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Understanding Asphaltene Fraction Behavior through Combined Quartz Crystal Resonator Sensor, FT-ICR MS, GPC ICP HR-MS, and AFM Characterization. Part I: Extrography Fractionations

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ABSTRACT: Multiscale characterization of asphaltenes and their extrography fractions titrated with *n*-heptane was performed. Chemical characterization via FT-ICR MS and GPC ICP HR-MS, stability monitoring via QCR, and AFM images of deposits indicate that "island"-enriched samples tend to form fewer, well-organized deposit aggregates, whereas samples with abundant "archipelago"-like molecules produce larger aggregates and less well-organized deposits. The combination of QCR and AFM leads to the conclusion that "island"-enriched samples lead to smaller deposits compared to "archipelago"-like molecules.

INTRODUCTION

General View of Asphaltene Chemistry. For more than five decades, the definition of asphaltenes has remained unaltered and constrained to the solubility of nanoaggregates in toluene and their insolubility in aliphatic solvents, such as pentane or heptane.¹ Asphaltenes are ultracomplex mixtures that include a polydispersed collection of nanoaggregates, with a high diversity of size, shape, and chemical properties such as solubility.²⁻⁴ Historically, asphaltene structure has been described as a single aromatic core with alkyl side chains, known as the island or continental structural model, which was introduced by Yen⁵ in 1961 and then more precisely by Dickie and Yen⁶ in 1967. The second and less accepted proposed structure is known as the archipelago model, which includes several (more than one) aromatic cores (multicore) linked by covalent bonds, and was proposed by Strausz et al.^{7,8} in 1992. The original Dickie and Yen⁶ model and the modified Yen model proposed by Mullins^{9,10} have ruled the understanding of asphaltenes for many decades and have perpetuated the idea that asphaltene aggregation is exclusively driven by aromatic stacking or $\pi - \pi$ interactions between the aromatic cores of single-core molecules.¹¹ Heteroatom-based intermolecular forces, such as hydrogen bonding, are not considered to be of main importance to asphaltene properties, according to the Yen–Mullins theory.^{11,12}

Conversely, the supramolecular assembly model for asphaltene aggregation, first proposed by Agrawala et al.¹³ and later refined by Gray et al.,¹⁴ suggests a more complex structure for asphaltene nanoaggregates, with the presence of different structural motifs (single-core and multicore), diverse intermolecular forces (e.g., $\pi - \pi$, hydrogen bonding, acid–base conjugation), and the occlusion of alkane-soluble compounds (or maltenes) inside asphaltene nanoaggregates.¹⁵ This theory is more consistent with several asphaltene properties, including

behavior in mild pyrolysis, gas-phase fragmentation (tandem mass spectrometry), adsorption on polar surfaces, occlusion of maltenes, and adsorption at the oil/water interface. Regardless of the inherent difficulties in understanding mild pyrolysis data, any asphaltene model should be suitable to the production of 1-5-ring alkyl-aromatics upon thermal stress.

These nanoaggregates undergo macro-aggregation and precipitation. Their solubility behavior is strongly linked to high heteroatom content and the presence of possible hydrogen bonding.^{16,17} The presence of Archipelago/Island-type asphaltene monomers can also influence precipitation.^{18,19} Modelization of asphaltene precipitation needs to divide the petroleum samples into different components/families such as saturates, aromatics, resins, and subdivision of asphaltenes into different families.²⁰

Asphaltene Fractionation Strategies. Recently, separation methods such as extrography coupled to molecular-level characterization by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) have allowed the detection of both island and archipelago structural motifs in asphaltene samples when applied to asphaltene investigation.^{21–23} Extrography involves the adsorption of petroleum samples on a polar adsorbent, such as silica gel, alumina, or cellulose. The subsequent fractionation is achieved by Soxhlet extraction with specific solvents. Chacon-Patiño et al.²¹ used acetone followed by an elutropic gradient composed of heptane, toluene, and tetrahydrofuran/methanol. The initial extraction with acetone,

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in which the predominant intermolecular forces consist of dipolar interactions, facilitates the selective separation of highly aromatic/condensed structures. The subsequent extraction with mixtures of heptane/toluene allows the isolation of alkyl-aromatic compounds. Finally, the use of tetrahydrofuran/ methanol produces asphaltene compounds with abundant polarizable functionalities that interact strongly, via hydrogen bonding, with the active silanol groups on the SiO₂ surface.

Molecular-Level Characterization by FT-ICR MS. Recent reports from FT-ICR MS and gas-phase fragmentation via infrared multiphoton dissociation (IRMPD) indicate that the acetone extrography fraction has a high concentration of single-core or island structural motifs.^{21,24} Moreover, the acetone fraction exhibits a high ionization efficiency in atmospheric pressure photoionization (APPI).²⁵ Conversely, the toluene/tetrahydrofuran/methanol fractions are more difficult to ionize, presumably because of their stronger aggregation tendency, and reveal abundant multicore or archipelago motifs. The authors concluded that single- and multicore motifs coexist in petroleum asphaltenes and the dominance of a particular structure depends on the sample.^{21,26} For instance, Wyoming deposit asphaltenes, known to be consistent with the modified Yen model because they produce high amounts of coke in thermal cracking, revealed abundant single-core motifs. In contrast, Athabasca bitumen asphaltenes, known to produce a high yield of distillable products in the thermal cracking, were shown to be enriched in multicore species. Therefore, the extrography methodology confirmed that asphaltenes are composed of different structural motifs. Importantly, because of the lesser aromaticity of multicore-type compounds, $\pi - \pi$ interactions are not the dominant force that drives nanoaggregation, consistent with recently published theoretical calculations.²

Among all of the available analytical techniques, high-field FT-ICR MS offers the most comprehensive molecular analyses because it can reveal tens of thousands of elemental compositions present in petroleum-derived samples.^{29,30} The high mass accuracy and resolution exclusively offered by FT-ICR MS allows the assignment of a unique elemental formula to each detected peak. Commonly, the assigned formulas are sorted by heteroatom content (e.g., all of the compounds with C, H, and one S atom belong to the class S_1), carbon number, and double bond equivalent (DBE = number of rings plus double bonds to carbon), and the information is represented by contoured plots of DBE versus carbon number with the relative abundance shown by a color scale. Although FT-ICR MS only reveals molecular formulas, when coupled to gasphase fragmentation such as IRMPD and collision-induced dissociation, it can supply useful structural information. However, all MS-based techniques are limited because of selective ionization, ion suppression, and matrix effects.³¹⁻³⁶ Currently, there is not a "universal" ion source that allows for ionization of complex mixtures without any discrimination toward specific compound classes and structures. Therefore, prior sample fractionation is critical to achieving more complete molecular characterization of complex samples such as asphaltenes.^{37–39}

Gel Permeation Chromatography Hyphenated with Inductively Coupled Plasma Mass Spectrometry. Gel permeation chromatography combined with inductively coupled plasma mass spectrometry (ICP-MS) has been recently used to understand metal (V and Ni) and heteroatom (S) content as a function of nanoaggregate size distribution in asphaltene samples.^{40–43} The results reveal that asphaltenes exist as a trimodal distribution of nanoaggregates. GPC chromatograms for geologically diverse samples suggest that asphaltenes can be separated into high molecular weight (HMW), medium molecular weight (MMW), and low molecular weight (LMW) aggregates and nonaggregated species (called "tailing" fraction).^{38,43,44} Fraction collection and their reinjection into the GPC system yields a chromatogram in which the compounds are mostly eluted at the same retention time as in the initial sample, which demonstrates the stability of the collected nanoaggregate and the reproducibility of the technique.³⁸ Thus, GPC/ICP-MS allows comparison of nanoaggregates because it reveals differences in hydrodynamic volume as a function of metal/heteroatom content.

Atomic Force Microscopy for Asphaltene Characterization. At the nanoscale level, atomic force microscopy (AFM) is an interesting technique that offers access to threedimensional information. For asphaltene characterization, AFM has been applied from single asphaltene molecule imaging (Schuler et al.)^{45,46} to observation of asphaltene aggregates in different media/support.^{47–50} Therefore, AFM is a technique of choice for observation and comparison of the type and form of macroaggregates deposited on metal surfaces or sensors.

Quartz Crystal Resonator for Trace Asphaltenes Flocculation. Due to the simplicity and versatility of this technique, quartz crystal resonator sensors (QCR or QCM) are increasingly used to understand asphaltene destabilization, aggregation, and deposition. In recent years, many studies have been published on this aspect.⁵¹⁻⁵⁶ The QCR sensor consists of a quartz disc with electrodes deposited on both faces and oscillated by applying an AC current between them. The oscillation is achieved due to the piezoelectric properties of the quartz. The resonance frequency at which the oscillation occurs depends on the characteristics of the crystal and can vary due to changes on its surface (mass adsorption, roughness) and in the surrounding media (viscosity, temperature, pressure, etc.).⁵⁷⁻⁶⁰ A simplified model can be used to correlate changes in the frequency (eq 1) and dissipation (eq 2) with the properties of the system, such as mass absorbed on the quartz surface and viscosity, when the QCR is immersed in a liquid:⁵⁴

$$\Delta f_n = -n(2C_m \Delta m) - \sqrt{n} \frac{C_m}{\sqrt{\pi f_0}} \sqrt{\rho \eta}$$
(1)

$$\Delta\Gamma_n = \sqrt{n} \frac{C_m}{\sqrt{\pi f_0}} \sqrt{\rho \eta} \left(1 + R\right) \tag{2}$$

where C_m is a constant that depends on the crystal characteristics, Δm is the theoretical mass deposited on the quartz surface, $\rho\eta$ is the density-viscosity product of the medium, f_0 is the fundamental resonance frequency of the crystal, and *R* is an empirical correction term that accounts for viscous friction on rough surfaces.

This work focuses on the study of asphaltene extrography fractions by QCR, AFM, GPC, and FT-ICR MS to establish correlations between molecular composition, nanoaggregate size and shape, and asphaltene precipitation trends.

EXPERIMENTAL SECTION

Asphaltene Fractionation by Extrography. Asphaltene samples were adsorbed on silica gel with a mass loading of 1%. The

mixture was dried under nitrogen, the temperature in the Soxhlet reservoir was below 50 $^{\circ}$ C, and it was protected from light. The dried material was extracted in a Soxhlet apparatus using three different solvents: acetone (100%), Hep/Tol (1:1), and Tol/THF/MeOH (10:10:1). Fractions were dried under nitrogen and stored in the dark for subsequent analyses. Gravimetric mass yields for the fractions and vanadium content are included in Table 1.

Table 1. Extrography Fractionation: Gravimetric Yields for Asp-1 and Asp-2 with V and S Content

sample	extract	extracted mass (% of the initial asphaltene)	V content in ppm	S content in ppm
Asp-1	Asphaltene	-	338	34 140
	Acetone	15	909	68 700
	Hep-Tol	46	275	29 110
	Tol-THF- MeOH	25	275	30 037
	Mass Balance (%)	86.0 ± 2.5	98	92
Asp-2	Asphaltene	-	588	43 300
	Acetone	19	1397	66 779
	Hep-Tol	29	340	29 450
	Tol-THF- MeOH	48	468	43 220
	Mass Balance (%)	96.1 ± 3.7	97	100

Materials. High-performance liquid chromatography (HPLC) grade heptane (Hep or C_7), toluene (Tol), tetrahydrofuran (THF), methanol (MeOH), and acetone from J.T. Baker (Phillipsburg, NJ) were used as received. Silica gel (100–200 mesh, type 60 Å, Fisher Scientific) was used in extrography. High-purity glass microfiber thimbles were used in Soxhlet extraction.

Samples. Two asphaltene samples were obtained by the standard method ASTM D6560-12 for precipitation of C_7 insolubles applied to Middle East atmospheric residues. Table 2 includes elemental analysis and weight content for both atmospheric residues.

GPC-ICP HR MS. After dilution in THF by a factor of 100, all samples were analyzed by the GPC-HR-MS method, as published elsewhere.^{42–44,61} In short, the liquid chromatographic system was set up with three Styragel gel permeation chromatographic columns in series (HR 4, HR2, HR 0.5 (7.8 × 300 mm) from Waters (Saint Quentin en Yvelines, France) and combined with a high-resolution ICP mass spectrometer (Thermo, City) with a custom-built interface. The isocratic THF (with 250 ppm of butylated hydroxytoluene (BHT) as a stabilizer) flow rate was 1 mL/min, and the injection volume was 40 μ L. Three isotopes were followed: ⁵¹V, ⁶⁰Ni, and ³²S.

FT-ICR MS. Asphaltene samples were diluted in toluene to a final concentration of 50 μ g/mL. The solutions were directly infused at 50 μ L/min into an atmospheric-pressure photoionization (APPI) Ion Max source (Thermo Scientific) operated with a vaporizer temperature of 350 °C. Gas-phase neutrals were ionized with 10.2 eV photons, and positive ions were transferred to the mass spectrometer through a heated metal capillary operated at ~350 °C. Ions were analyzed with a dynamically harmonized FT-ICR cell.⁶² For each sample, 200 time-domain transients were summed and Fourier transformed. Data collection and mass spectra calibration were

assisted by Predator custom software. PetroOrg software facilitated molecular formula assignment and data visualization.

Quartz Crystal Resonator (QCR). Stock solutions (1000 ppm) were prepared by dissolving the dried asphaltenes and fractions in toluene and placing them in a temperature-controlled oven at 30 °C for 72 h. A dilution with toluene was performed, resulting in 200 ppm solutions. Amounts of 17.5 g were used in titration with n-heptane. The experimental setup of the titration is shown in Figure 1. The quartz sensor (4) was placed inside the custom double-wall vessel (3), and the isothermal bath was set at 25 °C. Transmission of electrical signals and monitoring of the QCR sensor response were conducted through a network analyzer (Agilent E5071C) (2) connected by coaxial cables to a computer (1) with an internally automated LabVIEW program. The sensor was allowed to stabilize (frequency changes of <0.5 Hz), and the frequencies in air (background) were recorded. The sample solution was placed in the cell, and the system was held for approximately 30 min to reach a stable signal. The titration was performed with n-heptane (8) supplied at a constant speed of 0.25 g/min, and the mixture in the vessel was stirred at a constant rate using a magnetic stirrer and a stir bar (6) rotating below the quartz. The titration was stopped once a concentration of 80 wt % of n-heptane was reached. Gold coupons (5) immersed in the same container in the immediate vicinity of the resonator were used in the AFM images.

Estimation of the destabilization onset was obtained using a simple approach based on the model used. When a titration is performed in a system without any mass load on the quartz, the first term in eq 1 becomes 0, and all frequency shifts are due to liquid loading, and thus the following equality can be obtained:

$$\Delta f_{n,m} = \frac{-\Delta \Gamma_{n,\eta}}{(1+R)} \tag{3}$$

A plot of Δf as a function of $\Delta\Gamma$ (Figure 2, left) presents a linear behavior with a slope equal to -1/(1 + R). Deviations from this linearity must be linked with mass loading effects and thus can be used to detect asphaltene destabilization.

The amount of deposit on the sensor surface was estimated by analyzing the behavior of Δf for the different overtones (third, fifth, seventh, and ninth) and plotting the linear relation of $\Delta f/n$ vs $1/\sqrt{n}$.

$$\frac{\Delta f_n}{n} = -2C_m \Delta m - \frac{1}{\sqrt{n}} \frac{C_m}{\sqrt{\pi f_0}} \sqrt{\rho \eta_l}$$
(4)

AFM Images of Coupons after Deposition. After titration, the gold coupons were rinsed in *n*-heptane and dried in air. Atomic force microscopy (AFM) images of the surface were collected with a Multi-Mode VIII (BRUKER) instrument using Nanoscope ver. 8.15 software. To image these samples, the peak force quantitative nanomechanical mapping (QNM) mode was selected. Silicon nitride cantilevers with a calibrated spring constant of 0.36 N.m⁻¹ and a typical tip radius of approximately 10 nm were used.

RESULTS

Molecular Characterization by FT-ICR MS. Figures 3 and 4 (upper panel) present the isoabundance contoured plots of DBE versus carbon number for HC-, N-, and O-containing compounds (upper row); all species with at least one S atom (S-containing, middle row); and vanadyl porphyrins or class $N_4O_1V_1$ (lower row). The lower panels of Figures 3 and 4 present the gravimetric yields for extrography separation. The

Table 2. Elemental Composition and Asphaltene Content for Middle East Atmospheric Residues⁴

sample	N (%)	Ni (ppm)	V (ppm)	Fe (ppm)	S (%)	Na (ppm)	Asphaltene (wt %)	CCR (%)
AR-1	0.32	23	60	12	4.16	4.1	4.9	11.5
AR-2	0.47	60	82	13	4.33	5.8	8.0	13.6

^aCCR Corresponds to Conradson Carbon Residue.



Figure 1. Experimental Setup. (1) Computer, (2) Network analyzer, (3) Double-walled glass vessel, (4) QCR sensor, (5) Gold coupons, (6) Magnetic stir bar, (7) Peristaltic pump, (8) *n*-Heptane, and (9) Balance.



Figure 2. Destabilization onset determination. Left panel - Frequency shift (Δf) as a function of dissipation shift ($\Delta \Gamma$). Right panel - Frequency shift (Δf) as a function of *n*-heptane composition.

major difference is that Asp-2 contains a higher concentration of the most polarizable extrography fraction, Tol/THF/MeOH (~48 wt %). According to Table 1, Tol/THF/MeOH and Hep-Tol from Asp-2 have lowest concentrations of vanadium compared to the acetone fraction that reveal vanadyl porphyrins ($N_4O_1V_1$ class). The lower panels of Figures 3 and 4 also present the ionization efficiency, or monomer ion yield (MIY), as determined by APPI FT-ICR MS. MIY is inversely proportional to the accumulation period required to hit a target signal magnitude optimal for data collection in FT-ICR MS. Samples that ionize efficiently in APPI, such as PAHs and aromatic fractions from light crude oils, require a short accumulation period in an external ion trap before transferring to the ICR cell (~5-50 ms). Conversely, difficult-to-ionize samples, such as asphaltenes, polar petroleum fractions, and vacuum residues, require a longer accumulation, up to ~5000 ms. Thus, poor ion production translates into a longer accumulation period and thus lower MIY. The results indicate that the acetone fractions from both asphaltenes samples ionize ~25-90-fold more efficiently than the Tol/THF/MeOH fractions. Thus, analysis of whole asphaltene samples (without prior fractionation) preferentially reveals the acetone species. From Figures 3 and 4, it is clear that the acetone fractions closely resemble the compositional range of the whole samples (upper panels). However, the Hep/Tol and Tol/THF/MeOH fractions, with a lower monomer ion yield, present a completely different compositional range. The results highlight that the most strongly adsorbed compounds on the silica gel (Tol/THF/MeOH) have lower DBE values than the acetone

and Hep/Tol fractions. The major difference is shown again by the Tol/THF/MeOH species, which for the S-containing compounds of the sample Asp-2 extend to carbon numbers beyond 40, suggesting a higher content of carbon atoms in the alkyl side chains.

All samples (and fractions) contain vanadium, but porphyrins were detected only in the whole samples and the acetone fractions. For instance, the Tol/THF/MeOH Asp-2 fraction, with similar concentration of vanadium than whole asphaltene, displayed no porphyrin mass spectral peaks compared to whole asphaltenes which reveal some. Previous reports demonstrate that the Tol/THF/MeOH fractions from several asphaltene samples have a stronger precipitation tendency when titrated with heptane.²² We hypothesize that the stronger aggregation tendency of the Tol/THF/MeOH fractions is responsible for the lack of MS detection of vanadyl porphyrins. It is likely that porphyrin species are locked into asphaltene nanoaggregates and thus are not detected in the mass range to which the ICR cell is tuned ("monomeric"/ nonaggregated ions, $m/z \sim 100-1200$ g/mol).

Gas-phase fragmentation studies conducted for the extrography fractions indicate that the acetone and Hep/Tol fractions for both samples contain abundant single-core motifs (or island), whereas the Tol/THF/MeOH fractions reveal a significant amount of multicore (or archipelago) compounds. The results are summarized in Figures S1–3 of the Supporting Information.⁶³

The compositional range of S-containing compounds reveals abundant low-DBE species with higher content of CH₂ groups



Figure 3. Upper panel: Combined isoabundance contoured plots of DBE vs carbon number for HC-, N-/O-containing compounds (upper row), Scontaining species (middle row), and vanadyl porphyrins (lower row) for whole Asp-1 asphaltenes and extrography fractions. Lower panel: Gravimetric yields for extrography separation (gray bars) and monomer ion yield (red bars) or ionization efficiency as determined by APPI-MS.

(longer homologous series), in particular, for the most polar extrography fraction (Tol/THF/MeOH). Previous reports by Chacon-Patiño,²² Xu,^{49,64} Kilpatrick,^{65,66} and Stanford^{67,68} suggest the existence of asphaltene molecules with low aromaticity or low DBE but high heteroatom content. In particular, Xu et al. highlighted that "atypical" S-containing species with low aromaticity could be sulfoxides (R-S=O), which can participate in hydrogen bonding.⁶³ Therefore, heteroatom-based intermolecular forces, such as hydrogen bonding and acid/base interactions, likely dominate the aggregation/solubility behavior of atypical low-DBE compounds that are abundant in the Tol/THF/MeOH extrography fraction, which exhibits, as discussed below, the strongest deposition trends and the most irregular aggregate microstructure. This hypothesis seems to be consistent with the aggregation model proposed by Gray¹⁴ and Yarranton et al.¹³

GPC ICP HR MS Analysis of Both Samples and **Extrography Subfractions.** Figure 5 (sample Asp-1) and Figure 6 (sample Asp-2) show the S and V chromatograms of the whole asphaltene samples and their extrography fractions. The chromatograms of the extrography fractions clearly show that the acetone fraction has a completely different hydrodynamic volume than the two other fractions. The acetone fraction elutes primarily in the MMW and LMW region of the chromatogram. Conversely, the Hep/Tol and Tol/THF/ MeOH fractions are both eluted in the HMW region. The results indicate that the reconstructed chromatogram based on the summed chromatograms of each fraction for both elements (S and V) is different than the one for the whole sample, suggesting that the extrography separation partially disrupts the nanoaggregation behavior of the original asphaltene solution, as previous softer fractionation, by liquid-liquid extraction, has



Figure 4. Upper panel: Combined isoabundance contoured plots of DBE vs carbon number for HC-, N-/O-containing compounds (upper row), Scontaining species (middle row), and vanadyl porphyrins (lower row) for whole Asp-2 asphaltenes and extrography fractions. Lower panel: Gravimetric yields for extrography separation (gray bars) and monomer ion yield (red bars) or ionization efficiency as determined by APPI-MS.

shown that the reconstructed chromatogram was similar to the original asphaltene. 69

Figure 7 shows a comparison of the S and V chromatograms obtained for each sample and subfraction. Both whole asphaltene samples have a similar S chromatogram, but analyses of the extrography fractions suggest that there are more S-containing compounds in the Asp-2 Tol/THF/MeOH fraction than in the Asp-1 fraction. The behavior is the opposite for the Hep/Tol and acetone fractions. For the GPC profile, all members of the families of both samples have the same S chromatographic profile. The V chromatograms show behavior similar to that of S, except for the acetone fraction, where the MMW V nanoaggregate appears in Asp-1 and more LMW compounds appear in Asp-2.

Quartz Crystal Resonator (QCR) Sensor Analysis of Both Samples and Extrography Fractions. Destabilization of whole asphaltenes and their extrography fractions in toluene was achieved using *n*-heptane as a destabilizing agent (titrant). The flocculation and deposition processes were followed using a QCR sensor. The frequency shift (Δf) signals shown in Figures 8 and 9a exhibit a smooth increase during the entire titration for a nonflocculating system (pure toluene) due to reduction of the viscosity-density product ($\eta\rho$) by the addition of *n*-heptane. This behavior is also observed for the whole asphaltene and fraction samples at a low weight% of *n*heptane (wt %) in which the flocculation process has not yet begun. A progressive reduction of the signal is observed as the unstable compounds in solution are destabilized and flocculation begins, followed by an abrupt change in the slope (negative) due to the aggregation process. Ultimately, the changes in slope become less negative, indicating the end pubs.acs.org/EF

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Figure 5. Sample Asp-1 and its extrography fractions—GPC ICP MS of ³²S and ⁵¹V and reconstructed chromatogram.



Figure 6. Sample Asp-2 and its extrography fractions—GPC ICP MS of ³²S and ⁵¹V and reconstructed chromatogram.

of the aggregation process (clear for Tol/THF/MeOH fraction).

Once the destabilization begins, the aggregation process occurs more rapidly for the whole asphaltenes, Tol/THF/ MeOH and Hep/Tol fractions (from both samples), than it does for the acetone fraction. The Tol/THF/MeOH fraction is the one that destabilizes more rapidly, as expected and as previously discussed, and the Hep/Tol fraction is the one that destabilizes last. In Figures 8 and 9b, deposition onto quartz is shown as Δm . Both figures highlight that the acetone fraction tends to adsorb less on the quartz surface compared with the other fractions. Interestingly, the Asp-2 Tol/THF/MeOH fraction presents a maximum near 68 wt % of composition, and then a "decrease" of the deposit is observed. Rather than a desorption process, this diminution could be attributed to a slippage effect of the deposit on the quartz surface. This

slippage causes a positive frequency shift, which represents a "negative mass" loading, causing an underestimation of the Δm value. ^{54,70–72}

Figure 10 shows the destabilization onset and mass deposit values for all samples, when the system reaches a mass composition of 80% heptane added. If we compare the behavior between samples with similar chemistries, (i.e., whole/whole; acetone/acetone, etc.) the phenomenon observed in the solution is contrary to the one observed in the quartz surface: the sample that requires greater volume for destabilization generates less deposit. This occurs for both asphaltenes and their corresponding fractions. It is also clear that the difference in stability between both whole asphaltene samples can be related with the difference in content of both less stable (Tol/THF/MeOH) and most stable (HepTol) fractions. In other words, Asp-2 which destabilizes first



Figure 7. Sample Asp-1 (solid line) and Asp-2 (dotted line) and their extrography fraction—GPC ICP MS of ³²S and ⁵¹V.



Figure 8. QCR titration curves for Asp-1 samples. (a) Frequency shifts (Δf) of the third harmonic and (b) deposited mass (Δm) on the quartz surface vs composition of *n*-heptane.

contains a higher amount of Tol/THF/MeOH (46 wt %) than Asp-1 (25 wt %) and a lesser amount of HepTol (29 wt % vs 46 wt %).

AFM Images of QCR Coupon after Asphaltene Deposit. Representative height images $(1 \times 1 \ \mu m^2)$ of the deposit formed on the coupon gold surface at the end of QCR titration experiments are presented in Figure 11. These images visualize the "macrostructural" differences between deposits formed for each fraction. The whole asphaltene, Tol/THF/ MeOH, and Hep/Tol fractions of both samples displayed a layer of aggregates of irregular shapes, whereas both acetone fractions presented an organized structure of aggregates. The size of the aggregates varied in accordance with the amount of deposit estimated by the QCR experiments. The Asp-1 Tol/THF/MeOH fraction presented the largest aggregates ($\emptyset \sim 120$ nm), and both acetone fractions presented the smallest

aggregates ($\phi \sim 50$ nm). A difference was observed between the distribution of the aggregates for the Hep/Tol fraction; Hep/Tol fraction from Asp-1 is distributed in an irregular way, while the Asp-2 Hep/Tol fraction is distributed in a more homogeneous way.

DISCUSSION

Fractionation by Extrography. All of the analytical techniques used (AFM, FT ICR MS, GPC ICP MS) show that extrography fractionation allows asphaltene separation into fractions with similar behavior (e.g., both acetone fractions have similar composition, GPC elution); thus, they likely comprise nanoaggregates with similar size and chemistry. For QCR, although the destabilization onsets for the two whole asphaltene samples are different, after extrography fractions for the flocculation behaviors of Asp-1/Asp-2 extrography fractions



Figure 9. QCR titration curves for Asp-2 samples. (a) Frequency shifts (Δf) of the third harmonic and (b) deposited mass (Δm) on the quartz surface vs composition of *n*-heptane.



Figure 10. Destabilization onset (left) and deposited mass on the quartz surface at 80 wt % of *n*-heptane (right) comparison between Asp-1 (orange bars) and Asp-2 (red bars) whole asphaltenes and corresponding fractions.



Figure 11. AFM micrographs $(1 \times 1 \ \mu m^2)$ of the deposit formed on the gold surface at 80 wt % of *n*-heptane.

are similar. For the deposited mass, the acetone fraction revealed the same trend for both samples, whereas Tol/THF/ MeOH and HepTol fractions exhibited different deposited masses. Collectively, the results show that the acetone fraction from both samples, enriched with island-type structural motifs (FT ICR MS characterization), feature the same behavior for nanoaggregation (GPC) and macroaggregation (QCR). The macroaggregation is spatially well-organized (AFM), and this well-organized molecular layer emphasizes that the main interaction between each molecule might be π stacking



Figure 12. Derivation of the deposited mass $(d\Delta m)$ on the quartz surface vs composition for Asp-1 (left) and Asp-2 (right) whole asphaltenes and fractions.

between the aromatic cores. The size of these macroaggregates is the smallest (near 50 nm) of all fractions, consistent with the elution behavior of the acetone fractions in GPC. Conversely, the Hep/Tol and Tol/THF/MeOH fractions have larger nanoaggregates (GPC) and macroaggregates (AFM). As expected for the Hep/Tol fraction of Asp-2, the macroaggregates are less spatially organized, suggesting that aggregation is less driven by $\pi-\pi$ interaction, and it is more consistent with a supramolecular network similar to the structures hypothesized by Gray et al.¹⁴

In Figure 12, the plot (derivation of the deposited mass $(d\Delta m)$ on the quartz surface vs composition in heptane) discriminates clearly between the aggregate growing in size versus the aggregate growing in number in the solution. The acetone and Hep/Tol fractions, which contain abundant island molecules (FT-ICR MS characterization), tend to deposit less material than Tol/THF/MeOH (with more archipelago content) in both samples. In this fraction, heptane titration induces larger aggregates that progressively increase in size. The acetone fractions produce highly organized/regular macroaggregates with similar and smaller sizes than the other extrography fractions.

Thus, it appears that asphaltene precipitation is strongly linked to the chemical composition of the molecules contained in the sample/fractions.

Properties of the Fraction-Link to the Crude Oil. The GPC results show that during the extrography process, a portion of the HMW compounds move to MMW and LMW. Because most of the MMW and LMW molecules are contained in the acetone fraction, we can assume that a subset of "island"type molecules are contained in the HMW nanoaggregates in the bulk samples and are found in the acetone fraction after extrography extraction. Thus, these results support the idea that asphaltene aggregation is highly heterogeneous and there may be cooperative effects between asphaltene fractions.¹⁴ The HMW portion of the GPC chromatogram is strongly linked to the deposited mass in the QCR sensor. For both asphaltenes, the AFM images of the deposit of the bulk asphaltenes are not as well structured as the image of the TOL/THF/MeOH fraction. It appears that macroaggregation (asphaltene destabilization) might be driven by the HMW nanoaggregate

and the presence of "archipelago"-type molecules in the samples.

Porphyrins in Fractions and Samples. Petroporphyrins that belong to the $N_4O_1V_1$ class were identified only in bulk samples and acetone fractions. As the GPC reconstructed chromatogram of V shows, a shift from HMW to MMW and LMW occurs during extrography; thus, we hypothesize that the $N_4O_1V_1$ porphyrins detected in the bulk sample are likely the ones identified in the acetone fraction. This result might indicate that porphyrins surround the nanoaggregate in the HMW portion of the chromatogram in bulk/whole samples. GPC ICP-MS analysis can detect a large amount of vanadium in the HMW region, but FT-ICR MS fails to detect any vanadyl porphyrins. This result might occur because of poor ionization efficiency for these HMW compounds and thus a notably low sensitivity for this trace compound.

CONCLUSION

A combination of chemical and physical characterization was applied to whole/unfractionated asphaltene samples and their extrography fractions to better understand the aggregation process. The results showed that the extrography extraction, which is linked to the polarity of the molecule/nanoaggregate adsorbed on silica, produces compound families with different behaviors in the aggregation process. The aggregation and deposition (QCR and AFM) of the samples during *n*-heptane titration are related to the structure (FT ICR MS) and size of the aggregates (GPC ICP HR-MS). The smallest and "island"type fraction (acetone) is the one that forms lesser deposit amounts with more organized structures, whereas the larger and "archipelago"-type fraction (Tol/THF/MeOH) is the one that produces a greater deposit amount with a less organized macrostructure. This multiscale characterization technique can be useful in understanding asphaltene behavior during precipitation processes on production facilities and catalysts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.0c02687.

Infrared Multiphoton Dissociation of the Acetone, Hep/ Tol, and Tol/THF/MeOH fractions of Asp-1 and Asp-2 (PDF)

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Notes

The authors declare no competing financial interest.

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