# Asphaltenes subfractions extracted from Brazilian vacuum residue: chemical characterization and stabilization of model Water-in-Oil (W/O) Emulsions

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## HIGHLIGHTS

- Three different asphaltenes fractions were obtained from a vacuum residue using different ratios of *n*-heptane/VR.
- Asphaltenes were analyzed by APPI-FT-ICR MS, UV-Vis spectroscopy and NMR.
- APPI(+)FT-ICR MS showed higher polarity for the 4:1 subfraction and higher aromaticity for the 10:1 subfraction.
- The 4:1 subfraction also presented the lowest onset of precipitation, i.e., lower solubility in n-heptane.
- Asphaltenes subfractions promoted a great stability in the produced emulsions.

**ABSTRACT**

Asphaltenes were obtained from a Brazilian vacuum residue (VR) by precipitation with different ratios of *n*-heptane/VR to have three subfractions of the asphaltene. The behavior of these different subfractions in the stability of water-in-oil (W/O) emulsions was evaluated. The whole asphaltene subfraction (AH) was obtained by addition 40:1volumes of *n*-heptane/VR followed by filtration. Two different asphaltene subfractions (A4 and A10) were obtained by precipitation with a successive increasing *n*-heptane/VR ratio, from 4:1 and 10:1, respectively. The properties of these precipitated subfractions of asphaltenes were analyzed by atmospheric pressure photoionization (APPI) coupled to Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) in a positive-ion mode, ultraviolet-visible (UV-Vis) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. The FT-ICR MS results showed that the 4:1 subfraction (A4) exhibited a profile with higher heteroatoms components, high polarity and molecular weight distribution ($M_w$). An inverse correlation was observed with respect to aromaticity degree and solubility in heptane/toluene solutions (onset point). The subfractions AH and A10 were more aromatic than the subfraction A4, being the results confirmed by $^1$H NMR analysis. Besides, asphaltenes subfractions promoted a great stability in the produced emulsions. The droplet size distribution and bottle test showed similar results for emulsion stability formed with the three different subfractions. After application of centrifugal forces, the formation of a dense packed layer emulsion was observed containing approximately 85% water that remained stable for 2 weeks.

**Keywords**: water-in-oil emulsion; asphaltene fractionation; dense packed layer; asphaltene onset; FT-ICRMS analysis.

## 1. Introduction

Asphaltenes are a complex mixtures of molecules, which consists of condensed aromatic rings with aliphatic side chains, heteroatoms such as N, O, S and metals such as Fe and V. (Dudásova *et al*., 2008; Speight, 2007). They are typically defined as the nonvolatile oil fraction, insoluble in n-alkanes, such as heptane, and soluble in aromatics solvents, such as toluene (Dudásova *et al*., 2008; Sjoblom *et al*., 2003; Speight, 2007). Asphaltenes have propensity to aggregate, and their tendency to self-associate depends on the aromaticity of the solvent, the thermodynamic conditions, such as temperature and/or pressure and the presence of co-solutes such as resins. Generally, their aggregate size increases as a function of the increase of the aliphatic solvent volume or due to the reduction of the pressure (Sjoblom *et al*., 2003). Asphaltenes are responsible for some problems in the petroleum industry, including precipitation and deposition during crude oil production, processing and transport (Sjoblom *et al*., 2015).

In the crude oil industry, water-in-oil (W/O) emulsions can be found in almost all processes of production and oil recovery. These emulsions increase the viscosity of the crude oil, and affect the flow operations, leading to enormous economic losses during the recovery, treatment, and transportation of crude oil. W/O emulsions are stabilized by several surface-active species usually found in the crude oil such as resins, asphaltenes, fine solids, organic acids and bases. Asphaltenes are commonly identified as compounds which have a higher tendency to migrate to the W/O interface introducing a barrier that prevents the droplets from coalescing, yielding high emulsion stability (Samaniuk *et al*., 2015; Yang *et al*., 2007).

A variety of standards procedures exist to precipitate asphaltenes from crude oil. The conventional method is first to precipitate the whole asphaltene fraction from

crude oil by adding excess of the *n*-heptane or *n*-pentane to crude oil (40 volumes of solvent to 1 volume of oil). Due to asphaltene complexity, whole asphaltene is often subfractionated aiming at a fine identification of its behavior. This fractionation process can be accomplished by different methods, including adsorption on solids (Nascimento *et al.*, 2016) and treatments with different solvents (Fossen *et al*., 2007b; Speight, 2007; Yang *et al*., 2004). Produced subfractions of asphaltenes may have different functionality, solubility and composition. The chemical and structural characterization of asphaltenes and subfractions are the key to understand their properties and their behavior (Castillo *et al*., 2015; Nalwaya *et al*., 1999; Trejo *et al.*, 2004).

Different analytical methods have been used to characterize asphaltenes and their subfractions, such as nuclear magnetic resonance (NMR) spectroscopy (Pereira et al., 2014b), infrared (IR) spectroscopy (Rogel *et al*., 2015), vapor-pressure osmometry (VPO) (Acevedo *et al.,* 2010) and ultraviolet-visible (UV-vis) spectroscopy (Nascimento *et al.,* 2016). Currently, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) is one of the few techniques that enable the analysis at the molecular level of complex mixtures such as asphaltenes and petroleum (Cho *et al.,* 2012). The ultra-high resolution and mass accuracy of the FT-ICR MScan define a unique elemental composition ($C_cH_hN_nO_oS_s$) and double bond equivalent (DBE), facilitating material classification by heteroatom content and degree of aromaticity (Pereira *et al*., 2014b).

Pereira *et al.*(2014b) analyzed Brazilian asphaltene sample using different ionization sources, such as electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), atmospheric pressure photoionization (APPI), laser desorption/ionization (LDI) and matrix-assisted laser desorption/ionization (MALDI)

to understanding the effects caused by the ionization parameters during the asphaltenes analysis. It was demonstrated that each source acquired a distinct chemical profile of compounds classes, revealing specific singularities of the sample. In addition to that, it was demonstrated that APCI and APPI accessed a wide range of compound classes, DBEs and carbon number distributions within the evaluated ionization sources (Pereira *et al*., 2014b).

In these study, we precipitated three asphaltenes fractions using a gradually increase of *n*-heptane/VR ratio (40:1, 4:1 and 10:1). The asphaltene fractions were characterized using APPI(+)FT-ICR MS. For each sample, relative abundance distributions of the heteroatom class, van Krevelen diagram and the graphical DBE *versus* carbon number images were generated. Based on the asphaltenes subfractions obtained by different toluene/*n*-heptane ratios, it was possible to determinate the solubility profile. The ability to stabilize W/O emulsion for the three different subfractions produced was analyzed through bottle test and droplet size distribution, and the results compared with the chemical properties of each subfraction.

## 2. Experimental

### 2.1 Materials

The vacuum residue (VR) used in this study was supplied by Petrobras (Presidente Getúlio Vargas Refinery - REPAR) and consists of an asphaltic residue formed during the vacuum distillation of a blend of 10 different crude oils. The *n*-heptane solvent applied in the asphaltene extraction (purity > 99.5%) was supplied by Sigma-Aldrich Chemicals Brazil (Rio de Janeiro-Brazil). Toluene (>98%) used in the APPI(+)FT-ICR MS analysis was purchased by Vetec®Química Fina Ltda (Rio de Janeiro-Brazil). All reagents were used as received.

## 2.2 Asphaltenes precipitation

The VR was submitted to an extraction procedure where whole asphaltene was precipitated by addition of *n*-heptane in a 40:1 solvent-to-VR ($cm^3/g$) ratio. Initially, VR was heated to $140^0C$ for at least 1hour and then stirred to provide homogenization. Subsequently, 4g of the VR were dissolved in 160 mL of *n*-heptane. This mixture was left on magnetic stirrer for 24 hours. After, the precipitate was recovered by vacuum filtration through a 0.45 μm filter (Unifil®) and washed with an excess of *n*-heptane, to remove the remaining soluble material. Then, the whole asphaltene, named AH, was dried in a desiccator at room temperature until the mass was invariant. The yield of this AH subfraction was 11.2 wt% (± 0.2).

Two other subfractions were obtained based in a procedure described by Fossen et al. (2007b), where asphaltenes were precipitated with a successive increase of *n*-heptane. Briefly, the first subfraction was obtained using a ratio of 4:1 *n*-heptane/VR (wt/wt). This mixture was shaken for 24 hours and the precipitated material, was then separated by vacuum filtration through a 0.45 μm filter and designated as A4, with a yield of 6.8wt% (± 0.4). The subfraction A10 was precipitated adding *n*-heptane to the supernatant of the first step and the *n*-heptane/VR ratio was adjusted to 10:1. This mixture was shaken for 24 hours and the precipitated material was then separated by vacuum filtration through a 0.45 μm filter, with a yield of 3.1 wt% (± 0.2). Both A4 and A10 were washed with an excess of hot *n*-heptane. The subfractions were dried in a desiccator at room temperature until the mass was invariant.

153 **2.3$^{1}$H nuclear magnetic resonance ($^{1}$H NMR)**

154 The degree of aromaticity of the VR and their asphaltenes subfractions were
155 obtained by $^{1}$H NMR analysis. $^{1}$H NMR experiments were performed on a Varian
156 VNMRS 400 spectrometer; operating at 9.4 T using 5 mm broadband $^{1}$H/X/D probe.
157 All experiments were performed at 25 $^{o}$C. The aromatic hydrogen content (%) was
158 determined through the integration of areas from 9.0 to 6.0 ppm regions, and aliphatic
159 hydrogen through the integration of areas 4.0 to 0.0 ppm regions (Da Silva de
160 Oliveira et al., 2014; Nascimento et al., 2016).

161

162 **2.4 APPI (+)-FT-ICR MS**

163 VR, AH and the subfractions (A4 and A10) were characterized by FT-ICR
164 MS. FT-ICR MS analyses were perfomed using a 9.4 T Q-FT-ICR MS hybrid
165 (Solarix, Bruker Daltonics, Bremem, Germany) equipped with commercially
166 available APPI source, set to operate over a mass region of *m/z* 200-1000. FT-ICR
167 mass spectra of VR, AH and subfractions (A4 and A10) were acquired using positive-
168 ion ionization mode for APPI, APPI(+). Briefly, all samples were diluted to
169 proximally 1 to 2 mg.mL$^{-1}$ in toluene. The solutions were then sonicated for 5 min to
170 ensure solubility. The resulting solutions were directly infused into the ionization
171 source at 10μL.min$^{-1}$.

172 The APPI(+) source conditions were as follows: nebulizer gas pressure of
173 2.0bar, capillary voltage of 2-3kV, transfer capillary temperature of 250$^{0}$C and
174 Krypton photoionization lamp. Ions were accumulated in a hexapole for 3.0s and
175 transferred to the ICR cell through the multipole ion guide system (another hexapole).
176 Each spectrum was acquired using 200 scans of time-domain transient signals in 4
177 mega-point time domain data sets. The front and back trapping voltages in the ICR

cell were +0.85V for APPI(+). All mass spectra were externally calibrated using a NaTFA solution (*m/z* from 200 to 1200) after they were internally recalibrated using a set of the most abundant homologous alkylated compounds for each sample (Pereira *et al*., 2014a; Pereira *et al.,* 2014b).

The mass spectra were acquired and processed using a custom algorithm developed specifically for petroleum data processing, Composer *software* (Sierra Analytics, Modesto, CA, USA). The heteroatomic containing compounds, Van Krevelen (1950) diagrams and DBE versus carbon number (CN) were constructed (Kendrick, 1963). DBEs represent the number of rings plus the double bonds involving carbon, and can be calculated by the following **equation 1**:

$$\mathrm{DBE} = \mathrm{c} - \frac{\mathrm{h}}{2} + \frac{\mathrm{n}}{2} + 1 \quad \textbf{(eq. 1)}$$

Where c, h, and n are the numbers of carbon, hydrogen, and nitrogen atoms, respectively, in the molecular formula.

## 2.5 Onset of Precipitation of asphaltenes subfractions in Heptane/Toluene mixtures

A serie of asphaltene subfraction/toluene solutions with a concentration of 5% wt/v were prepared. The solutions were homogenized in a shaker for 24 hours and left on a sonic bath for 15 min. For each solution, a known amount was sampled (1mL) and mixed with *n*-heptane/toluene solutions (9 mL heptol) with different heptane to toluene ratios (0:100, 10:90, 20:80, 30: 70, 40:60, 50:50, 60:40, 70:30, 80:20 and 90:10 heptol), reaching a final concentration of asphaltene in each centrifuge tube of 0.5wt%. These samples were shaken for 24 hours, followed by centrifugation at 3000 rpm for 30 min. The onset of precipitation of asphaltenes subfractions was obtained using a Varian Cary 50 ultraviolet visible spectrometer at wavelength of 875nm

(Loureiro *et al.,* 2015).

**2.6 Emulsion stability test**

Model emulsions using asphaltenes subfractions dispersed in heptol were prepared to examine the influence of these different subfractions in the stability of emulsions. Mixtures of 60:40 heptol containing 0.5% of asphaltene subfraction (wt/v) were used as model oils. The aqueous phase was prepared with $50gL^{-1}$NaCl in deionized water. Equal volume of oil phase and aqueous phase were emulsified using Polytron homogenizer (PT 3100D) at 18000 rpm for 3 min. The emulsions obtained were placed in 15 mL centrifuge tubes and monitored using the bottle test method for 24 h at room temperature ($22\ ^{0}C \pm 2\ ^{0}C$). After, the emulsions were then centrifuged at 5000 rpm for 15 min to separate the free oil phase from the remaining emulsion phase, with this latter one looking dense and opaque, suggesting the formation of a dense packed layer (DPL). Aliquots of the free oil phase were sent for asphaltene content characterization as analyzed by UV-VIS spectrum and the emulsified phase(the so-called DPL) was analyzed at the Karl Fischer.

**2.7 Emulsion characterizations**

Emulsion properties such as droplet size distribution (DSD), water content and asphaltene content were characterized before and after each stability test. The droplet size distribution was measured by optical microscopy analysis using an inverter microscope Zeiss Observer D1 (Zeiss Vision GmbH, Germany) set to 1600X and a camera attached to the microscope was used to capture images. The images were processed in Axio Vision software. The stable emulsions were analyzed at room temperature after 24 h under the influence of gravity. The DSD analysis was

performed on three different micrographs, and at least 300 droplets were counted for obtaining the average droplet diameter.

A Karl Fisher volumetric titrator KEM-EBU, model KF-610 - Automatic Potentiometric Titrator AT-510 was used to measure the water content in the emulsions formed after centrifugation process, according to ASTM D 1744. Water content was reported as a weight percentage.

Asphaltene contents in the free oil phase obtained after centrifugation were analyzed by UV spectroscopy performed with the spectrophotometer Shimadzu Corporation in a wavelength of 336 nm (Kelesogluet al., 2014). Prior to measurement, calibration curves were constructed by preparing a series of asphaltenes in 9 ml of toluene and 1 ml of 60:40 heptol solutions, with concentration ranging from 0.01 $g.L^{-1}$ to 0.06 $g.L^{-1}$. The free oil phase was then diluted in toluene to match the calibration curve range. The concentration of asphaltenes was then calculated by evaluating the absorbance at $\lambda$= 336 nm.

## 3. Results and discussion

### 3.1 $^{1}$H NMR analysis

The VR and all subfractions of asphaltenes (AH, A4 and A10) were characterized by $^{1}$H NMR spectroscopy, where the results are described in **Table 1**. The NMR results show lower aromatic hydrogen content ($H_{ar}$) for the VR sample, whereas for the asphaltenes subfractions, higher and similar $H_{ar}$ values are reported. Note that a slight increase in the values of $H_{ar}$ is observed from subfraction A4 to A10, with this latter exhibiting a more aromatic profile.

253 **Table 1**.[1]H NMR analysis of vacuum residue (VR) and its asphaltenes subfractions.

| Samples | Chemical shift (ppm) | |
|---|---|---|
| | (%mol) $H_{ar}$ (6.0-9.0) | (%mol) $H_{alk}$ (0.5 -4.0) |
| VR | 5.9 | 94.1 |
| AH | 10.4 | 89.6 |
| A4 | 10.3 | 89.7 |
| A10 | 10.6 | 89.4 |

254

255 **3.2 APPI(+)FT-ICR MS**

256 **Figure 1**shows the APPI(+)FT-ICR mass spectra of the VR sample and its
257 asphaltenes subfractions (AH, A4 and A10). The FT-ICR mass spectra show broad
258 band profiles from *m/z* 200-650, with average molar distribution ($M_w$) centered at
259 approximately *m/z*412, 431, 511 and 428 for VR, AH, A4 and A10, respectively. $M_w$
260 values increases in the following order for the subfractions: A10 < AH <A4. For the
261 subfraction AH (**Figure 1b**), a broader range mass profile and a shift toward larger
262 *m/z* values is observed when compared to sample VR. For the other two subfractions
263 (A4 and A10) (**Figure 1**, **c** and **d**) a shift toward larger *m/z* values are also observed.
264 The higher $M_w$ presented by A4 subfraction (**Figure 1c**) could be due to higher
265 proportion of VR added to solvent (ratio of 4:1 *n*-heptane/ RV (wt/wt). This favors at
266 a higher abundance of heavier components that were accumulated in precipitated
267 subfraction. Other studies have reported $M_w$ values similar to the ones showed in
268 work. Nascimento *et al.*(2016) precipitated, by adsorption onto silica particles, three
269 different subfractions from Brazilian light oil and analyzed by APPI(+)FT-ICR MS.
270 The subfractions showed $M_w$ values lower than 600 Da. Pereira *at el.*(2014a)
271 characterized asphaltenes precipitated from three different Brazilian crude oil in *n*-
272 heptane using APPI(+) FT-ICR MS. The three different subfractions also showed
273 $M_w$< 600 Da.

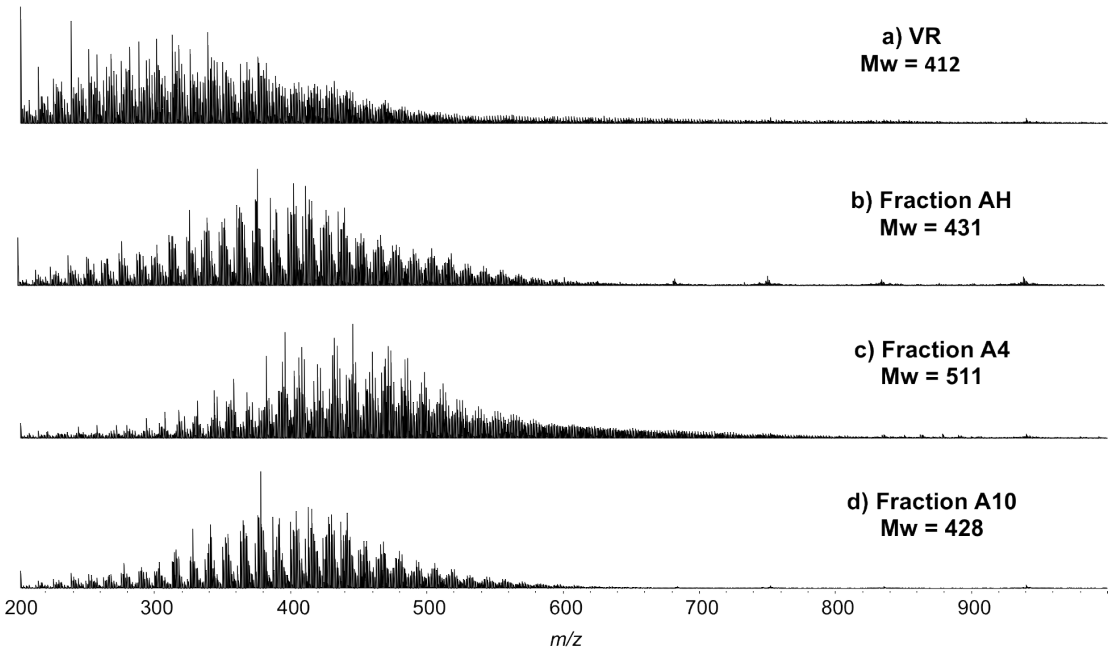



**Figure 1.** APPI(+)FT-ICR mass spectra of vacuum residue and the its asphaltene subfractions.

**Figure 2**shows the polar and nonpolar compounds class distribution of VR sample (**Figure 2a**) and its asphaltenes subfractions (**Figure 2b**). For the VR sample (**Figure 2a**), a higher abundance of N[H] compounds is observed, following by HC[H], N, and HC classes. On the other hand, asphaltenes subfractions (**Figure 2b**) exhibit a higher variety of highly polar compounds classes ($N_2$, $N_2$[H], NO[H] and $NO_2$[H]), which in turn represents a behavior expected for a typical asphaltene sample. Among the asphaltene subfractions, the sample A4 presents the highest concentration of polar compound species, thus suggesting that this subfraction is the most polar.

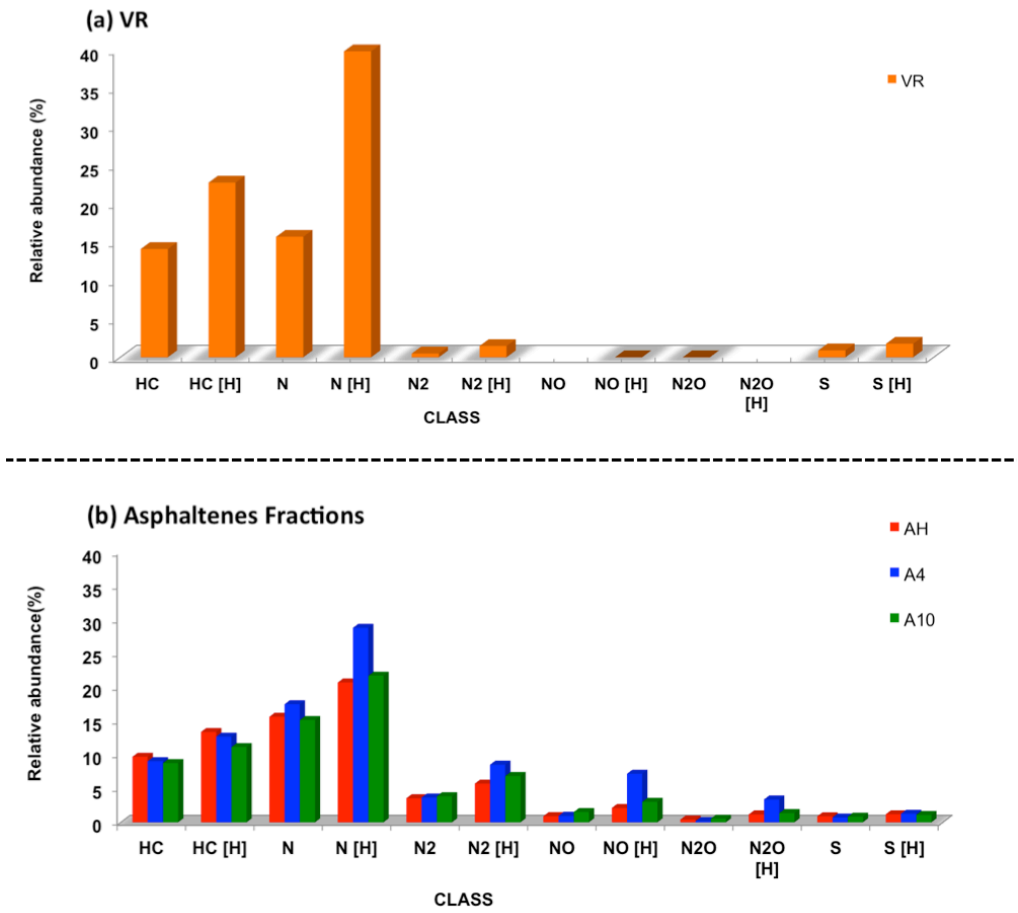



**Figure 2**. Class distribution generated from APPI(+)FT-ICR MS data for (**a**) VR sample and its (**b**)asphaltene subfractions.

The DBE relative abundance distributions of HC, HC[H], N and N[H] classes for the VR sample and its asphaltenes subfractions (AH, A4 and A10) are shown in **Figure 3(a-d)**. DBE distribution for asphaltenes subfractions shows a progressive shifting to higher DBE value when compared to VR, as seen in **Figure 3a-d**. Furthermore, DBE distribution ranges from 12 to 34 for all asphaltene subfractions and shows a maximum abundance of DBE centered on average at 26 for HC and HC[H] classes and 23 for N and N[H] classes. For the protonated classes (HC [H] and N[H]) (**Figure 3b** and **d**), it is more evident that the subfraction A4 presents a less

aromatic profile than other subfractions (AH and A10), corroborating with the $^{1}H$ NMR analysis (**Table 1**).

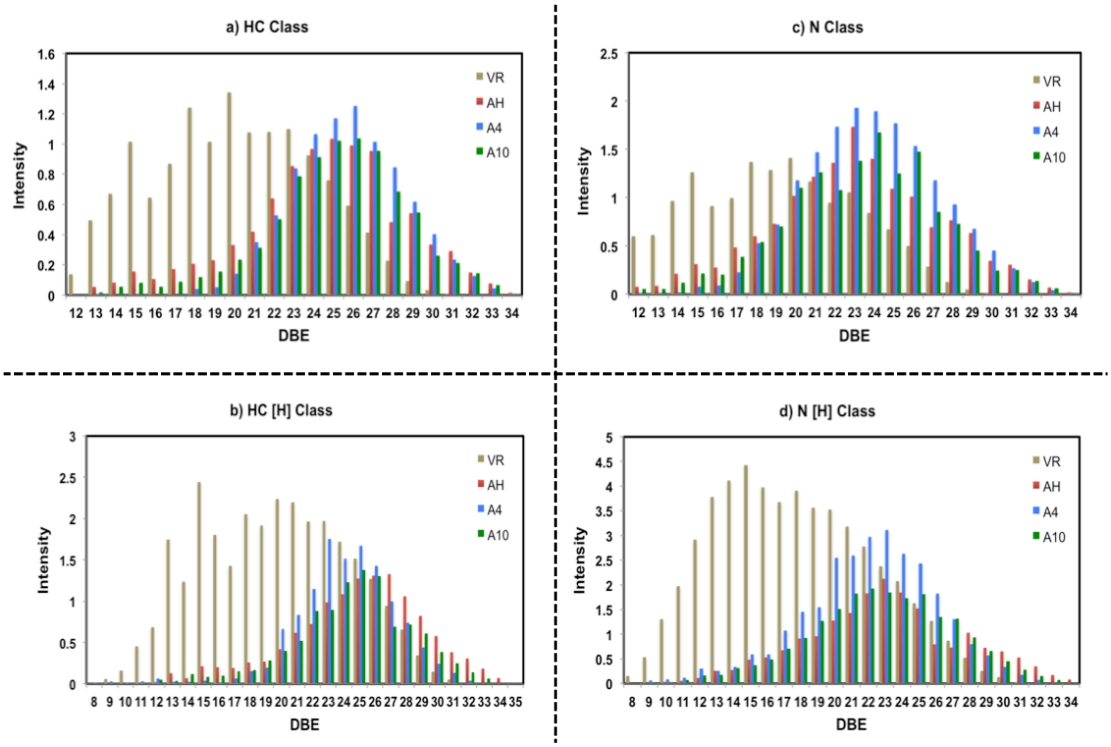



**Figure 3.** DBE relative abundance distribution for the **(a)** HC, **(b)** HC[H], **(c)** N and**(d)** N[H] classes for VR sample, and its asphaltene subfractions (AH, A4 and A10).

**Figures 4** and **5** show the DBE *versus* carbon number (CN) plots for the most abundance classes of radical and protonated molecules detected, HC and HC[H] classes (**Figure 4**) and N and N[H] classes (**Figure 5**), respectively. Structural interpretation is possible by the concept of planar slopes, which are defined as lines that connect maximum observed DBE values with specific carbon numbers. The slopes of these lines were calculated by linear regression, where the increase of slope of line is proportional to the increase in the $H_{ar}$ values, giving the possibility to extract the aromaticity degree for each sample (Pereira et al., 2014a).

**Figure 4a-f** exposes the DBE *versus* CN for HC and HC[H] classes of subfractions AH (**4a-d**), A4 (**4b-e**) and A10 (**4c-f**). A wider polyaromatic compounds

distribution is observed for subfraction AH, with DBE and CN ranging from 10 to 35 and $C_{10}$ to $C_{50}$, respectively. For subfraction A4, a shorter DBE and CN distribution is observed (DBE = 18-32 and CN of $C_{25}$-$C_{52}$). The slopes decrease in the following order: subfraction AH ~ subfraction A10 > subfraction A4, indicating that the subfraction A4 has a higher aliphatic character compared to the other asphaltenes.

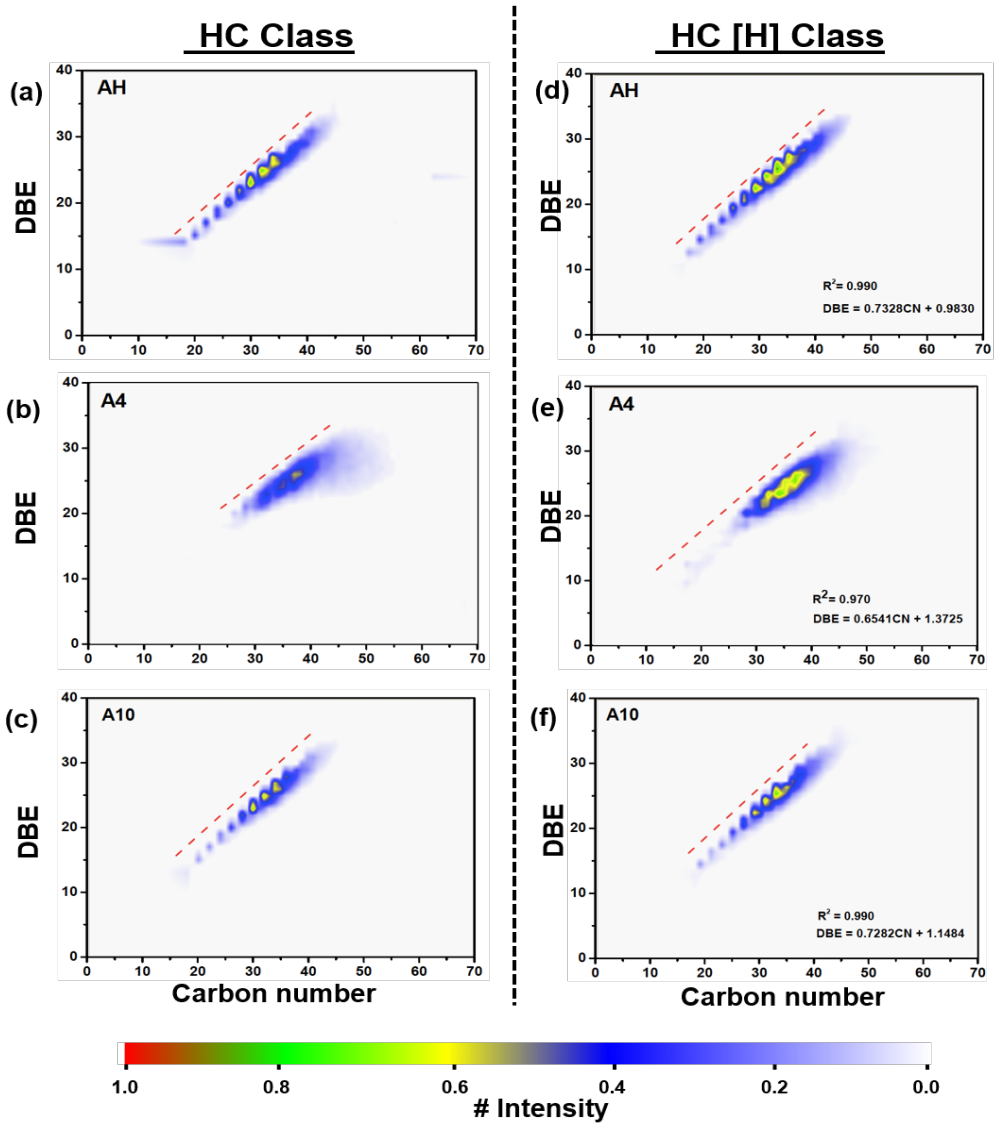



**Figure 4**. DBE *versus* carbon number plots for HC and HC[H] classes for asphaltenes subfractions AH **(a-d)**, A4 **(b-e)** and A10 **(c-f)**.

For the N and N[H] classes (**Figure 5a-f**), the asphaltenes subfraction samples exhibit a higher amplitude of distribution of DBE and CN values, ranging from 10 to

35 and from $C_{15}$to $C_{50}$. Similar to **Figure 4**, an increasing of the inclination of the planar line of DBE *versus* CN plot obeys the following order: subfraction AH >subfraction A10 >subfraction A4. Note that a higher population of nitrogenated compounds and low aromaticity is observed for subfraction A4, **Figures 5b-e**.

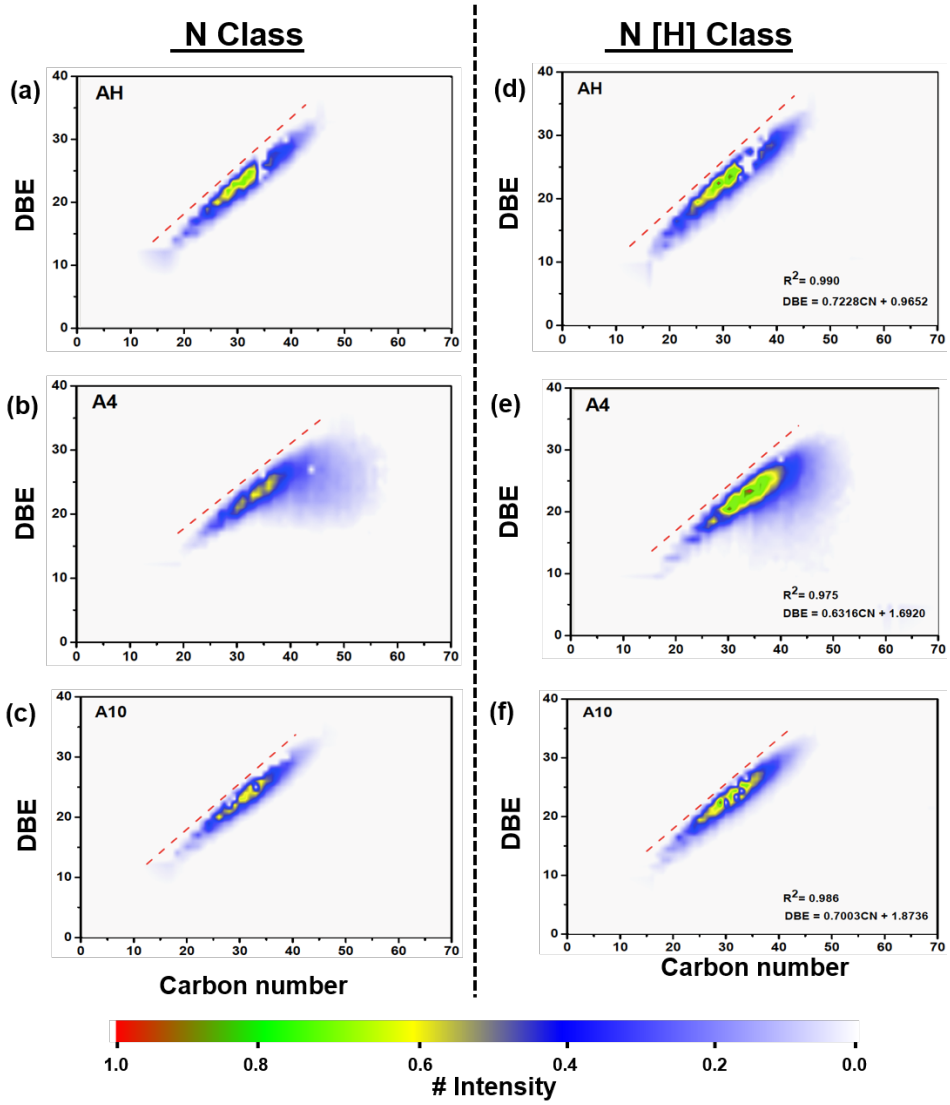



**Figure 5**. DBE *versus* carbon number plots for N and N[H] classes for asphaltenes subfractions (AH, A4 and A10).

The van Krevelen diagrams consist of iso-abundance contours as function of H/C ratio and N/C ratio for each compound containing those atoms (Klein et al.,

2006a). The van Krevelen allows a convenient visual separation of heteroatom class, DBE (type) and alkylation pattern (Klein et al., 2006b).

**Figure 6a-f** illustrates the $N_x$ and $N_xO_y$ profile classes of asphaltenes subfractions. The subfraction A4 (**Figure 6b**) exhibits a greater amplitude compounds at the H/C ratio varying from 0.5 to 1.7, with maximum centered at 0.7 for the $N_x$ profile classes. Whereas, the subfractions AH (**Figure 6a**) and A10 (**Figure 6c**) show a lower amplitude of compounds detected, with H/C ratio from 0.3 to 1.0, with maximum centered at 0.5. When the H/C ratio decreases, the number of rings plus double bonds increase, proving that the higher aromatic character is present in subfractions AH and A10 (Klein et al., 2006b).

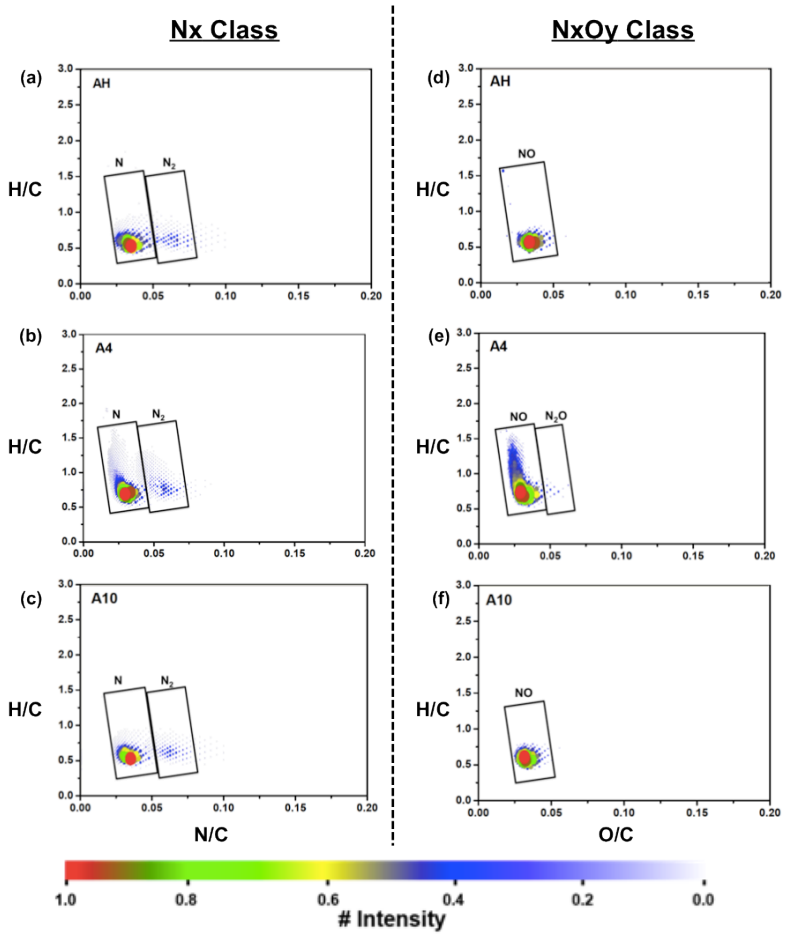



**Figure 6.** van Krevelen diagrams for $N_x$ and $N_xO_y$ containing species generated from APPI(+)FT-ICR MS data of asphaltene subfractions.

352 The $N_xO_y$ profile classes (**Figure 6d-f**) present similar behavior in relation to
353 data of **Figure 6a-c**. Subfraction A4 (**Figure 6e**) exhibits again greater amplitude of
354 compounds (H/C ratio varying from 0.5 to 1.5, with maximum centered at 0,7) when
355 compared with the other (subfractions AH and A10). The last two subfractions
356 (**Figure 6d** and **f**) show lower amplitude of $N_xO_y$ compounds, with H/C ratio from 0.3
357 to 0.7, with maximum centered at 0.5). Therefore, the FT-ICR MS data are in
358 agreement with the $^1$H NMR analysis (**Table 1**).
359
360 **3.3 Asphaltene precipitation onset results**
361 The onset point was obtained through the ultraviolet-visible (UV-Vis) and the
362 results are shown in **Figure 7**. Note that the absorbance values remain constant until
363 the 40:60 ratio of *n*-heptane/toluene for subfraction A4 and 50:50 for subfractions AH
364 and A10. After these ratios, it can be observed a decrease in absorbance values,
365 indicating a reduction on asphaltene concentration in the solution. The point in which
366 the absorbance began to decrease indicates the onset of precipitation of asphaltenes.
367 For the subfractions AH and A10, the precipitation onset occurred in the 60:40 ratio
368 of *n*-heptane/toluene. For the subfraction A4, the onset happened in the ratio 50:50 of
369 *n*-heptane/toluene. These data indicate that subfraction A4 is the least soluble of all
370 the subfractions. Spiecker *et. al.*(2003) studied the solubility of the asphaltenes
371 fractions in the *n*-heptane/toluene mixtures to four different oils, similar results were
372 presented, where the most polar fractions had low solubility.
373

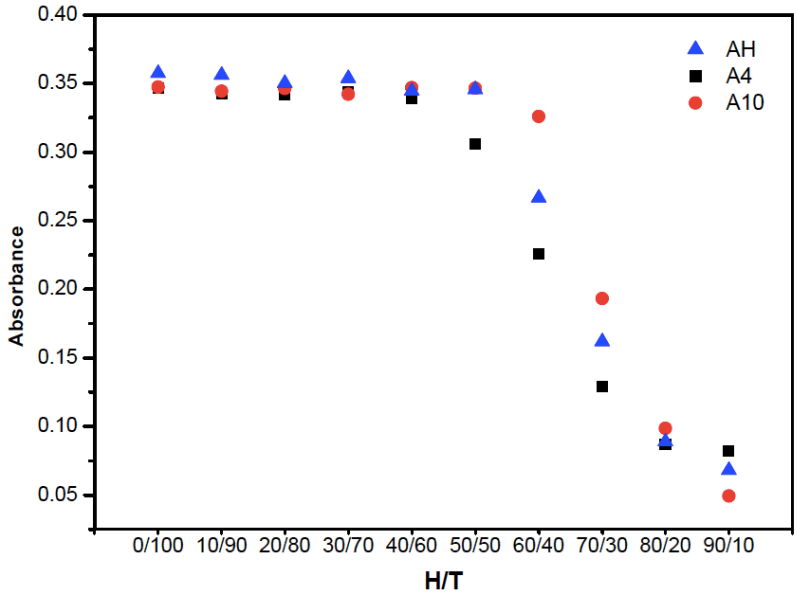
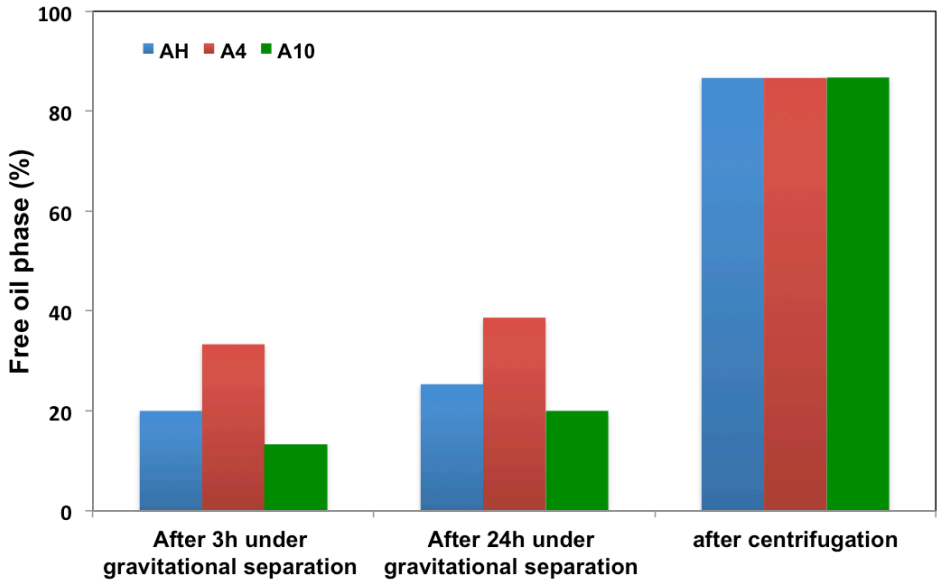



**Figure 7**. Onset of precipitation results for asphaltene subfractions AH, A4 and A10 into heptol.

### 3.4 Emulsion Stability

Emulsions were prepared with a 60:40 ratio of heptane/toluene because this heptol composition is beyond the precipitation onset point for all subfractions. A water percentage of 50% was selected to obtain a sufficient volume of emulsion.

The stability of asphaltenes emulsions was evaluated through the water and oil resolution during 24h under gravitational forces. **Figure 8** shows the separation phase evolutions. After 3h under gravitational separation, a free oil layer was observed at the top of the centrifugation tube for all emulsions. However, the free oil amount of the emulsion synthesized with subfraction A10 was smaller, showing that this subfraction has been more efficient in stabilizing emulsions (Zaki *et al*., 2000). In the period from 3h up to 24 h, all emulsions remained stable, no distinguishable water phase was observed and free oil phase remained practically the same.




391

392 **Figure 8**. Phase separation evolution of model water-in-oil emulsions involving
393 subfractions AH, A4 and A10.

394

395 After gravitational separation, to accelerate the process of destabilization, the
396 emulsions were centrifuged at 5000rpm for 15 min. **Figure 9** shows the image of the
397 system after centrifugation. The centrifugal forces were insufficient to separate the
398 water in the emulsions containing the asphaltenes subfractions AH, A4 and A10. On
399 the other hand, the separated oil phase increased significantly. It can be observed that
400 the droplets settled forming a dense packed layer. The DLPs formation can reduce the
401 emulsion separation efficiency (Kelesoglu *et al*., 2014) because portions of the oil
402 remain dissolved in the aqueous phase. All the DLPs formed remained stable for more
403 than 2 weeks.

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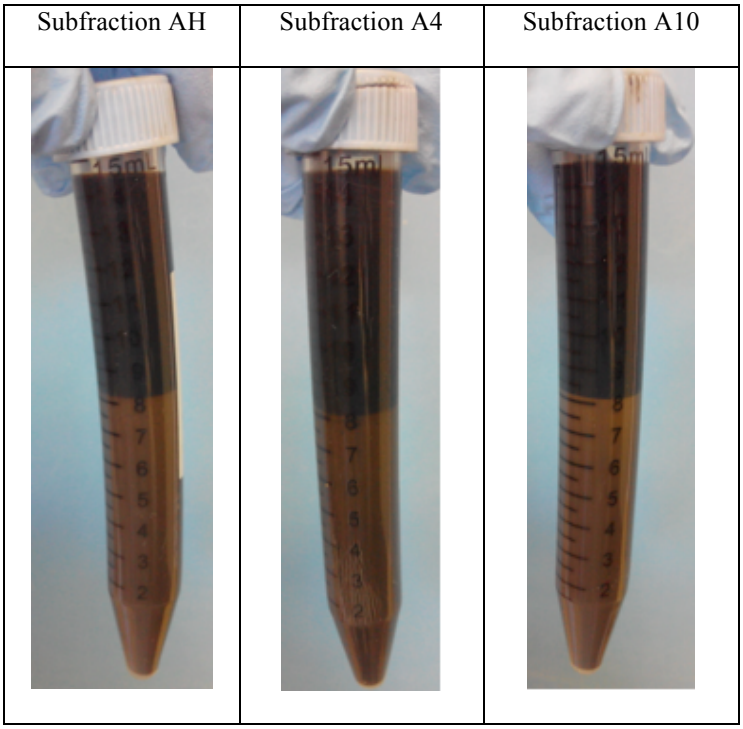
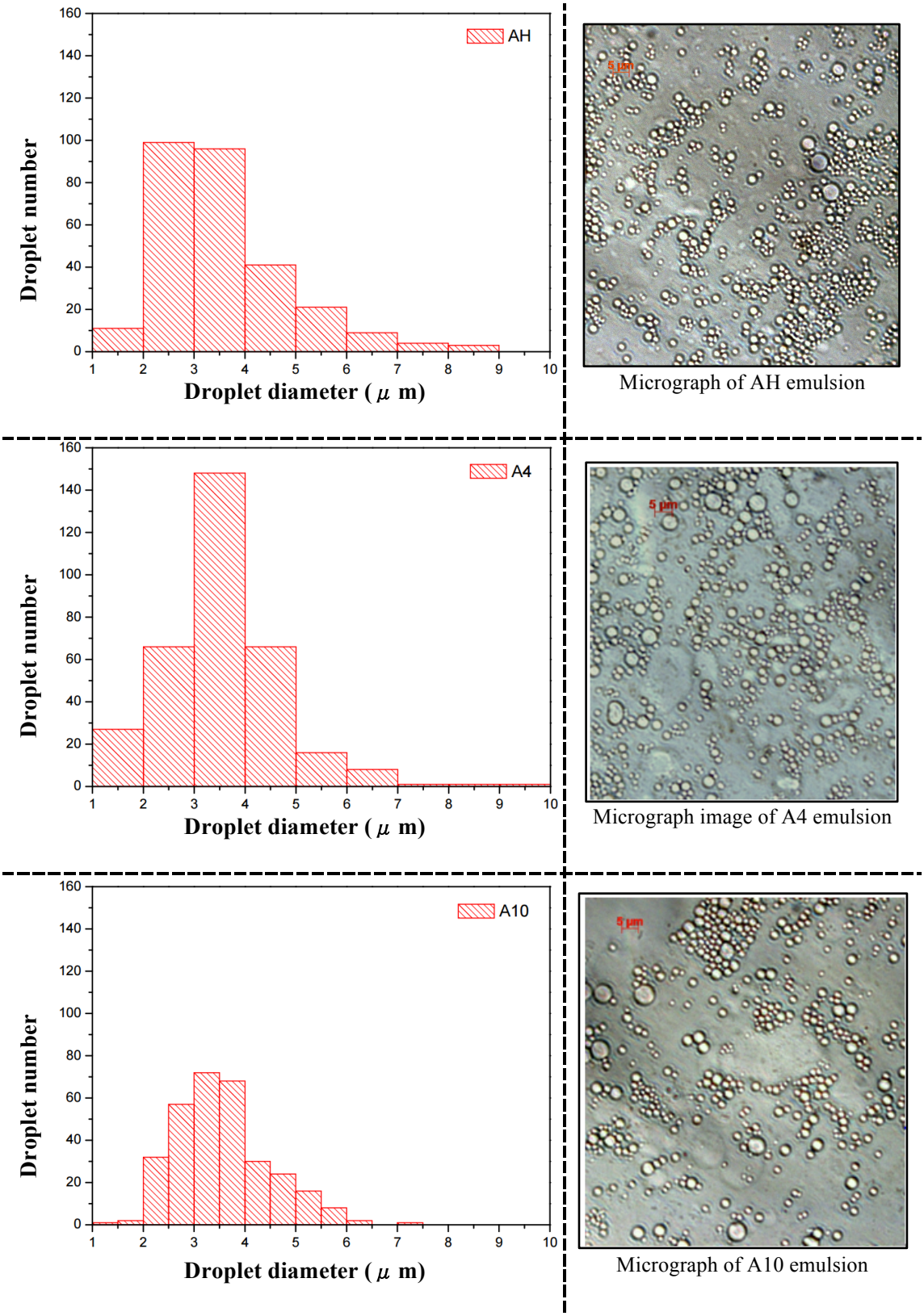



**Figure 9**. Centrifugation results of model water-in-oil emulsions involving subfractions AH, A4 and A10.

**Figure 10** shows the droplet size distribution generated from the micrographs obtained 24 h after the emulsification using an inverted microscopy. The droplet sizes varied between 2 μm and 6 μm for all samples. However, the droplets of the emulsions stabilized with the subfractions AH and A10 had value well distributed on this range and droplets in the emulsion stabilized with the A4 subfraction had diameters more concentrated in the range 3–4 $\mu$m. The average droplet size were very similar, approximately d = 3.27μm to subfraction AH; d = 3.52 μm to subfraction A4 and d = 3.49 to subfraction A10.




420 **Figure 10**. Histograms of the droplet size distribution generated through of the
421 micrographs obtained 24 h after the emulsification using an inverted microscopy.
422

**Figure 11** shows the calibration curve of solutions of the subfraction AH, subfraction A4 and subfraction A10 in toluene at concentrations ranging from 0.01 to 0.06 $g.L^{-1}$, for which UV-visible calibration curves were built at 336nm. It is possible to observe a perfect linear dependence of absorbance with concentration. Based on the linear regression of the absorbance-concentration data for each subfraction, it was possible to evaluate the final concentration of the asphaltene subfractions adsorbed on DLP.

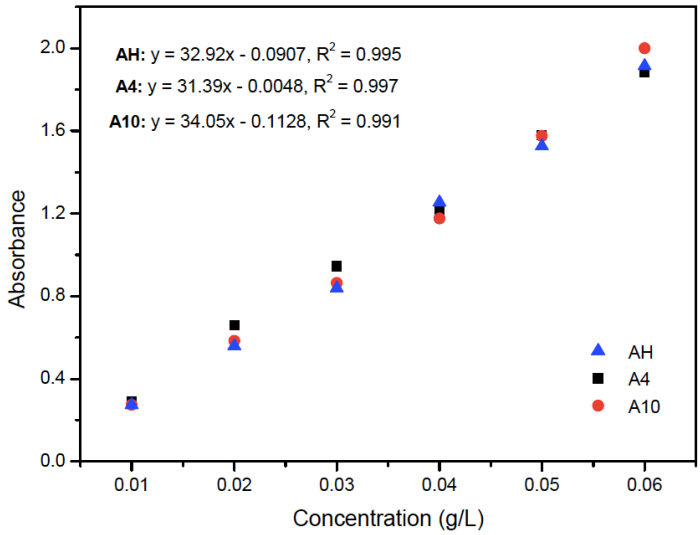



**Figure 11**. Calibration curves of solutions of subfraction AH, A4 and A10 in toluene.

**Table 2** compares the initial concentration of asphaltenes in the oil phase, asphaltene concentration in the oil phase after centrifugation and the water content in the DLP. The adsorbed amount of the asphaltene A4 in the DLP was the higher, approximately 54%, however, a lower percentage of water was observed among all samples. Is most likely driven by polar interactions, the A4 subfraction migrated preferentially to the aqueous phase destabilizing the DLP. The subfraction A10 showed higher efficiency in the stabilization of the emulsion. Due aromaticity, the A10 subfraction migrated in more quantity to the oil phase, even with lowest

concentration adsorbed on DLP, approximately 48%, A10 was able to keep the model emulsions stable containing more than 87% of water.

**Table 2**. Concentration of asphaltene subfractions AH, A4 and A10 in the oil phase after centrifugation and the water content in the DLP formed

| | Conc. of asphaltene in oil phase ($g.L^{-1}$) | Conc. of asphaltene in oil phase after separation of DLP ($g.L^{-1}$) | % Water in DLP |
|---|---|---|---|
| Subfraction AH | 5.0 | 2.6 ± 0.1 | 87 - 90% |
| Subfraction A4 | 5.0 | 2.3 ± 0.2 | 85 - 87% |
| Subfraction A10 | 5.0 | 2.9 ± 0.1 | 87 - 89% |

## 4. Conclusion

Asphaltenes were extracted from a Brazilian vacuum residue by two different methods. The whole asphaltene was precipitated with excess of *n*-heptane at the ratio of 40:1 (*n*-heptane/VR). The subfraction obtained from this first precipitation called AH, represented 11.2wt%. In the second stage, two successive precipitations were made based on the ratio of *n*-heptane/VR 4:1 and 10:1, obtaining two different subfractions of asphaltenes, A4 and A10, which yields 6.8 wt% and 3.1wt%, respectively. The precipitation in stages proved to be very effective; with an addition about 40% less solvent, 89% of all asphaltenes present in the vacuum residue were recovered.

Important parameters of the three subfractions as: polarity, aromaticity, chemical composition and molecular weight were obtained through the analytical technique of APPI(+)FT-ICR MS and NMR. The analysis of APPI(+)FT-ICR MS showed similarities between the AH and the subfraction A10. The A4 subfraction

showed a higher molecular weight distribution and a higher percentage of nitrogen compounds, being the most polar asphaltene subfraction among them. However the data show that whole asphaltene AH and sub subfraction A10 involved higher aromaticity and solubility in *n*-heptane/toluene solutions.

The properties of the model emulsions with the different subfractions, such as water content, droplet size distribution and gravitational separation, showed that the effect of the whole asphaltene AH, A4 and A10 subfractions in the stability were generally similar, with all subfractions stabilizing the emulsions for more than two weeks and without the presence of a free water layer during that entire period. However, subfraction A10 was the one that maintained a higher percentage of stable water in the DLP with a lower concentration, in addition to presenting a better distribution in droplet size and a smaller separation of phase oil during the 24 hours on gravity action. These results suggest that the aromaticity and lowest molar mass of subfraction A10 contributed to their self-association this may reflect in a more rigid interfacial film formation responsible for the DLP more stable. This research also suggests that subfractions of asphaltene molecules are so effective as the "whole" fraction in emulsion stability.

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