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Trapping of Paraffin and Other Compounds by Asphaltenes Detected by Laser Desorption Ionization–Time of Flight Mass Spectrometry (LDI–TOF MS): Role of A1 and A2 Asphaltene Fractions in This Trapping

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Trapping of compounds by asphaltenes in guest–host complexes (GHC) is an important phenomenon relevant to many properties of the system, such as asphaltene structure, swelling and solvent trapping, geochemical impact, as well as the trapping of metalloporphyrins, free radicals, resins, and other crude oil components, such as, e.g., paraffin. Several trapping mechanisms, such as adsorption and occlusion, during asphaltene separation from crude oil can be considered, but most interest is attracted to GHC, in which the guest is firmly bound and cannot be completely liberated from the host by solvent extraction. An example of such trapping is presented, with the guest being paraffinic and other resin-like compounds hereafter called trapped compounds (TCs). TCs were isolated from asphaltenes by the partition of the asphaltene sample in fractions A1 (toluene insoluble) and A2 (toluene soluble). A small quantity (about 8%) of a heptane-soluble TC fraction was isolated along with the A2 fraction. The presence of TCs in asphaltenes and their absence in fractions A1 and A2 were detected by means of laser desorption ionization–time of flight mass spectrometry (LDI–TOF MS) in the 450–600 molecular-mass range. These findings suggest that the TC sample is probably trapped in a network formed by both A1 and A2 fractions.

Introduction

Trapping of various compounds by asphaltenes is an interesting and important phenomenon. It was proposed to account for the presence of free radicals and organometallic compounds, such as, e.g., porphyrins in asphaltenes, and for the presence of difficult-to-remove paraffins from asphaltenes.¹ Swelling of asphaltenes is also related to solvent trapping. Unusually high equilibrium constants for “charge-transference” complexes suggest that acceptor molecules become trapped after complex formation. Such trapping would be equivalent to a quasi-irreversible process, which displaces the $A + D \rightleftharpoons AD$ “equilibrium” to the right, thus affording unexpected high equilibrium constants.² Separation of asphaltenes in fractions A1 and A2 has been achieved using the *para*-nitrophenol (PNP)

method discussed below.³ The most important property of these fractions is the large solubility difference. The A2 fraction solubility usually equals that of the entire asphaltene sample (50–100 g L^{−1}, toluene, room temperature), whereas the solubility of A1 is about 0.1 g L^{−1}.³

This solubility difference was accounted for in terms of differences in the ability to fold;¹ A2-type molecules could be represented by molecular models where different polycyclic sectors are separated by flexible aliphatic-type or bridging chains. On the other hand, in A1-type molecules, the above polycyclic sectors are fused together by bridging aliphatic rings (see below). As a result, A2-type molecules can fold upon themselves and A1-type molecules cannot thus affect the solubility. This difference has been estimated using molecular mechanics and leads to the differences in solubility parameters, consistent with the expected high solubility difference.¹

It was proposed that asphaltene colloids in crude oils have a structure formed by a cluster of A1 and A2 molecules. The colloidal core would be formed by a stack of A1 molecules, and the periphery would be occupied by soluble A2 molecules and other crude oil components.^{1,3} The above trapping capacity of asphaltenes lets us suppose that other crude oil components would be trapped in the colloid periphery between A1 and A2

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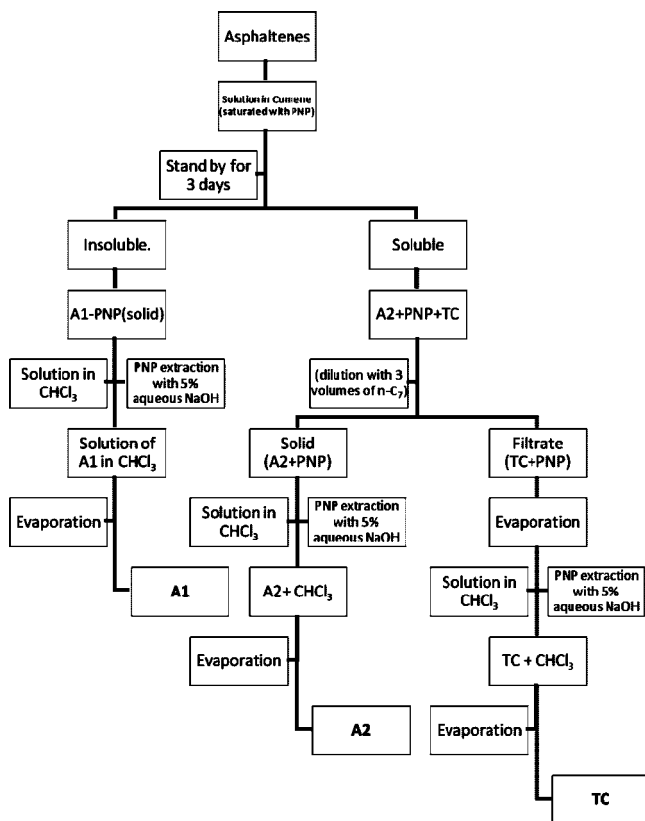
[§] LCABIE, UMR 5254, CNRS, Université de Pau et des Pays de l'Adour.

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(3) Gutiérrez, L. B.; Ranaudo, M. A.; Méndez, B.; Acevedo, S. Fractionation of asphaltene by complex formation with *para*-nitrophenol. A method for structural studies and stability of asphaltene colloids. *Energy Fuels* **2001**, *15*, 624–628.

Scheme 1. Separation of Asphaltenes in Fractions A1, A2, and TCs

Table 1. Percentages and Average Molecular Mass^a of Samples Studied

sample	percentage (%) ^b	M_n (VPO) ^c	M_n^d	M_w^d
asphaltene		1800	1500	2600
A1	57	2700	1800	3000
A2	35	1700	1800	3000
TC	8	900	1500	

^a In g mol⁻¹, with errors of about 10%. ^b With respect to asphaltenes. ^c In nitrobenzene at 100 °C. ^d Measured using LDI-TOF MS.

and would be very difficult to remove from asphaltenes when they are separated from the crude oil.

In this paper, we show that very well trapped compounds (TCs), including a mixture of homologous paraffin series and resin-like compounds, could be removed from asphaltenes after their fractionation in A1 and A2 fractions. Laser desorption ionization-time of flight mass spectrometry (LDI-TOF MS) allowed for the detection of the presence of TCs in asphaltenes and its absence in fractions A1 and A2. A possible trapping mechanism, involving the participation of both A1- and A2-type molecules is discussed together with some other aspects regarding asphaltene molecular mass (MM).

Experimental Section

Asphaltenes were obtained from extra-heavy (8 °API) Cerro Negro oil, after a modification of the IP-142 procedure. The crude oil was heated at 60 °C in a water bath and mechanically stirred while *n*-heptane (20 volumes) was added. Stirring was continued for 4 h, and the resulting mixture was set off for 24 h; after this time, the flocculated solid was filtered, pressed dry, and placed within a solid-liquid (Soxhlet) extractor, where the solid was thoroughly extracted with boiling *n*-heptane until the *n*-heptane emerged transparent from the Soxhlet thimble (about 4 days). To avoid incomplete extraction because of channel formation in the

Table 2. Elemental Analysis and Other Related Parameters

atom/sample	asphaltenes ^a	A1	A2	TC
C	81.23	80.74	80.6	80.44
H	7.72	6.88	7.4	8.1
N	2.13	2.12	2.07	1.28
S	5.5	5.19	4.92	4.56
H/C	1.140	1.023	1.102	1.208
N/C	0.022	0.023	0.022	0.014
S/C	0.025	0.024	0.023	0.021
DBE ^b	45.3	51.2	47.2	41.4

^a From ref 10. ^b Double-bond equivalents per 100 °C: DBE = (202 - H + N)/2.

Table 3. NMR Parameters Measured for Samples Studied

sample	f_H^a	f_C^b
asphaltenes		51
A1	84	52
A2	89	50
TC	89	

^a Percentage of aliphatic hydrogen; estimated errors of $\pm 2\%$. ^b Percentage of aromatic carbons; errors of $\pm 2\%$.

solid during this extraction, the solid was transferred from time to time to a beaker, suspended in hot *n*-heptane, and stirred for a while. Then, it was transferred back to the Soxhlet, and the extraction continued as above. When required, resins were obtained after vacuum evaporation of the pooled *n*-heptane-washing fractions.

Fractionation of asphaltenes with PNP to obtain fractions A1, A2, and TCs was carried out using a modification of the procedure described elsewhere.³ Briefly, a cumene (*iso*-propylbenzene) solution of asphaltenes (8 g L⁻¹) saturated with PNP was mechanically stirred and set off for 72 h, followed by filtration on a microporous membrane (0.25 μ m). The precipitated solid (A1-PNP) was washed with cumene, dissolved in chloroform, and extracted with aqueous sodium hydroxide solution (5%) to remove the PNP.

The filtrate (A1-PNP) was diluted with 3 volumes of *n*-heptane, and the precipitated solid (A2 + PNP) was filtered and treated for removal of PNP as described for A1. The TC fraction was obtained from the filtrate after evaporation of the cumene + *n*-heptane solvents, dissolution in chloroform, and extraction of PNP, as described above. These steps are summarized in Scheme 1.

The PNP/A1 mass ratio was determined by dissolving a weighed quantity of solid A1-PNP complex in chloroform. This solution was extracted several times with aqueous sodium hydroxide (5%) until the aqueous extract contained not measurable PNP determined by UV at 401 nm. Then, the aqueous extracts were combined, and the PNP content was determined after measuring an aliquot and interpolation using a calibration curve constructed with 5% aqueous solutions of PNP.

Molecular mass determined by vapor pressure osmometry (VPO) and laser desorption ionization couple with a time-of-flight detector in the linear way (LDI-TOF MS) were measured using methods described earlier.^{1,4} Briefly, M_n (VPO) values, in the 2–7 g L⁻¹ range were measured in nitrobenzene at 100 °C after extrapolation to infinite dilution. LDI-TOF MS was determined using a Voyager DE-STR instrument (Applied Biosystems), at optimum laser shoot (LS) employing diluted (about 100 mg L⁻¹) tetrahydrofuran (THF) solutions. According to previous results, no matrix was required to obtain the MS of asphaltenes and TC samples.⁴ Laser power was optimized using procedures described earlier;^{1,4} briefly, samples were run using different laser power, where it is usually found that either too low or too high LS values lead to too low average MMs because of poor volatilization or fragmentation.¹

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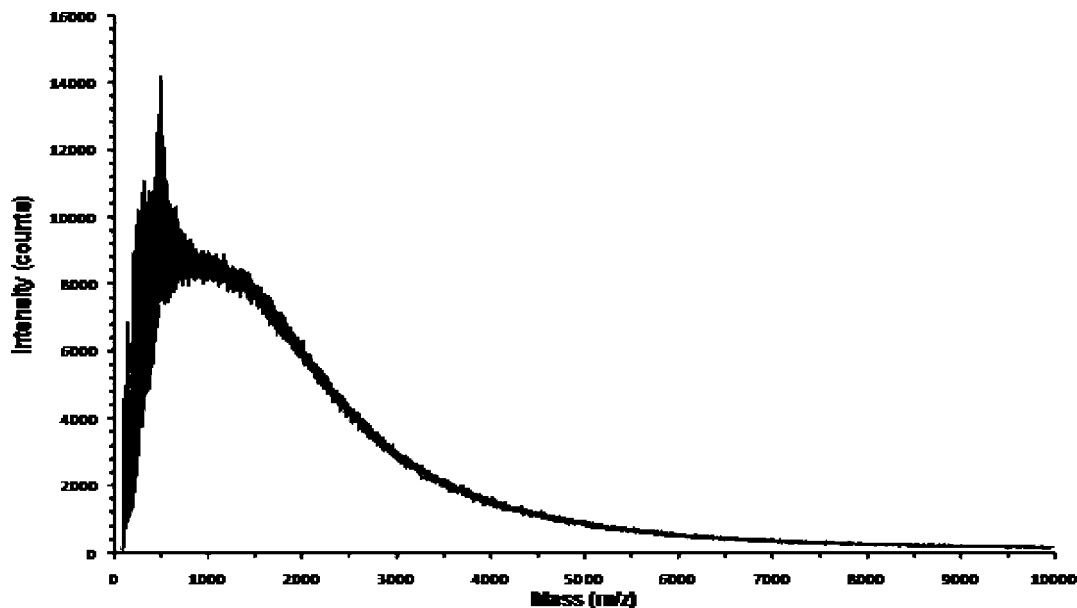


Figure 1. LDI-MS for asphaltenes in the 100–10 000 amu range. Note the bimodal MMD distribution of this sample. First band in the 100–1000 amu range.

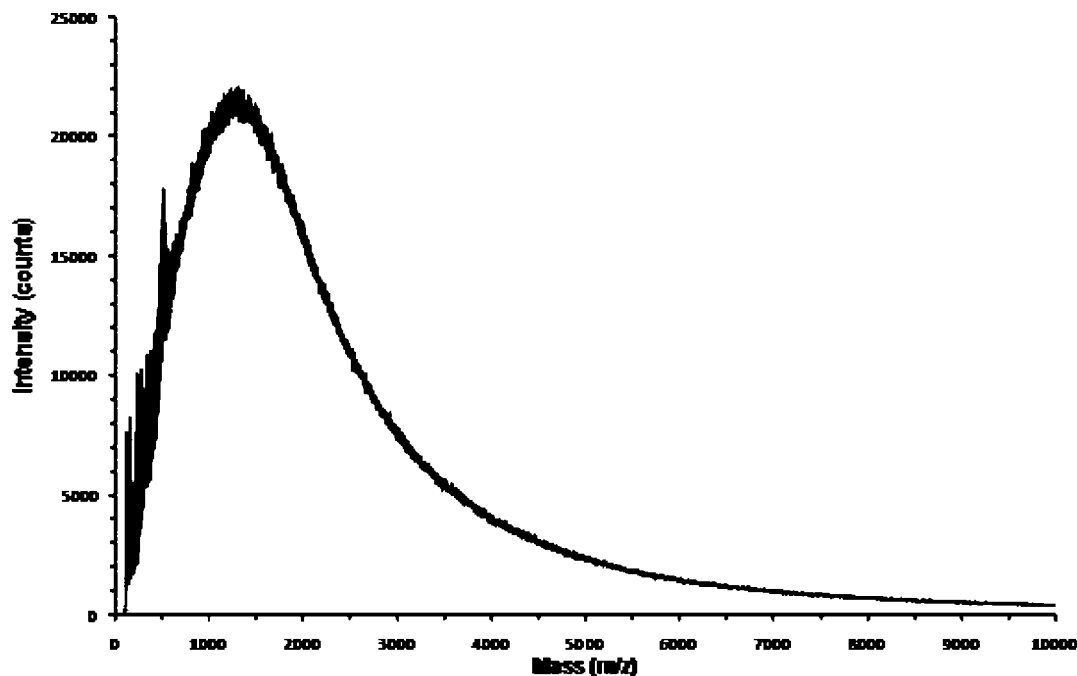


Figure 2. LDI-MS for the A1 fraction of asphaltenes in the 100–10 000 amu range. Note that the bimodal MMD distribution in Figure 1 is not present here.

Both ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were measured using a Jeol model Eclipse instrument. Elemental analysis was performed by Ultra Traces Analysis Aquitaine, University of Pau, France.

Results

The PNP/A1 ratio found (about 91 ± 4 mg/g, average of three determinations) was close to the values reported earlier;³ this is equivalent to a 1:1.11 PNP/A1 molar ratio for an asphaltene of average MM equal to 1700 g/mol. Considering the uncertainties in both the ratio and MM of asphaltenes, the molar ratio is not significantly different from 1.

Table 1 show the yields and the mean molecular masses of compounds investigated in this work. A significant amount of TCs (8%) was measured. As is usually the case, a large percentage of A1 was obtained.

Average molecular mass data obtained both by VPO and LDI are collected in Table 1. The very large difference in M_n (VPO) between A1 and A2 and the corresponding equal values obtained by LDI strongly suggest that aggregation in nitrobenzene is important for A1 but not for asphaltenes and A2. Similar results were reported earlier for Furiel asphaltenes.³ It is worth mentioning that techniques using LDI-MS for measuring the MM of asphaltenes were criticized because of the putative asphaltene aggregation during measurements.^{5,6} In such a case, the measured LDI-MS molecular mass for A1 would have been higher than that measured

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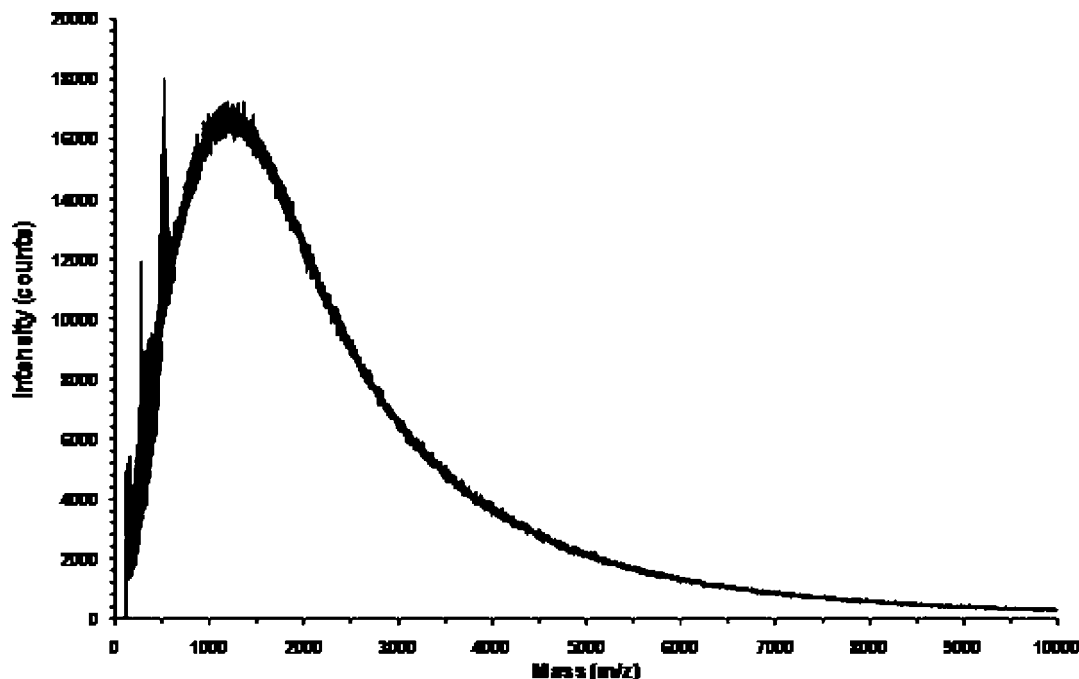


Figure 3. LDI-MS of fraction A2 of asphaltenes in the 100–10 000 amu range. Note that the bimodal MMD distribution in Figure 1 is not present here.

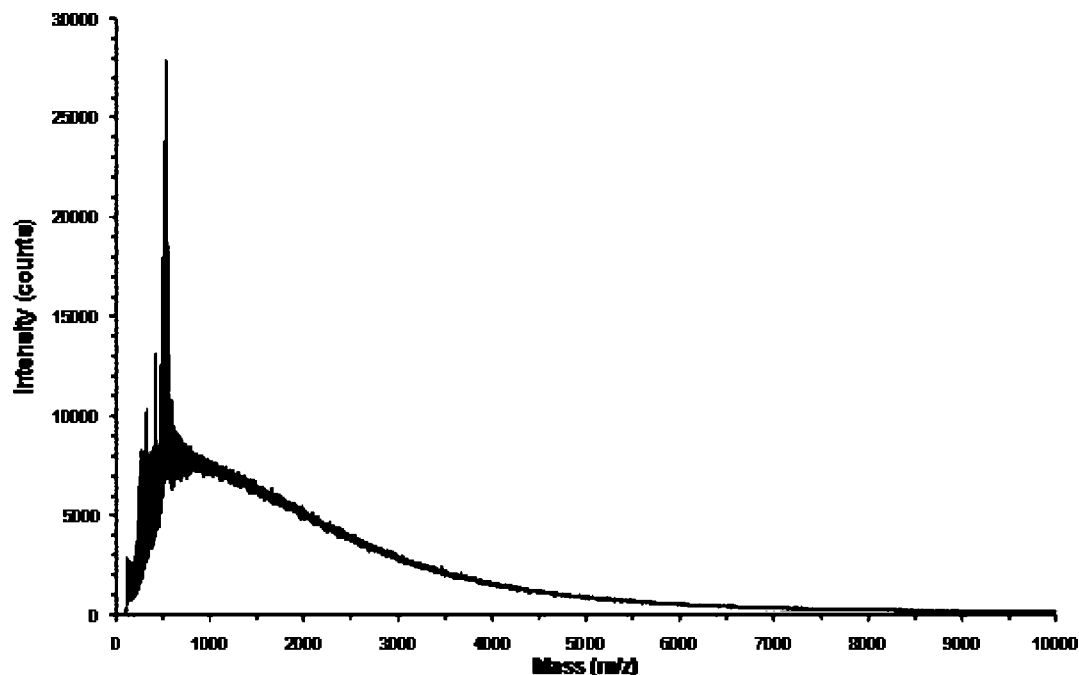


Figure 4. LDI-TOF MS of TCs showing the 100–10 000 amu range.

for A2. This is not the case according to the results in Table 1. MM and molecular mass distribution (MMD) similar to those reported here were reported using matrix-assisted laser desorption ionization (MALDI),⁷ LDI,⁸ and field-desorption (FD)⁹ mass spectrometry techniques. Dimerization was observed in LDI techniques with resins¹ and other relatively low-MM model

compounds,⁸ that is, compounds with MM or average MM < 1000 g mol⁻¹. Presumably, the significant difference between M_n values for TC in Table 1 is the consequence of some dimer formation during the LDI measurement.

Table 2 shows the elemental analysis, atomic ratios, and DBE data, whereas Table 3 shows some NMR results. In comparison to H/C values for resins previously reported¹⁰ for the same crude oil (H/C of around 1.4), H/C values for the TC sample appears low. This could be due to a higher aromaticity of the sample. The difference in H/C between A1 and A2 leads to higher DBE values for A1, which is consistent with more rigid structures

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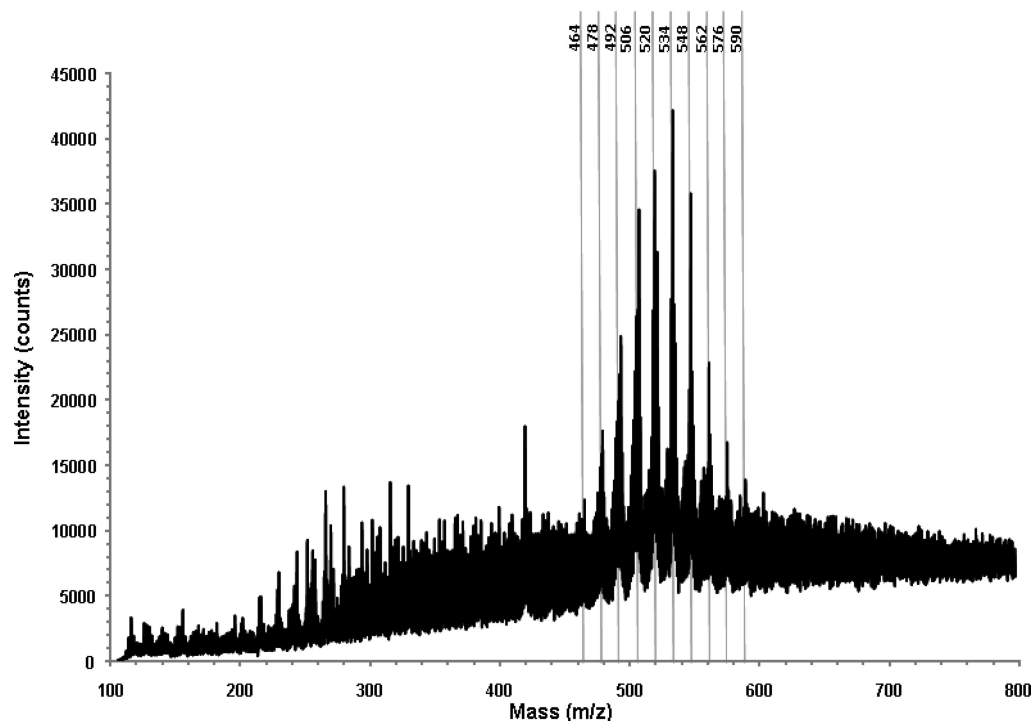


Figure 5. Expansion of the 100–800 MM range corresponding to the LDI–TOF MS of TCs; see Figure 4. The constant separation of 14 amu, corresponding to CH_2 and characteristic of paraffin, is clearly shown in the spectra. Corresponding mass values are 464, 478, 492, 506, 520, 534, 548, 562, 576, and 590.

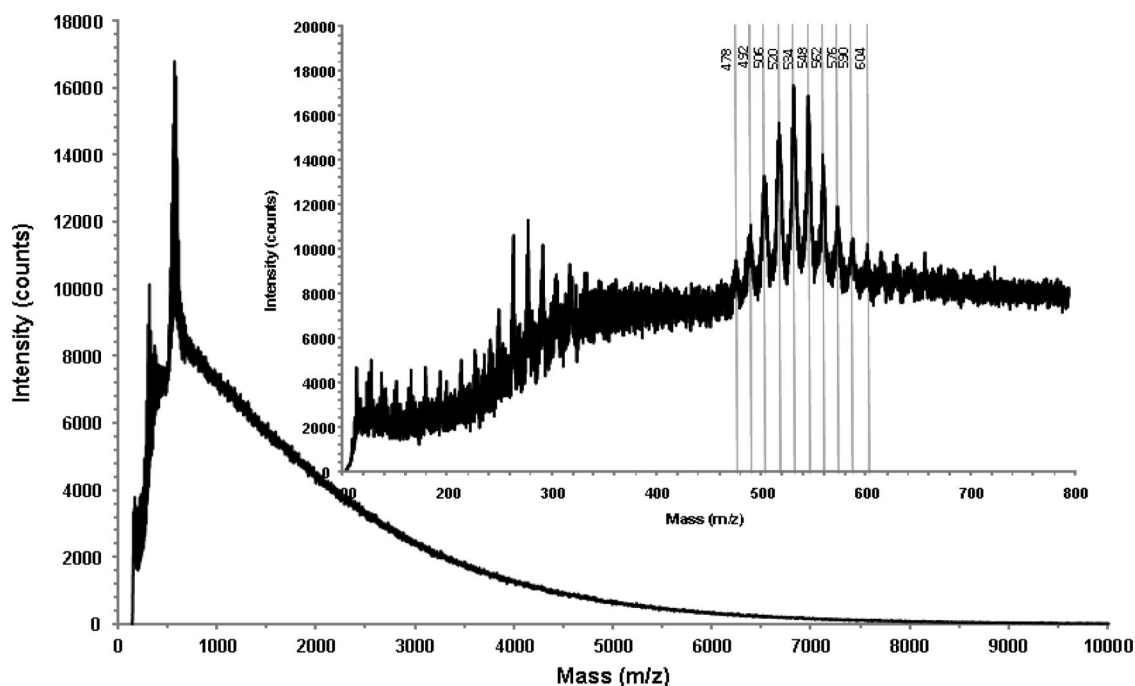


Figure 6. LDI–TOF MS corresponding to resins; the spectrum on the right is the expansion of the 450–650 mass range clearly showing the presence of paraffinic compounds in this sample. The paraffinic cluster goes from 478 to 604 amu.

for A1; in particular, A1 would contain aliphatic rings joining different aromatic sectors of the molecule (see Figure 8 for a simple A1-type model and Figure 9 for a A2-type model).

As was the case for other asphaltenes,³ differences in f_C are small and within the experimental error. Thus, the above results substantiate the hypothesis according to which the large solubility difference between A1 and A2 is the result of differences in molecular folding (cf. the Introduction).

Figures 1–4 show the LDI MMD of asphaltenes, A1, A2, and TC samples. Note that the bimodal nature of MMD corresponding to asphaltenes, clearly shown in Figure 1, is not present in the

spectra corresponding to the A1 (Figure 2) and A2 (Figure 3) samples; this is consistent with the removal of low molecular mass or TC compounds from asphaltenes. It is important to note that, after the removal of trapped compounds or TC, the MMD of both A1 and A2 is described by a single band with a very small “contamination” by residual TC compounds.

Figure 4 shows an LDI–TOF mass spectrum corresponding to the TC compounds trapped in the asphaltenes (see the Experimental Section). The spectrum is characterized by a cluster of well-defined peaks below 600 amu (see Figure 5) and a hump extending to higher MM. Average mass differences

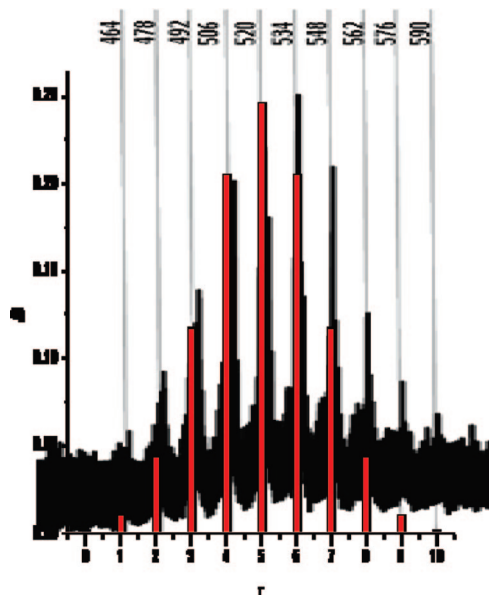


Figure 7. Comparison of the experimental paraffin distribution cut from Figure 5 with the binomial distribution of Figure A1 in the Appendix. The mass value corresponding to $r = 0$ should be 450 amu.

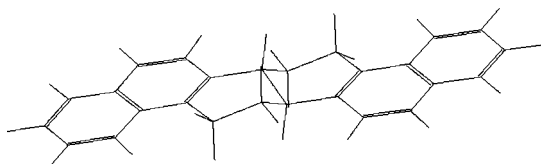


Figure 8. Simple M1 model illustrating the A1-type molecular model. Note the two aliphatic rings “bridging” polycyclic sectors of the molecule.

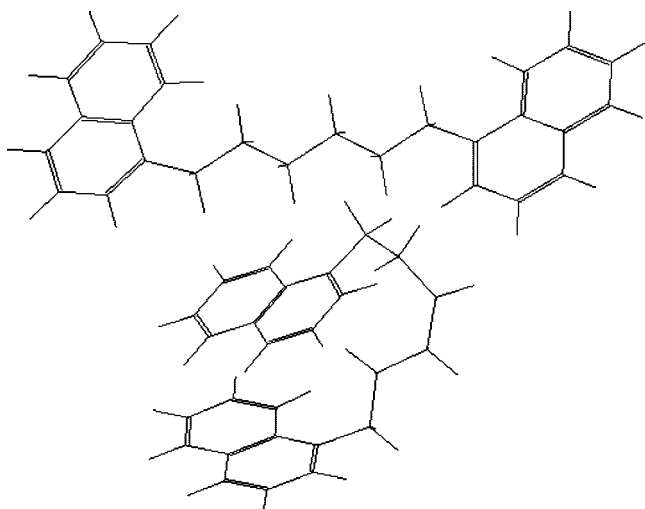


Figure 9. Two conformers of molecular model M2 representing simple examples of A2-type molecules: (top) unfolded and (bottom) folded conformers. Note the aliphatic chain bridging the polycyclic sectors.

between consecutive groups of prominent peaks in the 450–650 mass range were close to 14, indicating that paraffin compounds in this molecular range are among the TCs trapped by asphaltenes. Figure 5 is the expansion of the paraffinic sector showing a homologous series with nominal mass between 464 and 590. A similar homologous series of paraffins, measured by MALDI–TOF, was reported earlier for technical waxes.¹¹

An LDI–TOF mass spectrum of resins (Figure 6) shows an expansion in the 450–650 mass range; a comparison to Figures 4 and 5 shows important similarity, in particular, in terms of the presence of paraffinic compounds in both TCs and resins.

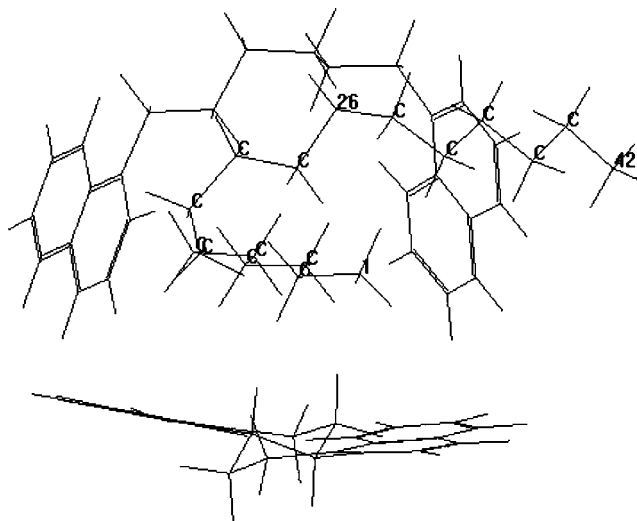


Figure 10. Molecular model depicting trapping of heptadecane by molecules M2 and M1. M2 is on the top, and M1 is on the bottom. Carbon atoms marked with C are from heptadecane. Carbons 1 and 42 are far from the viewer, and carbon 26 is close to the viewer; in this way, heptadecane adopts a “U” shape, where the section going from C1 to C26 is to the left and below the aromatic section (on the right) of M2 and the section going from C26 to C42 is to the right and on top of the same aromatic section of M2.

In Figure 7, the paraffin distribution shown in Figure 5 is compared to the simple binomial distribution described in the Appendix. The reasonable match between the two suggests that trapping has been effective enough to avoid a selective loss of members of the series.

Models of A1- and A2-type molecules are illustrated with simple examples in Figures 8 and 9. The idea with these models is to illustrate the molecular aspects relevant to this paper and not to represent details of any particular asphaltene molecule. When approaching each other, all atoms in A1-type molecules could interact simultaneously, leading to strong van der Waals interactions (the so-called cofacial interaction). Thus, aggregation in this case is expected.

On the other hand, M2 is a flexible model that could fold to give the folded conformer shown (note that M2 is obtained from M1 after aliphatic ring opening and “hydrogenation” with two hydrogen molecules). Simple molecular mechanic calculations show that the folded conformer is much more stable, and this conformation should prevail over the unfolded one. Hence, when these folded conformers approach each other, the number of atoms interacting simultaneously is limited, and this leads to weak van der Waals interactions. Thus, in good solvents, aggregation for A2-type molecules is not expected.

Figure 10 illustrates one of the many structures leading to the trapping of a paraffin molecule (heptadecane in this case) by M1 and M2. It is not difficult to image that this structure could interact with other A2 or A1 molecules, leading to aggregates where the paraffin will be trapped in a sort of labyrinth from which it would be very difficult to escape.

Discussion

According to the separation procedure described above, TCs are released from the mixture after asphaltene fractionation in fractions A1 and A2. This is confirmed by comparing the LDI mass spectra of asphaltenes to those corresponding to A1 and A2. The bimodal nature of MMD of asphaltenes, because of presence of TCs in the low MM range (Figure 1), is not present in the MMD corresponding to A1 (Figure 2) and A2 (Figure

3). The high solubility of TC in heptane suggests that the sample is not another asphaltene component. The comparison between LDI mass spectra (Figures 4 and 5 with Figure 6) strongly suggests that TCs are constituted by resin components. Other similar bimodal MMD measured using LDI could be seen in Figure 1 of ref 7 for Maya asphaltenes.

A comparison of M_n (VPO) values shown in Table 1 clearly develops the higher aggregation tendency of A1 when compared to A2. The present LDI-MS results (Table 1), as well as earlier size-exclusion chromatography (SEC) results,¹ show that these samples have very similar MM and MMD and that the higher M_n (VPO) of A1 is due to aggregate formation. On the other hand, the relative low M_n (VPO) value of sample A2 is consistent with the weak aggregation tendency expected for A2-type molecules. Hence, the MM of sample A2 should correspond to the MM of asphaltenes.

Although evidence for trapping of compounds by asphaltenes is now abundant,^{1,12,13} it is the first time that a direct nondestructive method is used to isolate them. It is an important topic in geochemistry, where unaltered paraffin and other geochemical markers are required for geochemical studies of crude oils.^{12,13} Because these compounds cannot be completely released by a thorough solid-liquid extraction of flocculated asphaltenes (see above), they must be trapped within the colloidal network formed by A1 and A2 compounds (cf. the Introduction).

A way to understand such trapping is presented in Figure 10. Because of the folding capacity of A2-type molecules, models such as M2 could effectively "catch" the guest (heptadecane in this case). Once the guest has been trapped, the structure could interact with other asphaltene molecules (A1 or A2), leading to the permanent trapping of the guest. We presume that such a mechanism would not be effective with A1 or A2 alone; intermolecular interactions between two A1-type molecules would be too strong and will expel any molecule placed between them. On the other hand, A2-type molecules are too soluble, and eventually, any trapped compound will escape.

As described above for asphaltene colloids, A1-type molecules should prevail in the colloidal core, whereas A2-type should prevail at the core periphery; it is quite reasonable that other molecules, such as the paraffin seen in the above spectra, could become trapped between the core and the periphery, which contributes to the stabilization of these colloids in crude oils.

Conclusions

Trapping of compounds by asphaltenes in permanent guest-host complexes has been established by examining the release of TCs initially trapped in these complexes. Both trapping and release after treatment were determined by LDI-TOF MS, which clearly show the presence before and absence after the treatment of the TCs or guest compounds. A hypothetical mechanism of trapping requires both the A2-type molecules for holding the guest and the A1-type molecules for permanent trapping. Thus, when asphaltenes are split in the above fractions, the TCs are released from their molecular traps.

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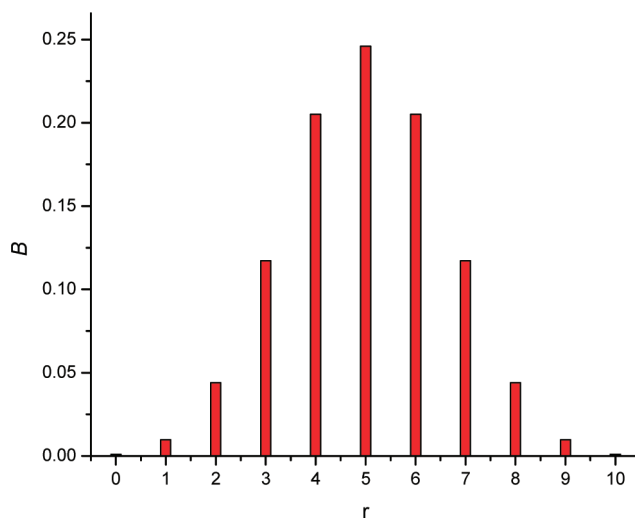


Figure A1. Binomial distribution given by eq 1 with $n = 10$ and $r = 0, 1, 2, \dots, 10$.

A conclusion from the above and earlier experiments^{1,3} is that asphaltenes are a mixture of A1- and A2-type molecules; A1- and A2-type molecules, also called continental- and archipelago-type molecules in the literature,^{14,15} are likely to be present in all asphaltene samples studied. Thus, the dilemma as to whether asphaltene molecules are continental- or archipelago-type appears to be a false one.

The main objective of this and earlier research in these laboratories is to find as much evidence as possible consistent with the main structural aspects related to fractions A1 and A2,^{1,3} that is, with the flexibility of A2-type molecules and "stiffness" of A1-type molecules. As proposed above, trapping and asphaltene aggregation are both related to these features.

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Appendix

We used the well-known binomial distribution shown in eq 1

$$B = \frac{n!}{r!(n-r)!} p^n, \quad r = 0, 1, 2, \dots, 10 \quad (1)$$

In this equation, we set $n = 10$, to match the number of bands or paraffin compounds in the experimental paraffin distribution (11 bands; see Figure A1). $p = 1/2$ would be the probability for the presence of the compound, and r takes values from 0 to 10. The binomial value or B gives the relative concentration or frequency of any of the 11 members in the mixture. Figure A1 was obtained after solving eq 1 in the usual manner. The experimental and theoretical distributions are compared in Figure 7.

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