal in LDI-IMS experiments, agrees well with the quasi-planar structure of the same molecular weight. Formation, with significantly higher mobility than a corresponding \(Vc\) \(m/z\) maintaining threshold laser power and constant field strength (15 \(V/cm\)).

Figure 2. LDI-IMS plot of arrival time distributions (ATDs) vs \(m/z\) for asphaltene ions, demonstrating a change in slope in the asphaltene trend line. \(C_{\text{gas}}\) spectra were graphically overlaid onto the asphaltene plot for comparison.

The presence of gas-phase aggregates in IM-MS spectra can also be investigated using molecular modeling. Although asphaltene structures can be somewhat ambiguous to model because an exact model is lacking, model systems that share structural features with asphaltenes can be studied. Because face-to-face interactions between the planar aromatic core of asphaltene ions are a primary feature of asphaltene aggregates,\(^{(41,42)}\) PAHs present an ideal candidate because they can be modeled accurately. PAHs and their multimers were modeled for structures with 4–40 fused aromatic rings in a single semicondensed aromatic core. Most optimized structures resulted in face-stacked geometries with intermolecular spacings of 3.4–3.8 Å, in agreement with previous physical and theoretical studies.\(^{(43–45)}\) A plot of computed collision cross section versus \(m/z\) is contained in Figure 4. It is noted that each group of multimers falls on a separate trend line with progressively decreasing slope from monomer on to higher-order multimers. The respective slope change results in a broad distribution of collision cross sections in a common region, reflecting the same trend that is observed for IM-MS spectra of asphaltenes (Figure 2) around \(m/z\) 2500.

**Petroleum Vacuum Residue Structures.** The relationship between gas-phase structure and collision cross section has been the subject of numerous studies.\(^{(46–50)}\) Briefly, collision cross sections obtained from IMS experiments provide a direct measure of the ion surface area. Molecular modeling can then be used to generate a large pool of candidate structures which are compared to experimental cross sections to select one or a few representative conformers. In the absence of known compositions and primary structures needed for detailed modeling, it is possible to make structural generalizations based on comparisons to known structures. To estimate the structure of asphaltene molecules, we compared IM-MS trend lines of asphaltene with three model systems: polystyrene 1400, polywax 650, and fullerene clusters. Raw data for these comparisons are shown in Figure 5. First, it is noted that peak widths of asphaltene samples are approximately 2–3 times the width of the linear polymers or fullerenes, implying a high degree of structural diversity at a particular nominal mass. Polystyrene 1400 and polywax 650 are on the top edge of the asphaltene trend line, whereas fullerenes are well below the trend line of asphaltenes. To further contrast the differences, we plotted the trend lines using the centroid of the ATDs of the four systems as shown in Figure 6. First, asphaltenes are much less condensed than are fullerenes, which have zero hydrogen content. The cross section of polywax is only slightly smaller than that of polystyrene, and both are larger than that of asphaltenes. These differences in cross section are expected because both polywax and polystyrene are linear polymers, whereas asphaltenes are believed to be


\[\text{(45) Marzec, A. Carbon 2000, 38, 1863–1871.}\]


mostly condensed aromatics with multiple alkyl substitutions. For example, the results of several studies have provided evidence that asphaltene structures consist primarily of a single, condensed, aromatic core containing a number of embedded heteroatoms. Such structures would have a higher gas-phase density and thus a higher mobility than a long-chained linear polymer where the gas-phase density is limited by the packing efficiency afforded by molecular structure (i.e., a high degree of bond hybridization and steric side chains between repeating units do not permit dense gas-phase structures).

Figure 3. (A) MW distributions of an asphaltene sample at various pressures in the drift cell and ionization source at 15 V cm⁻¹ Torr⁻¹. (B) LDI-IM-MS plot of arrival time distribution (ATD) vs m/z for asphaltene ions at 3 Torr of He bath gas. (C) LDI-IM-MS plot of ATD vs m/z for asphaltene ions at 8 Torr of He bath gas.

Figure 4. Plot of collision cross section vs m/z for polynuclear aromatic hydrocarbons (PAHs) and their multimers, derived from molecular modeling computations. See text for details.

Figure 5. LDI IM-MS plots of arrival time distribution (ATD) vs m/z for asphaltene ions (ASPH) and model polymeric systems.

Figure 6. Plot of arrival time distribution (ATD) vs m/z of asphaltene, deasphaltened oil (DAO), and polymers from Figure 5. Data were plotted as the centroid of observed ATDs.

Such structures would have a higher gas-phase density and thus a higher mobility than a long-chained linear polymer where the gas-phase density is limited by the packing efficiency afforded by molecular structure (i.e., a high degree of bond hybridization and steric side chains between repeating units do not permit dense gas-phase structures).

Figure 7 shows IM-MS spectra of asphaltene and DAO samples. Notably, the IM-MS spectra of DAO exhibit less ion signal at higher values of m/z than those of asphaltenes. In part, these differences in MW distribution could arise from differences in sample composition. Asphaltenene molecules are known to have more condensed aromatic ring structures (either fused or linked by alkyls or heteroatoms) than DAO. Consequently, there will be more substitution sites for alkyl attachment in asphaltenes, which contributes to higher observed molecular weights when compared to those of DAO. In addition, the lower aromatic and heteroatom content of DAO will decrease its tendency for aggregation in the gas phase, resulting in decreased signal at high m/z from aggregate species. Both distributions are very broad and similar in terms of width and cross section; however, the trend line of DAO is somewhat higher than that of the asphaltenes. To illustrate the difference between asphaltenes and DAO, we produced a 1D slice of the mobility data in Figure 7 bracketing 500–600 m/z.
At the selected molecular weight range, ASPH clearly has a shorter average drift time when compared directly to DAO, indicating a more condensed average structure for ASPH when compared to DAO. A similar difference in drift time can be observed over the entire region where these spectra overlap (Figure 6). Two representative molecules are constructed for asphaltene and DAO based on the aromatic content (46.5% vs 29.5%) and H/C ratio (1.2 vs 1.5) in Table 1 assuming a molecular weight of 558. The lower aromatic content and longer alkyl side chains dictate a greater flexibility for DAO molecules. The greater flexibility of the molecules permit for more extended gas-phase conformations which leads to the observation of larger collision cross sections such as that observed in Figures 7 and 8. In addition, the observed differences in cross section can be interpreted as evidence of multiple or less condensed aromatic cores for DAO compared to a single condensed core of asphaltenes.

CONCLUSIONS
We successfully applied LDI and IM-MS to study petroleum asphaltene and DAO. This data suggests careful consideration must be applied to the mass analysis of heavy MW petroleum samples. For example, we have shown that gas-phase aggregation can play a significant contributing factor to MW distributions observed in LDI-MS. The gas-phase aggregation was confirmed by ion mobility data which demonstrated most of the molecules with MW > 3000 g/mol are due to the presence of gas-phase aggregates. The potential for aggregation effects using other ionization techniques also cannot be ignored (e.g., ESI droplet desolvation would naturally lead to higher concentrations, thereby inducing aggregation). It should be noted that quantitative application of any MS technique (including LDI-MS) for determination of molecular weight distributions requires careful assessment of response factors. In addition, IM-MS trend lines were compared with model systems to show the following order of CCS: polywax > polystyrene > DAO > ASPH > fullerene, illustrating that ASPH has a more condensed average structure than DAO.

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