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Molecular Weight of Petroleum Asphaltenes: A Comparison between Mass Spectrometry and Vapor Pressure Osmometry

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Seven asphaltene samples and six octylated asphaltene (OA) derivatives were analyzed using laser desorption ionization−time-of-flight (LDI−TOF) mass spectrometry (abbreviated as MS) and vapor pressure osmometry (VPO) techniques. Molecular weight distributions (MWDs) that were determined using MS spanned, for all asphaltenes samples and their octylated counterparts, a similar range, from ~100 Da to ~10 000 Da. For asphaltenes, the number-average molecular weight (M_n) and weight-average molecular weight (M_w) afforded values in the 1900 ± 200 and 3200 ± 400 intervals, respectively. Consistently heavier values were observed for the OA derivatives ($M_n \approx 2300 \pm 200$ and $M_w \approx 3600 \pm 200$). To select the adequate laser power for these measurements, experiments at different laser powers were performed, to increase volatility and reduce fragmentation to a minimum. Several other experiments were performed to validate these results. First, good agreement between the measured and calculated M_n values was observed for OA materials (calculated from asphaltene M_n and n, the number of octyl groups introduced, as determined from elemental analysis); second, M_n values, as measured by VPO and MS, were determined to be equal, within an average standard deviation of ±27.0%. These results and calculations strongly suggest that the MWD, the molecular weight range, and the molecular weight averages determined using the present MS technique are reasonable estimates of the molecular weight properties of asphaltenes and not the result of artifacts such as fragmentation, polymerization, incomplete volatilization, etc., which may be occurring during the MS experiment.

1. Introduction

Determination of the molecular-weight-related properties of asphaltenes is an important step toward the characterization of these substances, and, thus, much effort has been devoted to this goal.[1−20,24,25] However, because of several factors (such as polydispersity of the sample), difficulties in isolation from crude oils, limitations of techniques used to measure the values, and the tendency to form aggregates, such determinations have

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been proven to be very difficult. Thus, it is not surprising that molecular weights between 300 000 and 1000 have been reported in the past.[1,2] It is now recognized that the major source of these discrepancies is the formation of aggregates or macrostructures formed through intermolecular interactions.

Vapor pressure osmometry (VPO),[1,2,14-16,20,24] size exclusion chromatography (SEC),[3,10,14-16,20] and mass spectrometry (MS)[4-9,17,18,24] are among the techniques most commonly used for molecular weight studies of asphaltenes and bitumen. Because of its simplicity and cost, VPO is used extensively. The VPO technique allows for the determination of an "absolute" value for the number-average molecular weight (M_n). When used for weakly or nonpolar low-molecular-weight compounds, such as resins and crude oils, the technique gives accurate values, similar to those obtained by mass spectroscopy.[8] However, aggregate formation, which is a factor to consider with asphaltenes, is always difficult to eliminate completely, even with the use of high temperatures and polar solvents.[1,2] Molecular weight distributions (MWDs) as well as the M_n and the weight-average molecular weight (M_w) for asphaltenes has been obtained using SEC.[3,16,19] However, complications that are due to inadequate calibration, flow rate effects, column adsorption, and detection of sample severely limits the application to asphaltenes. Moreover, being a relative technique, calibration with adequate standards is required and special methods must be used to obtain meaningful results.[16]

Satisfactory fittings to a log-normal distribution (LND) have been found for asphaltenes and octylated asphaltene (OA) derivatives when using SEC techniques.[3,15] This strongly suggests that compounds in the mixture are the result of a natural statistical process that occurs during asphaltene generation (probably a cracking of giant molecules). From a mathematical standpoint, polymerization and depolymerization are equivalent and the situation could be compare to a usual polymerization leading to MWDs similar to LNDs.[21]

Using thermal volatilization (from 50 °C to 300 °C), which is a low-voltage, low-resolution mass spectroscopy technique, molecular weights of ~400 have been reported.[5] As a result from laser desorption mass spectra (LD MS) techniques, it has been claimed that asphaltene molecular weights should not be higher than 1500, with average values of ~400.[6,7] Similar low values, using similar mass spectra techniques were reported previously[7] and more recently.[8] Molecular weight values in the range of 1000 or less have been reported using

interfacial tension data[9] and, more recently, using a fluorescence depolarization technique.[11,12]
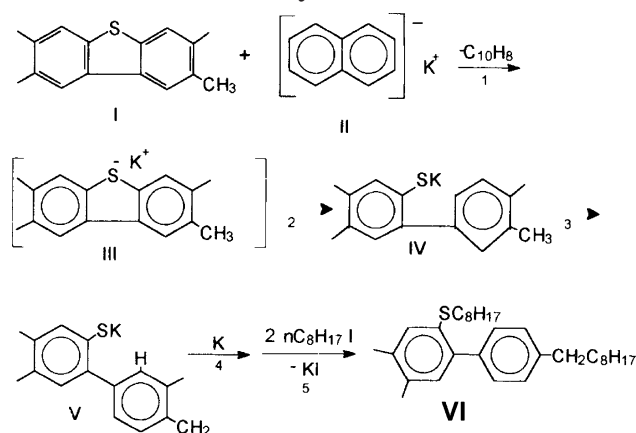
However, many other reports, using VPO, have indicated that M_n values are higher and probably in the range of 1500−2000.[1,2,14,16] Use of polar solvents such as nitrobenzene at high temperatures usually leads to VPO values in that range (see below). Similarly, MW ranges reaching high MW values−from 3000 (from ref 18) to 10 000 (from ref 24) and 20 000 (from ref 17)−have been reported using MS techniques.

It could be argued that some of the previously mentioned discrepancies are mainly due to either fragmentation, recombination, or incomplete volatilization of sample during the mass spectra analysis, or to sample aggregation during the VPO measurements. Volatilization is an issue that is particularly important in regard to MS methods. For instance, experiments with laser desorption show that the MWD obtained is dependent on the laser power used. Because of incomplete volatilization, MWDs that have been measured at low power are unreliable. On the other hand, excessive power leads to fragmentation (see below). Thus, a compromise is needed to obtain optimal conditions.

Because laser energies could be controlled to reduce sample fragmentation to a minimum, matrix-assisted laser desorption ionization−time-of-flight (MALDI−TOF) MS techniques are called "soft" MS techniques. As is well-known, MALDI MS has been used extensively to analyze biopolymers and synthetic polymers, as well as polycyclic aromatic hydrocarbons (PAHs).[22,23] Matrixes are used for samples such as proteins, peptides, and carbohydrates, which do not strongly absorb the laser energy. However, for absorbing high-molecular-weight compounds, such as asphaltenes, matrixes are not necessary (see below). This was determined to be the case for the asphaltene samples analyzed by Tanaka et al., using a LDI apparatus and techniques similar to those used here[24] (see below).

The possible reactions that could be occurring during asphaltene octylation have been discussed earlier.[25] Thus, only a brief and schematic account of these is given here. When treated with the reagent potassium naphthalenide, S atoms in thiophene-like structures react according to the reaction given in Scheme 1:

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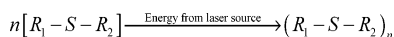(22) Hillenkamp, F.; Karas, M.; Beavis, R. C.; Chait, B. T. *Anal. Chem.* **1991**, *63*, 1193A.
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Scheme 1. Model Reactions To Illustrate Asphaltene Octylation[a]

[a] Here, the dibenzothiophene functional group **I** represents an asphaltene molecular section. Potassium naphthalenide is represented by groups **II** and **III**, groups **IV** and **V** are intermediaries, and group **VI** is the octylated product.

Scheme 2

$$n\left[R_1 - S - R_2\right] \xrightarrow{\text{Energy from laser source}} \left(R_1 - S - R_2\right)_n$$

There are two properties of OA worth mentioning at this stage. Changing aromatic (thiophene-like) S–C bonds to aliphatic bonds make OA materials more labile than asphaltenes. For instance, as shown by (unpublished) thermogravimetric analysis (TGA) experiments, OA materials loose up to 18% of their weight when the sample was heated from room temperature to 350 °C (compare with the 3% loss for asphaltenes) This occurs in one band (centered at ~250°) before sample pyrolysis, which occurs at temperatures of ~400° and above. This should be due to the cracking of aliphatic C–S bonds. Thus, should there be any significant fragmentation reactions during LD MS experiments, these would show clearly in the OA MS.

For similar reasons, it is expected that any possible reaction, such as free-radical recombination, leading to a polymeric species (see reaction Scheme 2), would be more likely to occur with OA materials than with asphaltenes. As shown below, any significant change in the MWD of asphaltenes that is due to this or any other related process could be excluded by the results obtained.

Another OA property is related to volatility and melting points. As shown below, contrary to asphaltenes, which do not melt, OA materials have melting points of ~100 °C. Thus, it is expected that OA materials would be volatile enough to set the adequate power required to get all of the asphaltene sample in the vapor phase during the MS measurements.

In this work, we present an MS study of 13 asphaltene samples using a LDI–TOF technique (no matrix used) that is capable of analyzing molecular weights of up to 30 000 Da and higher. The MS results obtained were compared with VPO values. Similarly, the M_n values for OA materials, measured using MS, were compared to the calculated values. As described below, the results of these comparisons and calculations lead us to believe that the MS results are reliable and, hence, that the averages and MW range of asphaltenes are those referenced in the previously mentioned Abstract section.

Experimental and Methods Section

2.1. Asphaltenes. Furrial, which is an oil with asphaltene precipitation problems, was obtained from Monagas State in the northeast part of Venezuela. DM 153, DM 115, and VLA 711 were from the Maracaibo Lake in northwestern Venezuela. Hamaca and Cerro Negro were extra heavy crude oils from the Orinoco basin in southwestern Venezuela. As described previously,[19] because of the high viscosity of these last oils, they were diluted with toluene (1:1) before the addition of *n*-heptane to obtain the asphaltenes. For the other samples, no dilution with toluene was required. In all cases, the precipitated solid was continuously extracted with boiling *n*-heptane in a Soxhlet extractor, to remove coprecipitated resins (usually 24 h).

A1 was a Furrial fraction isolated using the so-called PNP method.[20] In this method, a toluene solution of the asphaltene is treated with *para*-nitrophenol (PNP) and, from this mixture, a PNP–A1 complex is precipitated, from which A1 is separated by alkaline treatment. The solubility of the A1 fraction in toluene at room temperature is very low (0.09 g/L) when compare to the asphaltene from which is isolated (~57 g/L)

2.2. Reductive Octylation: Synthesis of Octylated Asphaltenes (OA). Octylated asphaltenes (OAs) were synthesized by treating the asphaltenes with potassium naphtenide in tetrahydrofuran (THF) and then with octyl iodide, as reported elsewhere.[16,25]

2.3. ¹³C NMR Experiments. NMR spectra were recorded on a JEOL model EX 270 Fourier transform NMR spectrometer using CDCl₃; tetramethylsilane (TMS) was used as an internal standard. The instrument was equipped with a 5-mm broadband probe head. Processing was performed using the DELTA V1.8 program, which was running on a Silicon Graphics workstation. The selected parameters were as follows: spectral window, 250 ppm; width of 30° pulses, 2.8 μs; relaxation delay, 5 s; and number of scans, 8000–12 000. The spectra were obtained using standard JEOL software.

2.4. Number of Octyl Groups (n). The number of octyl groups (n) (per 100 C atoms in the asphaltenes) incorporated into the asphaltene molecule after the octylation treatment was obtained using elemental analysis. For elemental analysis and from the corresponding H/C ratios, using eq 1, as described earlier:[16,25]

$$(\text{H/C})_O = \frac{100(\text{H/C})_A + 17n}{100 + 8n} \tag{1}$$

or

$$n = \frac{100((\text{H/C})_O - (\text{H/C})_A)}{17 - 8(\text{H/C})_O} \tag{2}$$

Expected errors in n were calculated using the procedure described below for the M_n(OA) case.

2.5. Mass Spectra. LDI mass spectra were recorded in a positive polarity, using an Applied Biosystems apparatus (MALDI–TOF Voyager DE-STR). A N₂ laser ($\lambda = 337$ nm) was used. Samples were dissolved in THF (10 g/L) and then 1 μL of the solution was deposited dropwise on the target.

To minimize fragmentation that occurred with inappropriate laser-power values, leading to noise and ions mainly in the low mass range (typically $m/z < 500$), the power selected was optimized both for OA and asphaltenes. The laser power used (measured in terms of the number of laser shots (LS)) were 1900, 2100, 2300, and 2500 LS. For the OA materials, low power (1900 LS) afforded reasonable spectra with little fragmentation. However, spectra with low intensities and poor resolution were obtained for asphaltenes under the same conditions. The optimal power (2100 LS) was selected by monitoring the change of the MWD of the OA material as the laser power was increased. Several trials were performed using a matrix (dithranol: 1,8,9-anthracenetriol). For this, asphaltenes and the matrix were dissolved in chloroform, the solvent was evaporated, and the resulting solid (2% in asphaltenes) was analyzed. No significant differences were obtained between these MALDI spectra and the LDI spectra measured for the asphaltene without matrix. Therefore, no matrix was used in the spectra reported here.

Moreover, all the spectra were recorded in the first few minutes after the introduction of the sample in the mass spectrometer, which avoided the fast volatilization of molecules of low molecular weight, leading to a modification of the sample's distribution.

2.6. Estimation of M_n for Octylated Asphaltenes. These were estimated from the M_n values of asphaltenes, using eq 3 below:

$$M_n(\text{OA}) = \left(1 + \frac{117n}{M_{100}}\right)M_n(\text{A}) \tag{3}$$

Here, M_{100} is the MW per 100 C atoms, which is obtained from the elemental analysis (~1400 in all cases).

Table 1. Elemental Analysis and Other Properties of Asphaltenes and Crude Oils

			Elemental Analysis (%)[a]					
sample	API of crude oil[a]	amount of asphaltene in crude oil (%)	C	H	O[b]	N	S	H/C[c]
Furrial	21	7.6	85.50	6.90	2.5	1.73	3.4	0.97
DM 153	14	10.0	81.05	8.17	2.0	1.64	6.6	1.20
DM 115	11.2	11.0	80.23	7.73	4.4	1.44	6.3	1.10
VLA 711	31.1	2.2	83.94	7.53	2.0	1.23	4.6	1.06
Hamaca	8	14	83.94	7.71	1.9	1.96	4.5	1.10
Cerro Negro	8	13	81.23	7.72	3.5	2.13	5.5	1.12

[a] In asphaltenes. [b] By difference. [c] With errors of ~3% or less.

Expected relative errors in $M_n(OA)$ were calculated using the usual procedure. This leads to eq 4:

$$100 \times \frac{dM_n(OA)}{M_n(OA)} =$$
$$100 \times \left\{ \frac{117d_n}{1400[1 + (117n/1400)]} + \frac{dM_n(A)}{M_n(A)} \right\} \quad (4)$$

The parameter $dM_n(A)$ is unknown; therefore, we assumed it to be equal to $0.2M_n(A)$.

2.7. VPO Measurements. With the described instrument,[16] VPO M_n were measured in nitrobenzene at 100 °C using five solutions in the 0–6 g/L range. Plots of ΔV (instrument readings) against the concentration C were fitted to parabolas such as those defined by eq 5.

$$\Delta V = aC^2 + bC + d \quad (5)$$

Here a, b, and d are constants. Equation 5 could be rearranged to eq 6:

$$\frac{\Delta V - d}{C} = aC + b \quad (6)$$

The M_n value was then obtained from eq 7, where K is the instrument constant:

$$M_n = \frac{K}{b} \quad (7)$$

Because eq 5 (and eq 6) contains three parameters, this procedure is generally more accurate than the usual $\Delta V/C$ vs C plot, which contains only two parameters (a different pair of parameters a and b).

3. Results

As shown in Table 1, the asphaltene samples span a significant range of H/C values and sulfur contents. Also, the corresponding oils span a wide range of asphaltenes content and API gravities from the extra heavy (Hamaca and Cerro Negro) to the light VLA 711. Therefore, these samples could be considered as a good general representation of the oil and asphaltenes.

The elemental analysis and other properties of the octylated derivatives are shown in Table 2. As expected, the H/C ratios of these samples were higher than those corresponding to asphaltenes. As shown in Table 2, all octylated samples melt at <105 °C, with reasonable melting ranges.

The ^{13}C spectra of DM 153 samples are shown in Figure 1. Similar spectra were measured for the other samples, and the complete results are shown in Table 3. As expected, the percentages of aliphatic carbons were higher for the octylated derivatives; n values in Table 3 were calculated using eq 2.

Table 2. Elemental Analysis and Other Properties of Octylated Asphaltenes

			Elemental Analysis					
sample	yield[a] (%)	mp range (°C)	C	H	O[b]	N	S	H/C[c]
Furrial	75	87–91	82.67	8.33	5.56	0.92	2.5	1.20
DM 153	80	80–85	81.87	10.15	1.93	0.55	5.5	1.48
DM 115	70	97–104	81.69	9.16	2.65	1.30	5.2	1.34
VLA 711	85	85–97	83.15	9.73	2.73	0.79	3.6	1.39
Hamaca	70	100–105	84.03	9.86	1.91	1.28	2.9	1.40
Cerro Negro	70	100–104	83.82	10.32	0.34	1.60	3.9	1.47

[a] Octylation reaction yield. [b] By difference. [c] With errors of ~2.7% or less.

Table 3. ^{13}C NMR Result and Calculated Number of Octyl Groups n From Elemental Analysis[b]

	Percentage of Aliphatic Carbons[a]		
	octylated	asphaltenes	n[b]
Furrial	62.4	50.0	3.3 ± 0.4
DM 153	75.0	61.8	5.5 ± 0.7
DM 115	76.5	71.0	3.1 ± 0.5
VLA 711	71.8	59.8	5.7 ± 0.6
Hamaca	75.4	65.9	5.3 ± 0.6
Cerro Negro	73.4	63.5	5.0 ± 0.6

[a] An error of 10% was assumed. [b] Calculated from elemental analysis using eq 2.

Table 4. Measured (MALDI–TOF, 2100 LS) and Calculated Molecular Weights and Other Results for Asphaltenes and Octylated Asphaltene Samples

sample	$M_n(ob)$[c]	$M_w(ob)$[c]	$M_n(calc)$[d]	difference (%)[e]	expected error (%)[f]
Furrial	2040	3500			
Furrial Oc[a]	2500	3770	2600	−4	±22
DM 153	1720	2715			
DM 153 Oc[a]	2370	3620	2510	−5.6	±28
DM 115	2020	3130			
DM 115 Oc[a]	2200	3640	2540	−13.5	±20
VLA 711	2240	3800			
VLA 711 Oc[a]	2510	3690	3300	−24	±21
Hamaca	1840	2980			
Hamaca Oc[a]	2500	3810	2655	−6	±28
Cerro Negro	1700	2840			
Cerro Negro Oc[a]	2100	3264	2410	−12.87	±25
A$_1$ Furrial[b]	2000	3540			

[a] Octylated asphaltene. [b] A1 fraction from Furrial asphaltene isolated using the PNP method (see text). [c] Experimental (observed) values. [d] Calculated using eq 3. [e] Calculated using the equation $100(M_n(ob) - M_n(calc))/M_n(calc)$. [f] Calculated using eq 4.

Contrary to asphaltenes, these octylated asphaltenes dissolved easily in heptane at room temperature. Moreover, these derivatives have melting points of <105 °C, and, in all cases, the octylation reaction yields were high (see Table 2).

As shown in Table 3, the values of n range from 3 to ~6. This means that at least three long octyl chains
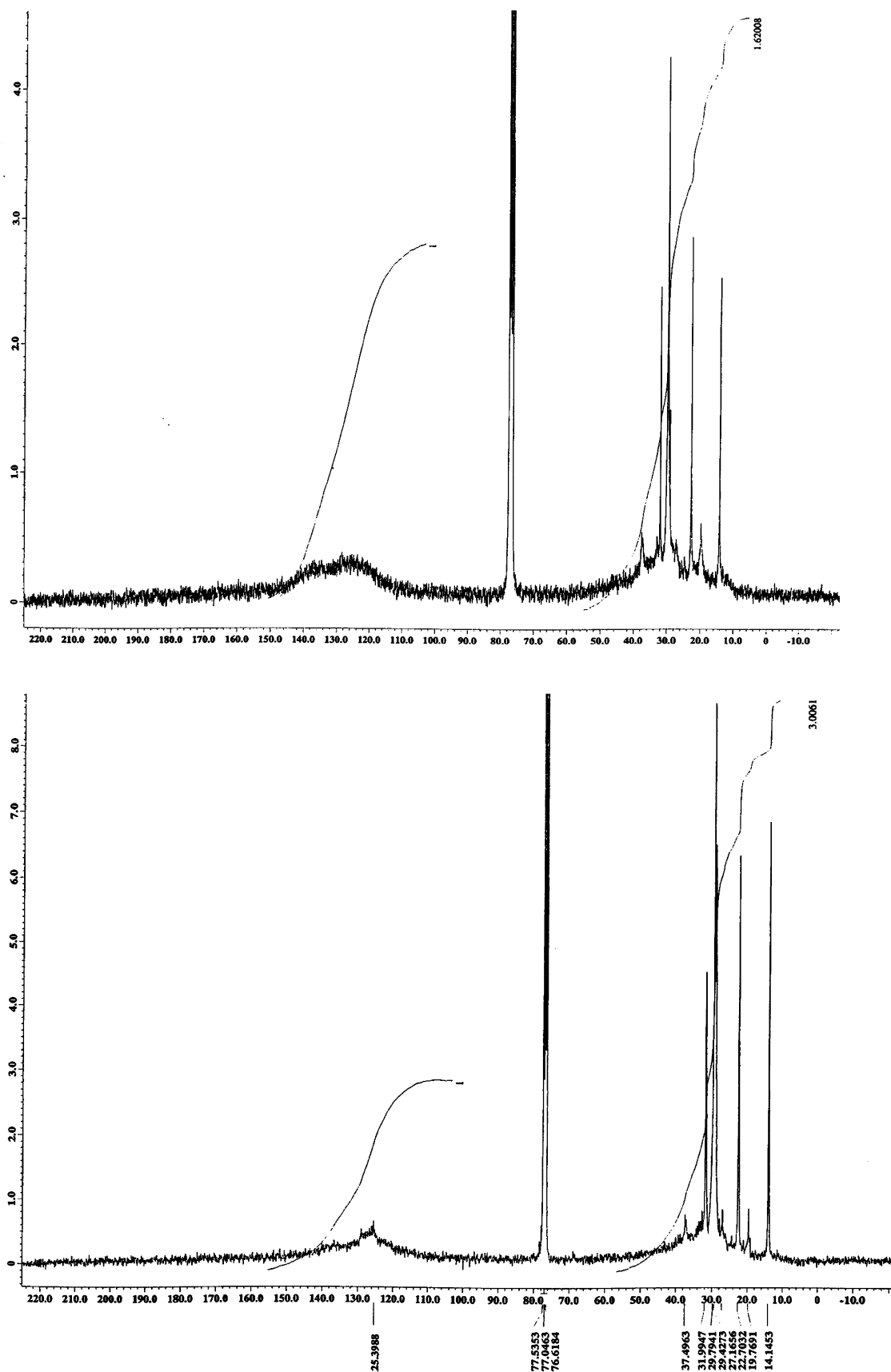
Figure 1. ^{13}C NMR spectra for DM 153 asphaltene samples: (top) asphaltene and (bottom) octylated asphaltene (OA).

were incorporated in the asphaltene molecule. The presence of these chains leads to profound differences in solubility and melting point, as shown in Table 2. As is well-known, asphaltenes do not have melting points and are insoluble in *n*-heptane and other paraffin solvents, whereas the opposite in true for the octylated derivatives. Because the presence of the octyl chains must lead to a large reduction in the self-assembling
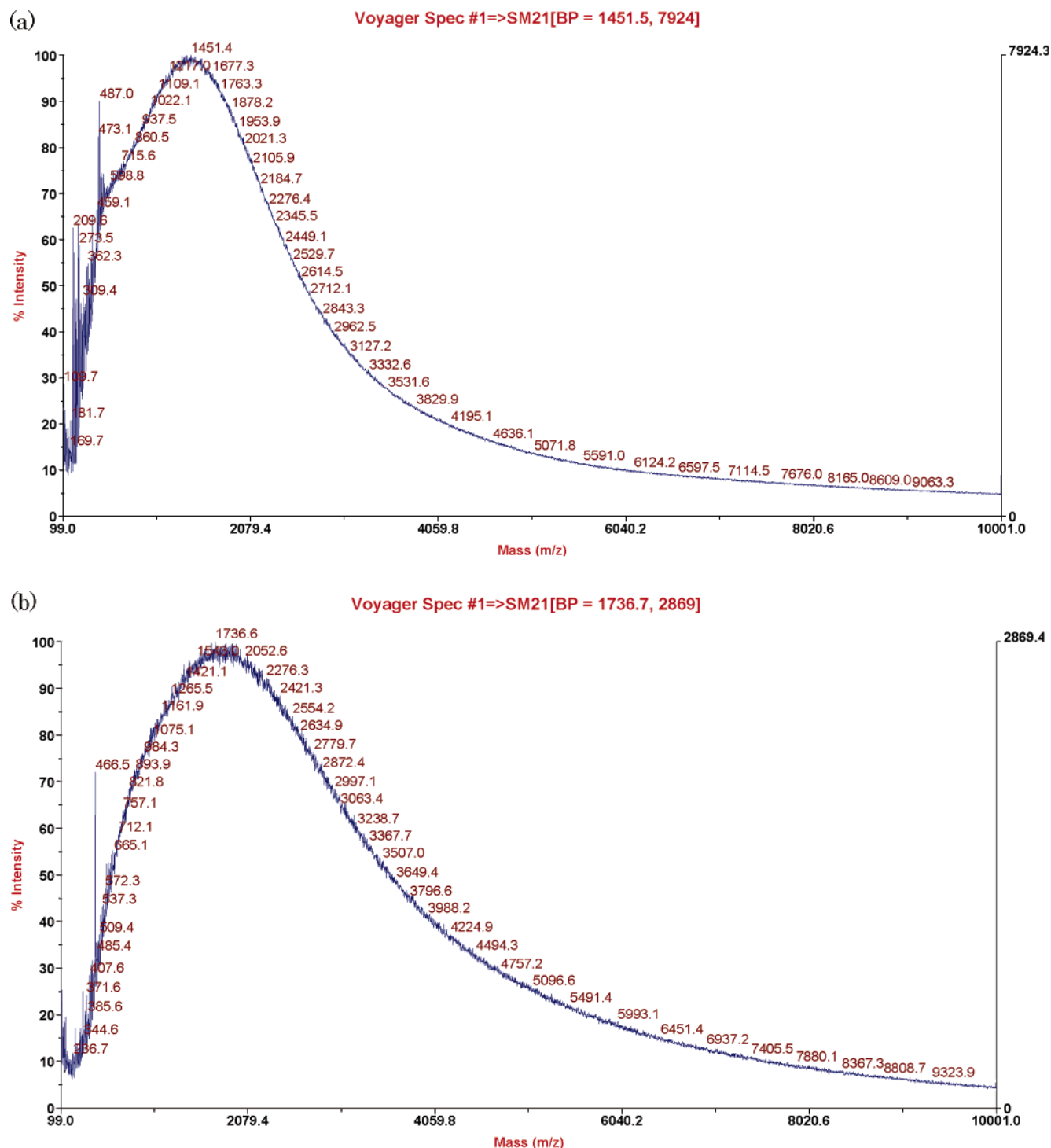
(a)

(b)

Figure 2. Laser desorption−time-of-flight (LD−TOF) mass spectroscopy (MS) for (a) Furrial asphaltene and (b) octylated Furrial asphaltene.
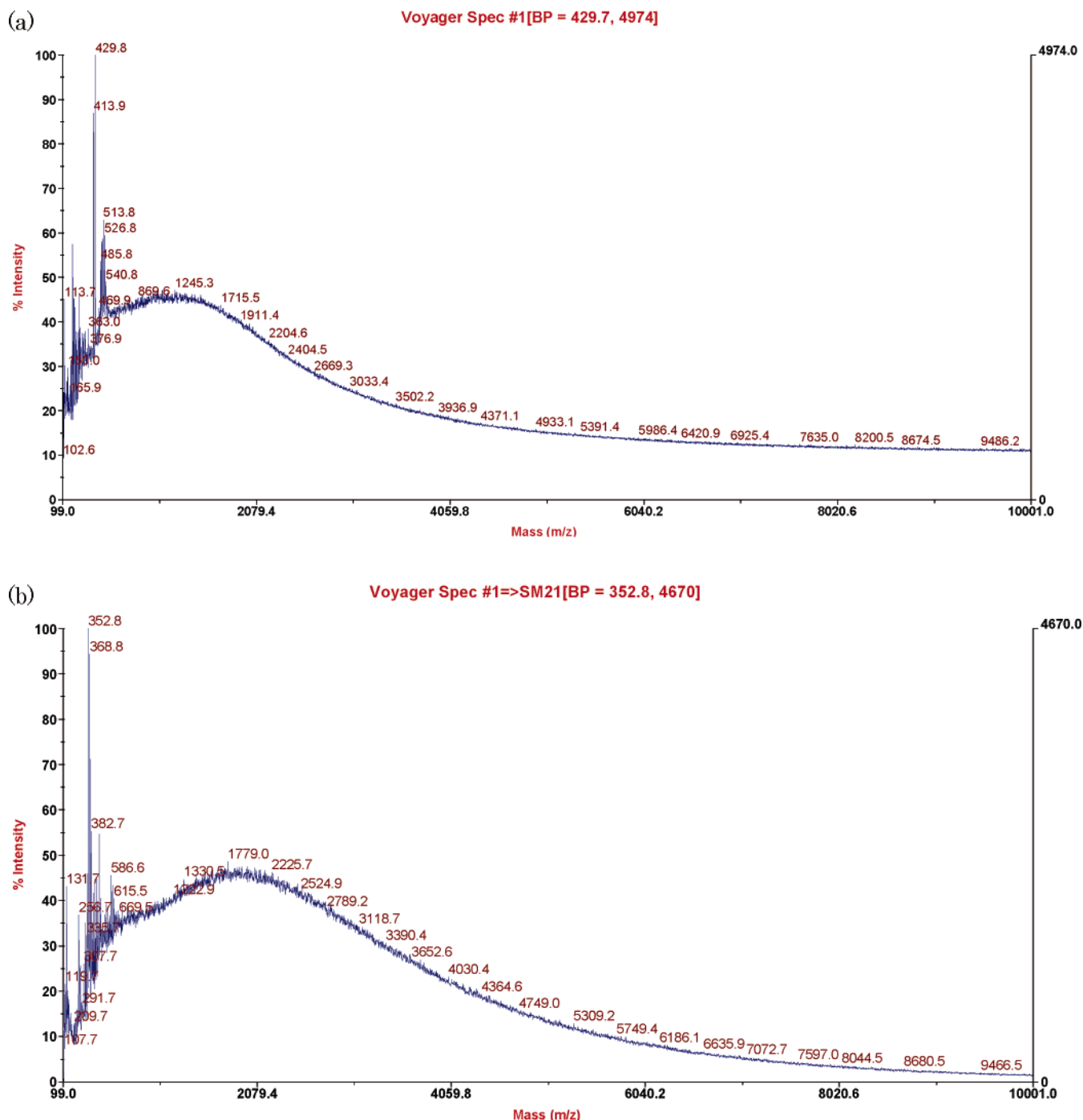
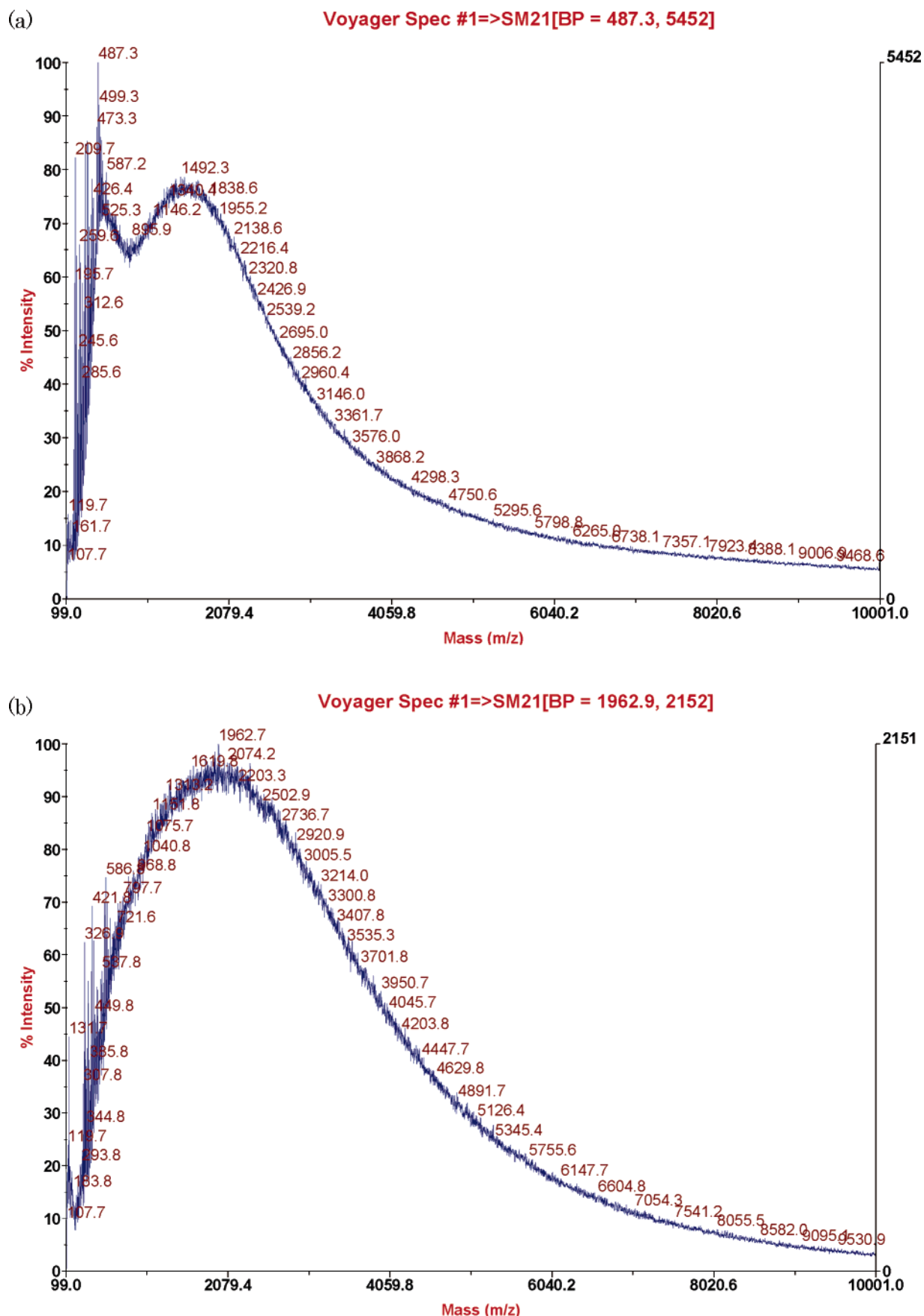capacity of the sample, these changes are expected.

3.1. Mass Spectra Results. The LDI−TOF MS results, measured at 2100 LS, are shown in Table 4. As shown in this table, the M_n and M_w values of the asphaltenes leads to values of $\bar{M}_n = 1900 \pm 200$ and $\bar{M}_w = 3200 \pm 400$. In other words, these M_n and M_w values are practically independent of sample type. Similar close results were found for the OA derivatives ($\bar{M}_n = 2300 \pm 200$ and $\bar{M}_w = 3600 \pm 200$). MW values for the OA materials were higher than those for asphaltenes. For the addition of n-octyl groups, this is the expected result. $M_n(OA)$, calculated using eq 3, were within 25% or

better of the observed results (see Table 4). Except in the VLA case, these differences are within the expected error for the calculation, which is an accumulation of errors determining $M_n(A)$ and n (see eq 4 and Table 4).

The Furrial A1 fraction was chosen because of its very low solubility in toluene at room temperature (see Experimental Section: Asphaltenes). However, no significant difference in the MW properties of the A1 fraction with the original sample (Furrial) was observed. This interesting result will be discussed elsewhere.

The spectra corresponding to some asphaltene and OA samples are shown in Figures 2−4. Some common
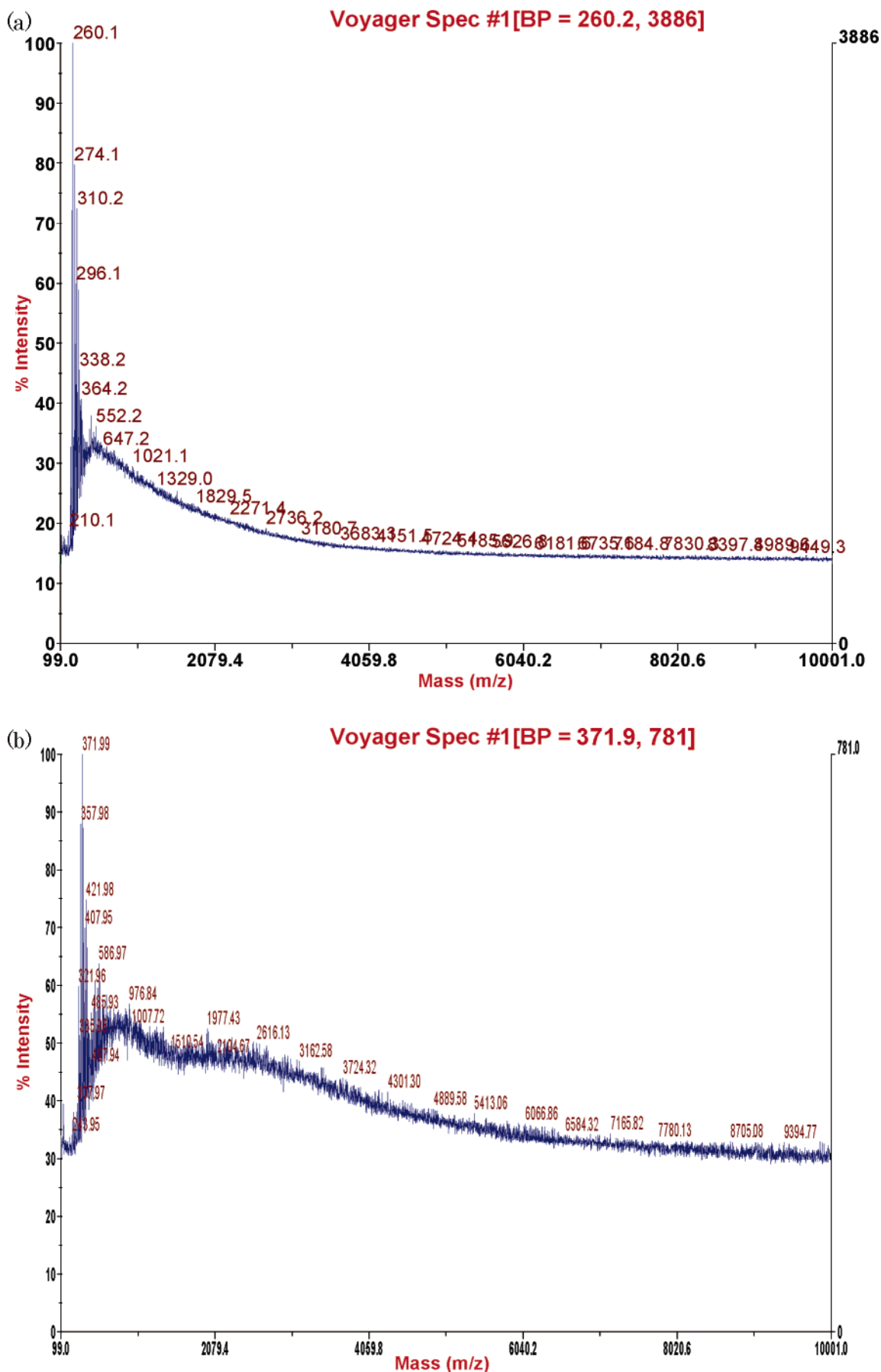
Figure 3. LD–TOF MS for (a) DM 153 asphaltene and (b) octylated DM 153 asphaltene.

features could be observed in these spectra. Both asphaltenes and OA samples span the same molecular weight range (between ∼100 and 10 000). As described previously, octylation leads to a relatively low-melting, and more-soluble, sample than the asphaltenes. Thus, it is expected that the volatilization of asphaltenes would be enhanced by octylation. We found this to be consistent with the MS measured at low power of 1900 LS. The case is illustrated in Figure 5 for the Furrial samples, where the high-molecular-weight components, which are clearly visible in the OA spectra (see Figure 5b), either are absent or have a lower intensity in the asphaltene spectra (see Figure 5a).

The effect of laser power on the asphaltene and OA spectra is shown in Figures 6 and 7, respectively. A glance at these figures shows that a drastic change in the MWD occurs between laser powers of 2100 and 2300 LS. At low power (1900 LS), a spectrum with poor resolution and low intensities was obtained (see spectra a in Figure 6; also see spectra a in Figure 5). At higher power (2300 and 2500 LS, see spectra c and d in Figure 6; and 2300 LS, see spectra c in Figure 7), extensive fragmentation is apparent from both spectra. The change is very sharp for the OA Furrial case (compare spectra b and c in Figure 7). As can be seen in these spectra, as the power is increased, the fragmentation shifts the MWD toward the low-molecular-weight values. From these findings, the laser power of 2100 LS was selected as the best compromise and was used to measure the values in Table 4.

(a)

(b)

Figure 4. LD−TOF MS for (a) VLA 711 asphaltene and (b) octylated VLA 711 asphaltene.

As shown in Table 4, calculated M_n(OA) were reasonable similar to the experimental values. Percentage differences were within the expected error in all cases.

This gives strong support to the laser power choice previously mentioned. However, it should be mentioned that differences between observed and calculated M_n

Figure 5. Comparison of furrial asphaltenes spectra measured at a laser power of 1900 LS: (a) asphaltenes and (b) OA.

were always negative. This suggests that, even at this relatively low power, some fragmentation is occurring.

As described previously, no matrix was required because no significant differences were found between

Figure 6. Power laser effect on the spectra of DM 153 asphaltenes. Laser power, from top to bottom, was as follows: 1900, 2100, 2300, and 2500 LS. Figure 2a is also included here (in Figure 6b), for comparison purposes.

the MALDI and the LDI (no matrix) spectra. A similar finding has been recently reported.[24]

3.2. VPO Measurements. The VPO M_n values measured in this work are shown in Table 5. In all cases,
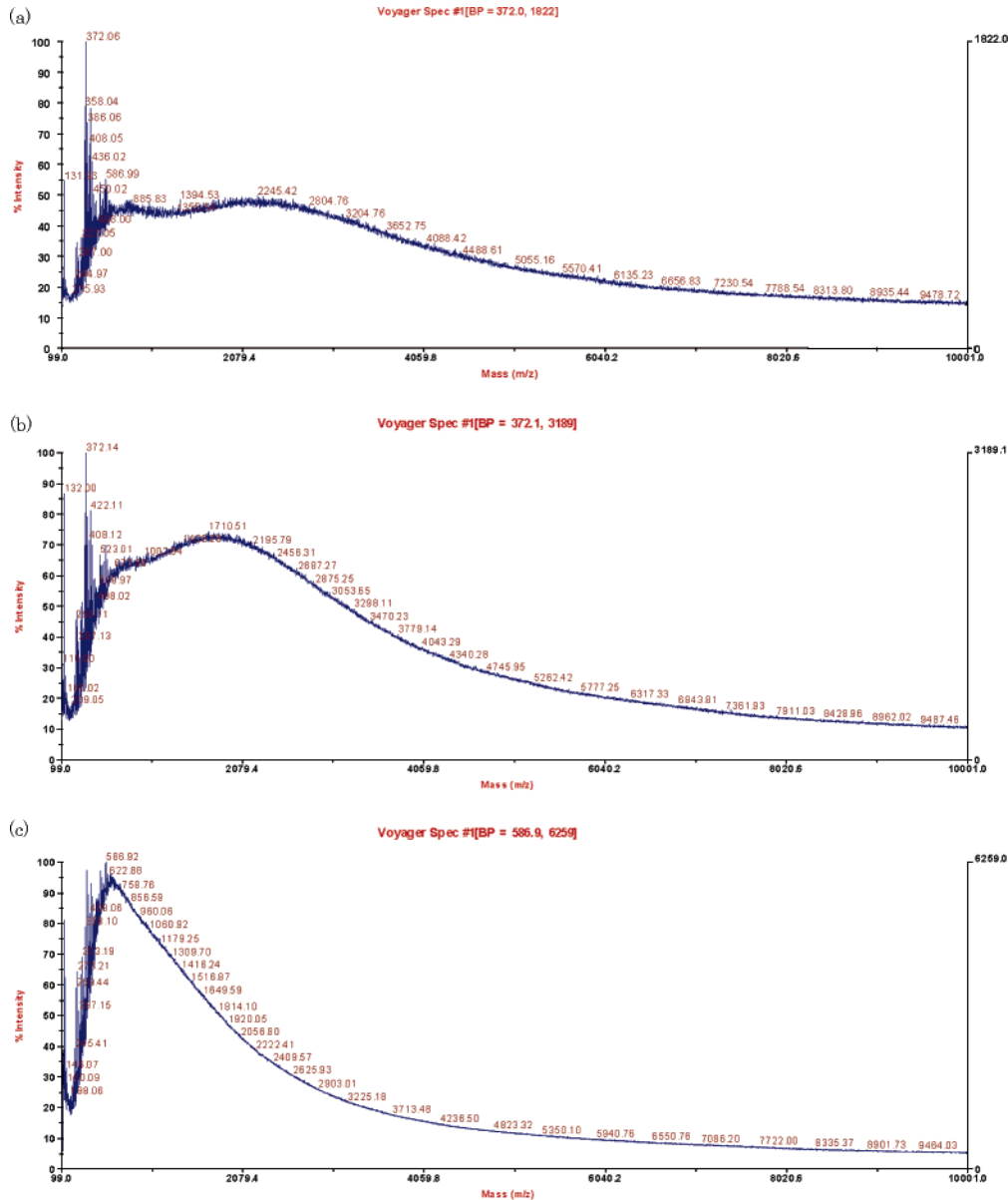
Figure 7. Power laser effect on the spectra of furrial OA. Laser power, from top to bottom, was as follows: 2000, 2100, and 2300 LS.

Table 5. Comparison of Vapor Phase Osmometry (VPO)[a] and Mass Spectroscopy (MS)[b] Number-Average Molecular Weight (M_n) Values for Asphaltenes

sample	M_n		difference (%)[c]
	VPO	MS	
Furrial	2440	2040	16.4
DM 115	1400	2020	−44.3
DM 153	1680	1720	−2.4
Cerro Negro	1760	1700	3.4
Hamaca	2420	1840	24.0
VLA 711	1720	2240	−30.2

[a] In nitrobenzene at 100 °C. [b] Data taken from Table 4. [c] Calculated using the formula $100(M_n(VPO) - M_n(MS))/M_n(VPO)$. The standard deviation of the differences was ±27.0%.

fittings to eq 5 were excellent with r^2 values equal or very similar to 1. As shown in Table 5, comparison of the two techniques afforded values which, on average, are within ±27.0% of each other. The M_n values in Table 5 are similar to other reported elsewhere using the same technique and similar experimental conditions.[1,2,14] The differences in Table 5 gave both negative and positive

values, suggesting that systematic errors were absent (see the discussion section).

4. Discussion

The good agreement between results from MS and VPO and the comparison between observed and calculated M_n are good arguments to warrant the reliability of the MS results summarized in Table 4. Thus, the same molecular weight range found for both asphaltenes and OA (100−10 000) and the comparison between calculated and measured M_n(OA) values (see first and third columns in Table 4) rules out any significant impact of incomplete volatility or fragmentation on the results measured at a laser power of 2100 LS.

The comparison in Figure 5 is consistent with the higher volatility expected for OA materials. Figures 6 and 7 clearly indicate that fragmentation is an important issue when the laser power applied is too high. According to these spectra, and the good comparison between the observed and calculated M_n(OA) values in
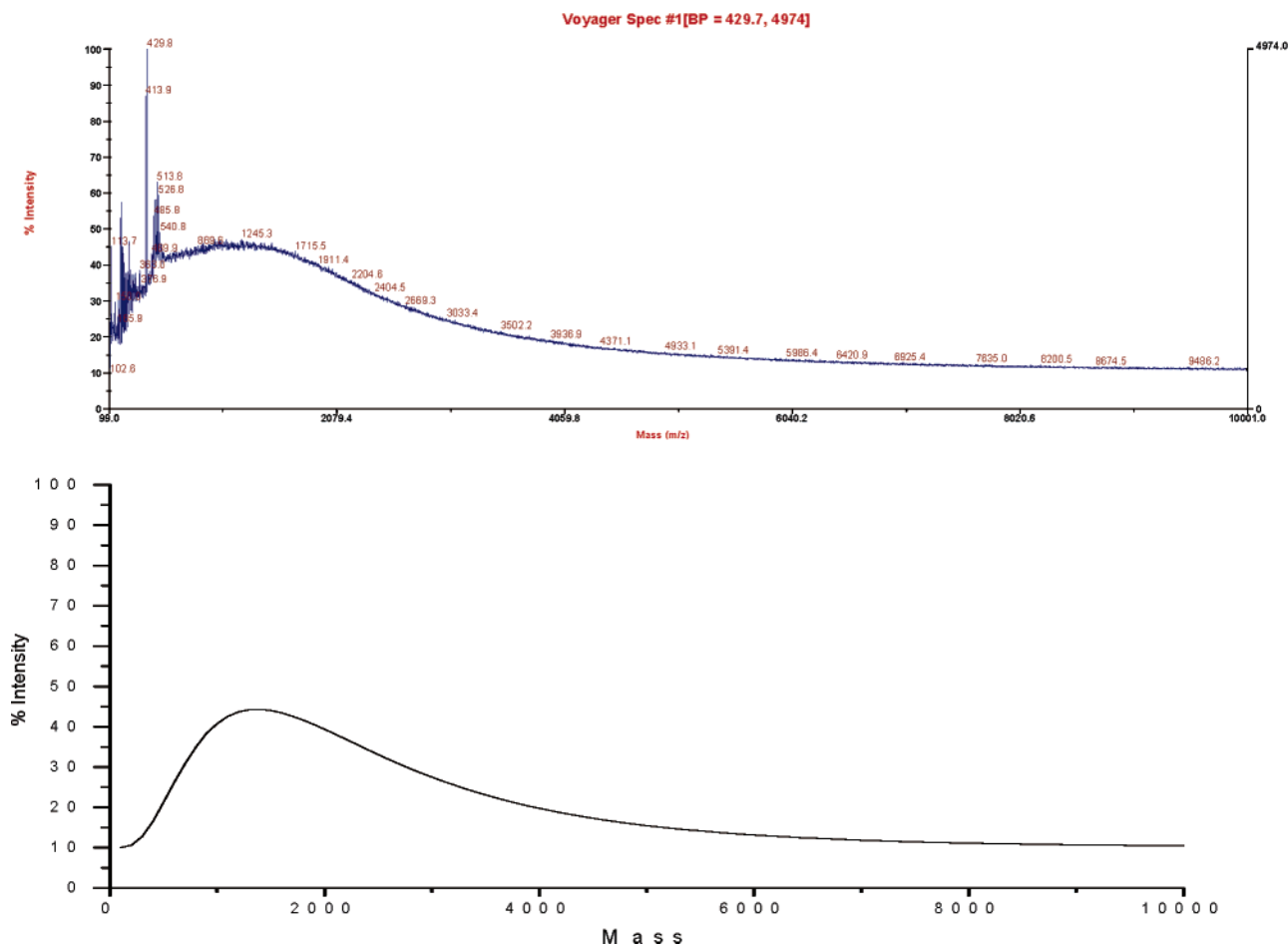
Figure 8. Comparison of (top) observed and (bottom) calculated MWD for the DM 153 asphaltene sample (see text).

Table 4, the power selected for these measurements (2100) is a good compromise in the present case.

Similar molecular weight values and ranges were reported in the previously cited paper by Tanaka et al.[24] Thus, using a similar LDI MS technique, a molecular weight range of 200−8000 amu and molecular weight averages of ∼1650 were reported by these authors for Maya asphaltenes. This value is close to those given in Table 4.

Of course, a significant increase in molecular weight averages should be expected if polymerization has any importance in the present measurements. As found by Tanaka et al., using low-molecular-weight (∼300) model compounds, polymerization was promoted in this case by increasing the laser power.[24] However, no such polymerization was detected when either a high-molecular-weight (∼700) aromatic model or asphaltenes were used.[24]

In agreement with these findings, increasing the laser power gave no evidence of polymerization in the present case. Instead, when power was increased, the MWD for both asphaltenes and OA shifted to lower-molecular-weight values (see Figures 6 and 7). Thus, based on these results, polymerization could be ruled out.

The previously mentioned conclusions are reinforced by the comparison with the VPO results (see Table 5). The differences between the M_n values measured using the two techniques were determined to be within an average standard deviation of 27%. In view of the expected errors for these measurements (between ∼10%

and 20%), the agreement is very good. Differences between the two techniques are either negative or positive, strongly suggesting that these are not systematic. Thus, systematic asphaltene aggregation in VPO or extensive fragmentation (at a laser power of 2100 LS) and polymerization in MS could be discarded.

Similar VPO M_n values for 14 asphaltene samples were reported some time ago for both nitrobenzene (M_n = 1900 ± 300, T = 100 °C) and pyridine (M_n = 2770 ± 490, T = 37 °C).[1] Values of ∼2000 (pyridine, T = 50 °C) were reported by other researchers.[19] When measured in other polar solvents, such as THF[16] or dibromomethane,[1] higher values are usually obtained, presumably because of aggregation promoted by lower solvent polarity and lower temperature.

The previously mentioned small standard deviations found for the reported VPO values in pyridine,[1] for the VPO values in Table 5, and for the average values in Table 4 are worthy of comment at this point. It suggests that, when molecular weight values are determined using adequate conditions, relatively small differences in the average molecular weight values will be observed.

Figure 8 is an example of how well the experimental MWD could be reproduced by a LND. The comparison is for the DM 153 sample. The only imputed data for the calculation were the experimental M_n and M_w values. The details of the calculated curve are given in the Appendix. The resemblance is very good. Using SEC, similar good fitting to LND has been reported for asphaltenes[3] and OA materials.[15] As mentioned in the

Introduction section, these fittings could be expected for a natural distribution of compounds. The good comparison shown in Figure 8 would not be expected in the case of extensive fragmentation or polymerization during the MS experiment.

5. Conclusions

As shown previously, the selection of the proper conditions for the laser desorption ionization (LDI) mass spectroscopy (MS) measurements is very important to obtain meaningful results. In this sense, a compromise between volatility and fragmentation must be reached. Using a power that is too low to avoid fragmentation leads to poor spectra, lacking the less-volatile, high-molecular-weight components. On the other hand, the use of a power that is too strong produces extensive fragmentation, leading to drastic changes in the molecular weight distribution (MWD). The molecular weight averages and ranges observed for asphaltenes in this work, using an intermediate laser power, were validated (i) by comparison with the observed and calculated molecular weight properties of the octylated asphaltene derivative (OA) materials, (ii) by comparison with VPO values, both from this work and with literature values, and (iii) by comparison with reported LDI MS performed under similar conditions. According to these comparisons and the previous discussion, these values are not significantly affected by artifacts such as polymerization, fragmentation, or incomplete volatilization.

Appendix

The normalized frequency f in a log-normal distribution (LND) is given by eq A-1:[3,21,26]

$$f = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-0.5\left(\frac{\ln M - \ln M_0}{\sigma}\right)^2\right] \quad \text{(A-1)}$$

Equation A-1 gives the distribution of mass in terms of $\ln M$.

To apply this equation, we must know the values of M_0 and σ. These are given by eqs A-2 and A-3:[3]

$$M_0 = \sqrt{M_n M_w} \quad \text{(A-2)}$$

$$\sigma = \sqrt{\ln\left(\frac{M_w}{M_n}\right)} \quad \text{(A-3)}$$

Using the DM 153 results (see Table 4), values of $M_0 = 2161$ and $\sigma = 0.675$ were obtained. For comparison with the MS distribution, eq A-1 must be divided by M, to covert the mass distribution to a molar distribution. Thus, we must consider the function f/M, rather than f. Moreover, for the same purposes of comparison, we plotted the function $10^5(f/M) + 10$. In this way, both the experimental and calculated distribution were placed in the same scale. The comparison is shown in Figure 8.

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