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1 **Asphaltenes, subfractions A1 and A2 aggregation and adsorption onto RH-SiO₂**
2 **nanoparticles: solvent effect on the aggregate size**

3

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22

23 **Abstract**

24 The aggregation and adsorption of asphaltenes in dilute solutions has been extensively studied
25 and is now well established. At low concentrations, asphaltenes are mainly found in the form of
26 aggregates of approximately 3 nm in size. One strategy to simplify the study of these systems has
27 been to fractionate the asphaltenes into subfractions called A1 and A2. The nature of these
28 subfraction aggregates, their behavior with the concentration and their interaction with other
29 aggregates and surfaces remain under debate. This work presents experimental results on the
30 aggregation and adsorption of asphaltenes and their subfractions A1 and A2 onto SiO₂
31 nanoparticles from rice husks (RH-SiO₂), and the evidence allows us to infer that the aggregates
32 are in equilibrium in solution over a wide range of concentrations. The size distribution for each
33 subfraction does not change with dilution but is sensitive to solvent media. Subfraction A1 has a
34 very similar behavior to asphaltenes, while subfraction A2 tends to form larger aggregates.
35 Larger aggregates more likely adsorb on surfaces than small aggregates. According to the results,
36 the interaction of the aggregates in different solvents can be studied as a phase change
37 phenomenon, where the aggregate can be considered a partially immiscible phase in a solvent.
38 The theoretical principles are described, and a hypothesis is elaborated in these terms.

39

40 **Keywords: asphaltene aggregation, adsorption, nanoparticle, asphaltene adsorption.**

41

42

43 **1 Introduction**

44 Asphaltenes comprise a series of molecules with a wide range of molecular weight distributions
45 and heteroatoms, such as nitrogen, oxygen, sulfur, and metals, which modulate their properties.
46 From the operational viewpoint, asphaltenes are defined as the crude oil fraction soluble in light
47 aromatic hydrocarbons (e.g., toluene, benzene) and insoluble in low molecular weight alkanes
48 (e.g., n-pentane, n-hexane, n-heptane). Due to the complexity, their behavior is under study until
49 this date [1].

50 The behavior of asphaltene aggregates and their association is under debate, and the
51 existence of molecular units of natural asphaltenes has not been verified. Consequently, the
52 aggregates have shown stability in solvents, such as toluene, and the original petroleum mixture.
53 The size of the heterogeneous population of aggregates has been measured with a range of
54 analytical techniques, and the mean aggregate size is 2-20 nm [2]. Evidence suggests a range of
55 sizes in a polydisperse distribution [3]. Other hypotheses propose the existence of
56 supramolecular assembly of molecules; according to the authors, this hypothesis presents a better
57 context to understand, model, and predict the asphaltene behavior. The driving forces for this
58 supramolecular assembly proposed by Gray et al. [4] include a different type of interaction
59 between polar and aromatic groups.

60 In this context, it is now widely accepted that asphaltenes form aggregates even in very
61 dilute solutions of good solvents such as toluene or THF, but experimental data that describe the
62 nature of the aggregates and aggregation process remain open to interpretation and are the
63 subject of various disagreements. According to the literature, asphaltenes begin to form
64 nanoscale aggregated structures at concentrations below 100 mg L⁻¹ [5]. These nanoaggregates
65 are considered to have a limited size because of steric inhibitions introduced by the alkyl chains

66 attached to asphaltene aromatic cores. In a colloidal approach to the problem, a critical
67 nanoaggregate concentration (CNAC) has been defined as the concentration at which the growth
68 of nanoaggregates starts [6]; at higher concentrations ($2\text{--}10\text{ g L}^{-1}$), these nanoaggregates undergo
69 additional association to form clusters or micelles. These aggregates and clusters have often been
70 referred to and considered nanocolloidal and colloidal structures, respectively.

71 In a solid–liquid phase approach, asphaltene solutions can undergo liquid–solid phase
72 separation to give a solvent-rich phase in equilibrium with asphaltene-rich droplets (clusters).
73 The asphaltene-rich particles formed upon phase separation can act as colloids, but
74 thermodynamically, it is a liquid or glass that exhibits coarsening and coalescence instead of
75 colloidal aggregation at elevated temperature or upon dilution. In discussing asphaltene
76 aggregation, it is important to clearly define the type of aggregates under consideration. In some
77 studies, particles in the size range of 5–10 nm are referred to as both aggregates and
78 nanoaggregates, which of course they are. However, in scattering work, there is a clear
79 distinction between an initial, limited association to form nanoaggregates approximately 2–3 nm
80 in size and subsequent aggregation of these particles to form mass fractal clusters in the size
81 range of 5–10 nm [7].

82 As reported in previous works [8–11], asphaltenes can be fractionated into two main
83 subfractions A1 and A2 using the p–nitrophenol (PNP) method, where A1 has very low
84 solubility (in toluene, under laboratory conditions) (approximately 90 mg L^{-1}), and A2 has
85 similar solubility to that observed for asphaltenes (5–12%, depending on the sample). This
86 method has been tested numerous times and with different samples and always affords the two
87 fractions with the main difference in solubility. The solubility parameters of asphaltenes A1 and
88 A2 are consistent: A1 is less soluble than A2 in more than 50 different solvents [12].

89 Asphaltene adsorption governs many aspects of crude oil recovery and production.
90 Generally, the effects produced are undesirable, since they can lead to consequences such as
91 deposition, wettability modification, and emulsion stabilization; thus, considerable efforts have
92 been directed at understanding the behavior of crude oils and their constituents at interfaces. In
93 general, the results from adsorption studies over the years have been fitted with classical
94 adsorption models. The interpretation of these classical models does not give a real answer to all
95 changes in the system, so new approaches to the problem remain under discussion [13–19] In
96 other researches, the use of nanoparticles (NPs) to reduce the size of asphaltene flocks formed in
97 *n*-heptane:toluene mixtures has been reported [19–21]. Large reductions in the average flock size
98 of up to 50% were observed when NPs were added to an asphaltene-toluene solution. We
99 propose that the removal of substantial amounts of aggregates by NPs disrupts the flocks by
100 increasing their solubility, which results in large-sized reductions. The adsorption of asphaltenes
101 on nanoparticles has been previously studied, and different behaviors have been found.

102 From a geochemical interpretation, asphaltenes are derived from geomacromolecules and
103 generally have high molecular weights and complex chemical structures. Some conceptual
104 structure models that represent the largest possible set of physicochemical analytical data for
105 geomacromolecules have been used to represent structures of humic matter, kerogen, and
106 asphaltenes. Kerogen, asphaltene, and solid bitumen are important for the geochemical
107 information encoded with them. Their macromolecular structures can adsorb and even occlude
108 other small molecules (e.g., biomarkers) [22]. In their works, Cheng et al. [22] present a different
109 view, since asphaltenes are not formed from molecular systems but appear from the cracking of
110 larger structures.

111 Combining experimental and theoretical studies, Moncayo-Riascos et al. [23] studied the
112 effect of the solvent on the rheological behavior of asphaltenes dissolved in aromatic solvents
113 such as benzene and the three isomers of xylene. Experimentally, differences in the viscosity of
114 the solutions were obtained, being higher in p-xylene than in benzene. Likewise, a
115 correspondence was observed by molecular dynamics simulations with the size of the aggregates
116 obtained in the solutions being o-xylene > m-xylene > p-xylene \approx benzene, which corresponds to
117 the dipole moment and the solubility parameter due to the location of the -CH₃ substituent. Jiang
118 et al. [24] studied the aggregation behavior of a model polyaromatic asphaltene compound was
119 evaluated. When heptane was added to a solution of the model in toluene, it increased the
120 aggregation especially due to the possibility of establishing interactions via van der Waals. When
121 water was added to the mixture, an increase in aggregation and a different rearrangement was
122 observed, in which the water molecules allowed the construction of a network to connect
123 aggregates (via hydrogen bonding) and consequently the formation of aggregate clusters. In
124 contrast, in the presence of an asphaltene inhibitor, it destroyed some interactions between the
125 model and water, dispersing the conglomerates in solution. Xiong et al. [25] studied the
126 adsorption on protonated silica using molecular dynamics of a polyaromatic compound with
127 fused rings similar to those reported for asphaltenes. They found that in heptane aggregates are
128 found in the form of a long strip and these tend to adsorb rapidly on the surface. While in toluene
129 the aggregates are more compact and tend to desorb from the silica surface remaining in the
130 solvent phase.

131 In the present work, experiments of asphaltene aggregation and adsorption onto SiO₂ NPs
132 are presented, and the results show that asphaltene solutions are composed of aggregates of
133 different molecular weights in equilibrium with the solvent. The solvent properties produce a

134 change in size distribution proportion in the solution. The tendency of asphaltenes to adsorb on
135 surfaces is greater for large aggregates than for small aggregates. These results can be interpreted
136 based on the existence of a solid–liquid equilibrium, which is consistent with the recent proposal
137 of phase separation suppression, where crude oil or certain solvents act by stabilizing different
138 asphaltene aggregates and preventing the phase separation. The stabilization of this solid phase
139 depends on the quality of the environment and the type of asphaltenes.

140 **2 Experimental Section**

141 *2.1 Materials and Methods*

142 **Reagents:** toluene (99.8%, Scharlau), *n*-heptane (HPLC grade, 99% Scharlau), chloroform
143 (synthesis grade, stabilized with ethanol, 99% Scharlau), cumene (99% Alfa Aesar),
144 tetrahydrofuran [THF, GPC grade, ACS, stabilized with 250 mg L⁻¹ of 2,6-di-*tert*-butyl 4-
145 methylphenol (BHT), 99%, Scharlau], sodium hydroxide (NaOH, synthesis grade, 98%,
146 Scharlau) and *p*-nitrophenol (PNP, synthesis grade, 99%, Scharlau).

147 *2.1.1 Asphaltenes Separation*

148 Asphaltenes were separated from Hamaca and Cerro Negro (also known as Carabobo)
149 Venezuelan crude oils, and their characteristics are shown in Table 1. The procedure for
150 asphaltene separation is based on the ASTM D6560-17 standard and has been widely
151 reported in different publications related to asphaltenes [9–12]. *N*-heptane was added at a
152 crude:heptane volume ratio of 1:40 to induce the precipitation of asphaltenes. After a resting
153 time of 48-72 h and filtration by suction in two stages, Soxhlet extraction with *n*-heptane
154 was performed for 6-8 days to remove the coprecipitated material. At this stage, the
155 asphaltenes are separated from the maltenes (saturated, aromatics, and resins).

156 **Table 1.** Crude oil characteristics and yields of the asphaltene separation and fractionation.

Crude oil	°API	Stability	% Asphaltenes	% A1	% A2	% TC
Hamaca	9.0	Stable	13.7	38	58	3
Cerro Negro	8.5	Stable	8.0	20	72	6

157

158 *2.1.2 Asphaltenes Fractionation*

159 Based on the fractionation by complex formation with PNP proposed for the first time by
160 Gutiérrez et al. [26], subfractions A1 and A2 and the trapped compounds (TC) were obtained.
161 The asphaltenes were dissolved in cumene saturated with PNP and refluxed for 6 h. During the
162 8-day resting time at room temperature, subfraction A1 precipitates as an insoluble asphaltene-
163 PNP complex, while in solution, subfractions A2 and TC remain in solution. After the filtration
164 steps, reduced pressure distillation of the cumene, and successive washing with *n*-heptane, the
165 solid subfractions were obtained. The PNP was removed by successive washing with a 5%
166 aqueous NaOH solution until colorless washing was obtained. The yields of subfractions A1 and
167 A2 and TC (saved for further analysis) are shown in Table 1. The A1 and A2 subfractions have
168 the same average composition and characteristic of previously reported [26] where the most
169 important difference between these fractions is in the H/C ratio with 0.90 for A1 and 0.99 for A2
170 and the Double Bond Equivalent (DBE) of 56 for A1 and 52 for A2.

171 *2.1.3 Asphaltene Solution Preparation*

172 Solutions of the whole asphaltenes and their subfractions A1 and A2 were prepared in THF and
173 CHCl₃ at a fixed concentration of 1000 mg L⁻¹ and in the concentration range of 50-2000 mg L⁻¹.
174 All solutions were analyzed by GPC-ICP HR MS, where ⁵¹V, ³²S, and ⁵⁸Ni isotopes were
175 monitored.

176 2.1.4 *SiO₂ nanoparticle preparation*

177 SiO₂ nanoparticles from rice husks (RH-SiO₂ NPs) were prepared using a modification of a
178 reported process [16]. In the first step, rice husks were leached with 100 mg/L HCl, washed to
179 neutral pH, and heated at 120 °C to remove water. Then, with a heating ramp of 500 °C h⁻¹, the
180 rice husks were heated at 500 °C for 1 h to burn carbonaceous residue and at 700 °C for 9 h to
181 produce loosely interconnected amorphous SiO₂. The amorphous silica size was reduced by a
182 ball milling process for at least 24 h, and mesoporous nanoparticles were obtained with an
183 average size of 40-60 nm, a porosity of 78%, and a specific surface of 234 m² g⁻¹. The BET and
184 porosity plots are shown in Figs. S5 and S6, respectively, in the supporting information.

185 2.1.5 *Asphaltenes Adsorption Experiment*

186 The adsorption experiments were based on previous works of Castillo *et al.* [16,18] and Acevedo
187 *et al.* [27]. In the first batch of experiments, the quantity of NPs was varied. For this purpose, 600
188 mg L⁻¹ asphaltene solutions in toluene and CHCl₃ were prepared and placed in contact for 72 h
189 with RH-SiO₂ NPs in the concentration range of 0-5 and 0-300 mg/L, respectively. The
190 remaining solutions after adsorption were analyzed by GPC-ICP HR MS and UV-Visible
191 spectroscopy.

192 Subsequently, the adsorption behavior of the asphaltenes was analyzed concerning their
193 A1 and A2 subfractions. Then, 600 mg L⁻¹ asphaltenes and their A1 and A2 subfraction solutions
194 in CHCl₃ were placed in contact with 300 mg/L RH-SiO₂ NPs for 72 h. After this time, the
195 remaining solution was separated from the solid phase by centrifugation (6000 rpm for 5 min).
196 From the experiments, the solutions before and after adsorption were analyzed, and the solid
197 material (RH-SiO₂ nanoparticle NPs adsorbed with the asphaltene or subfraction) was extracted
198 with THF to study the desorption of the material. From now on, the solution before adsorption is

199 called "original", the one after adsorption "remains", and the one from the THF extracts
200 "extract". All solutions were analyzed by GPC-ICP HR MS.

201 *2.1.6 GPC-ICP HR MS Analysis*

202 As reported in previous studies [18,27,28], GPC-ICP HR MS analyses were performed using a
203 Thermo Scientific Element XR sector field ICP HR MS instrument that operates at a resolution
204 of 4000 (medium resolution) to access spectrally interfered isotopes of ^{58}Ni , ^{32}S , and ^{51}V . The
205 spectrometer was equipped with a Fassel-type quartz torch shielded with a grounded Pt electrode
206 and a quartz injector (1.0 mm i.d.). A Pt sampler (1.1-mm orifice diameter) and a Pt skimmer
207 (0.8-mm orifice diameter) were used. An O_2 flow was continuously supplied to the nebulizer Ar
208 gas flow. The introduction system was fitted with a modified DS-5 microflow total consumption
209 nebulizer (CETAC, Omaha, NE) mounted on a laboratory-made, low-volume (8 mL), single-
210 pass-jacketed glass spray chamber of total consumption. The spray chamber was thermostated to
211 $60\text{ }^\circ\text{C}$. The ICP HR MS conditions were controlled and optimized daily using a 1.0 ng g^{-1}
212 multielement tuning solution in THF delivered via a syringe pump at a flow rate of $15\text{ }\mu\text{L min}^{-1}$.

213 Chromatographic separations were conducted using a Dionex HPLC 3000 with three
214 Styragel styrene-divinylbenzene gel permeation columns connected in series ($7.8 \times 300\text{ mm}$) that
215 works at a flow rate of 0.7 mL min^{-1} in THF. These columns were HR4 (particle size, $5\text{ }\mu\text{m}$;
216 exclusion limit, 600 000 Da of polystyrene [PS] equivalent), HR2 (particle size, $5\text{ }\mu\text{m}$; exclusion
217 limit, 20 000 Da) and HR0.5 (particle size, $5\text{ }\mu\text{m}$; exclusion limit, 1000 Da). A Styragel guard
218 column ($4.6 \times 30\text{ mm}$) was included before these three columns to protect them and prolong their
219 lifetimes. The separation achieved by the columns was evaluated using a mixture of PS standards
220 of 1,000,000–162 Da. According to the GPC column configuration, high-molecular-weight
221 compounds elute at shorter times, and low-molecular-weight molecules elute at longer times,

222 which allowed us to define integration intervals for super-high (SHMW), high (HMW), medium
223 (MMW), and low (LMW) molecular weights of the eluted components, which correspond to
224 $\approx 1,000,000$ – $67,000$ Da; $\approx 27,000$ – $6,600$ Da; $\approx 1,100$ Da and ≈ 162 Da in equivalent polystyrene,
225 respectively. For the calibration of chromatographic methods by GPC, polymers of known molar
226 mass are used, and the retention time in the column is correlated with the size of the polymer and
227 these values are used as a reference. In the case of asphaltenes the retention times of the
228 aggregates are measured and these are associated with their size, but the size of these aggregates
229 depends on the shape of the aggregates and the solvation, so the real size of the aggregates is
230 smaller than what is determined by GPC, so the graphs give us the relative size.

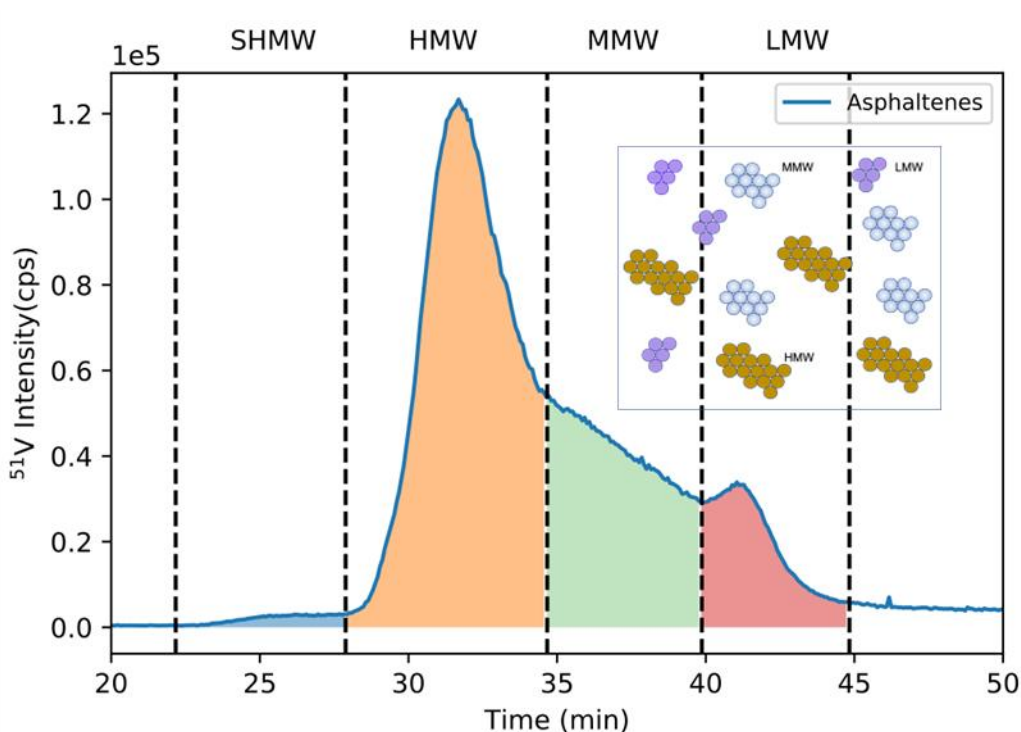
231 *2.1.7 UV–Vis Analysis*

232 The fractions of each sample were measured in UV–Visible equipment from Mettler Toledo
233 UV7 using a 1 cm cell. The absorbance signal is taken as a function of wavelength in the range
234 of 350–700 nm. For each sample, the absorbance exponentially decays with wavelength showing
235 a maximum at approximately 420 nm, which corresponds to the Soret band of the porphyrins.
236 For each concentration, the absorbance signal at 450 nm is taken, where the dispersive
237 component of the signal is negligible, and only the absorptive component is taken to construct
238 the absorbance vs. concentration plots.

239 *2.2 Methods*

240 In all adsorption experiments, once the solution reached the contact time with the RH-SiO₂ NPs
241 (72 h), aliquots of these solutions were removed and evaporated to dryness, redissolved in the
242 same amount of THF, and analyzed using GPC-ICP HR MS techniques. The aggregate
243 formation of different sizes depends on the chemical potentials of different aggregates present,
244 their interaction potentials, and the functional form of this potential with the size of the

245 aggregates. The chromatographic profile displays similar characteristics throughout the
246 concentration range, which indicates that the aggregate fractions were in equilibrium. Fig. 1
247 shows a typical GPC-ICP HR MS chromatogram for the asphaltene solutions following the
248 vanadium signal, and the SHMW, HMW, MMW, and LMW regions are detailed.



249
250 **Fig. 1.** Asphaltene vanadium GPC-ICP HR MS profile at 1000 mg L^{-1} in THF for Hamaca crude
251 oil, which shows the SHMW, HMW, MMW, and LMW regions, in the inset. Sketch of the
252 HMW, MMW and LMW aggregate models in THF solution

253 In Fig. 1, three different distributions of aggregates are presented in equilibrium in the
254 solution (assuming that the SHMW region is negligible for asphaltene samples). This
255 equilibrium is sketched in the inset of Fig. 1, where each group of aggregates has equal chemical
256 potential. According to the experimental results, different groups of species are present in the
257 asphaltene fraction, which are represented by three different distributions.

258 This fact may be expressed as:

$$259 \quad \mu_{LMW} = \mu_{LMW}^0 + k T \ln(X_{LMW}) = \mu_{MMW} = \mu_{MMW}^0 + k T \ln(X_{MMW}) = \mu_{HMW} = \mu_{HMW}^0 +$$
$$260 \quad k T \ln(X_{HMW}) \quad (1)$$

261 where μ_{LMW}^0 is the potential for low-molecular-weight aggregates or monomers, μ_{MMW}^0 is the
262 potential for medium-molecular-weight aggregates, and μ_{HMW}^0 is the potential for high-
263 molecular-weight aggregates. k is the Boltzmann constant, T is temperature, and X_{HMW} , X_{MMW} ,
264 and X_{LMW} correspond to the fraction of each region in THF solution. Assuming that a
265 nanoaggregate of radius r can be represented as a simple spherical structure, number of units N is
266 proportional to the volume ($4/3\pi R^3$), and α is the interaction factor between the particle and the
267 solvent:

$$268 \quad \mu_N^0 = \mu^0 + \frac{\alpha k T}{N^{\frac{1}{3}}} \quad (2)$$

269 From Equations 1 and 2, the concentration of aggregates of different sizes in equilibrium in the
270 media can be expressed by:

$$271 \quad X_{XMW}(r) = e^{-\alpha} = e^{-\frac{4\pi(r-r_0)^2}{kT}} \quad (3)$$

272 where r_0 is the average radius, and r is the radius of different aggregates. For this system of
273 two immiscible components (X_{XMW}), parameter α corresponds to the free energy of transferring a
274 solute molecule from the solute into the solvent phase. γ is the interfacial free energy per unit
275 exposed area of the nanoaggregate, and r is the radius of the aggregate. For a set of
276 nanoaggregates of different sizes $r_i > r_{i0}$, the fraction X_{XMW} is the sum of the set of aggregates in
277 that fraction that behave in an approximately similar manner.

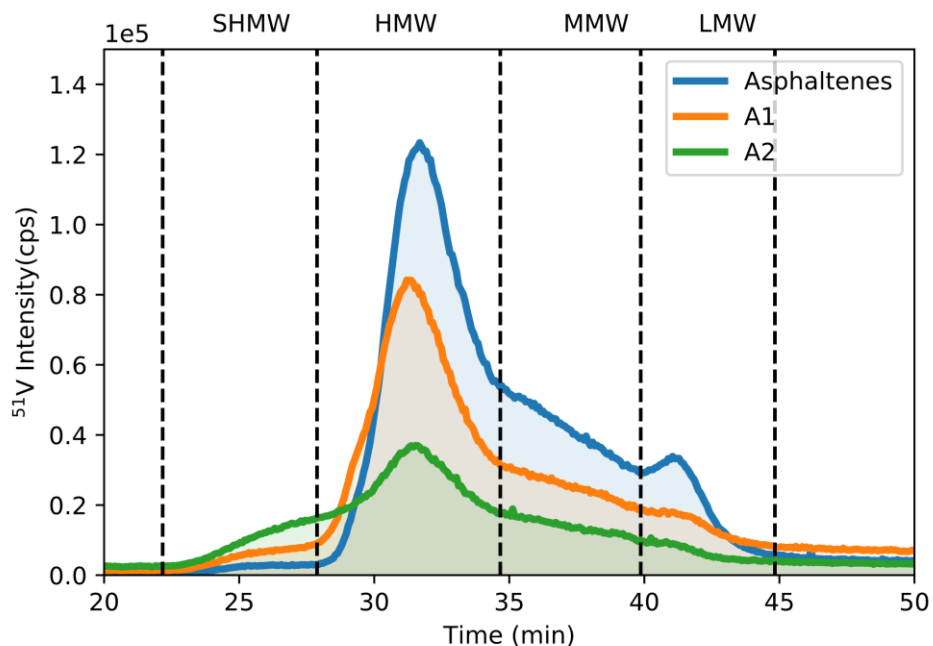
$$278 \quad X_{XMW} = \sum_i e^{-\alpha_i} = \sum_i e^{-\frac{4\pi r_i^2 \gamma}{kT}} \quad (4)$$

279 The properties of the solvent play a very important role in the dissolution and
280 stabilization of the aggregates and affect the aggregation process. The solvent interaction with
281 the aggregates drives the formation of aggregates and their structural conformation, since
282 depending on the properties of the solvent in which it is found, the aggregates may form
283 structures with different geometrical forms. In the experiment, it is assumed that the
284 aggregates behave as nanoparticles with defined sizes immersed in the solvent; despite
285 being soluble in the medium, due to their interactions, the surface energy of the aggregates
286 exceeds the dissolution energy.

287 **3 Results and Discussion**

288 ***3.1 GPC-ICP HR MS of asphaltenes, A1 and A2 subfractions in different solvents***

289 Fig. 2 shows the vanadium GPC-ICP HR MS profiles that correspond to the hydrodynamic
290 volume separation of asphaltenes and its subfractions A1 and A2 from Cerro Negro crude oil.
291 The samples showed a typical trimodal profile for the asphaltenes and small variations in the
292 profile for the subfractions. Subfraction A1 presents a similar size distribution to asphaltenes
293 with a shift toward high-molecular-weight compounds or larger hydrodynamic volume and a
294 decrease in the low-molecular-weight section. The A2 subfraction shows a notorious shift toward
295 high-molecular-weight compounds or larger hydrodynamic volumes and an evident decrease in
296 the low-molecular-weight section. Similar profiles have been presented in previous works for
297 different asphaltene samples [3,18]. The profiles obtained by GPC-ICPMS are similar in most of
298 the crude oils studied, in the present case, for the Hamaca crude oil, a greater definition of the
299 areas is observed and an area of super high molecular weight appears in a very important way,
300 corresponding to super-aggregates. All samples show that the A2 subfraction tends to form
301 compounds with larger hydrodynamic volumes than asphaltenes.



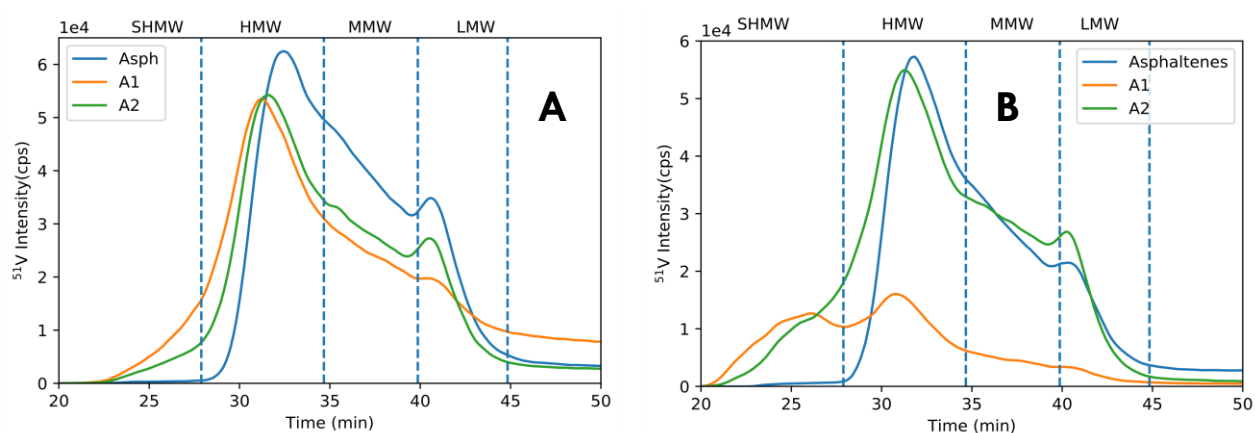
302

303 **Fig. 2.** Vanadium GPC-ICP HR MS profiles of asphaltenes, subfractions A1 and A2 at 1000 mg
 304 L⁻¹ in THF for Hamaca crude oil.

305 The A1 subfraction behaves similarly to the asphaltenes, which reinforces the previous
 306 results [28], where the stabilization of the asphaltene aggregates is due the interaction of
 307 subfractions A1 and A2. Variations in the profiles show that the aggregation of different
 308 fractions can be modulated by geometrical parameters, the structure of the formed aggregates,
 309 and their fractal dimension [29–31].

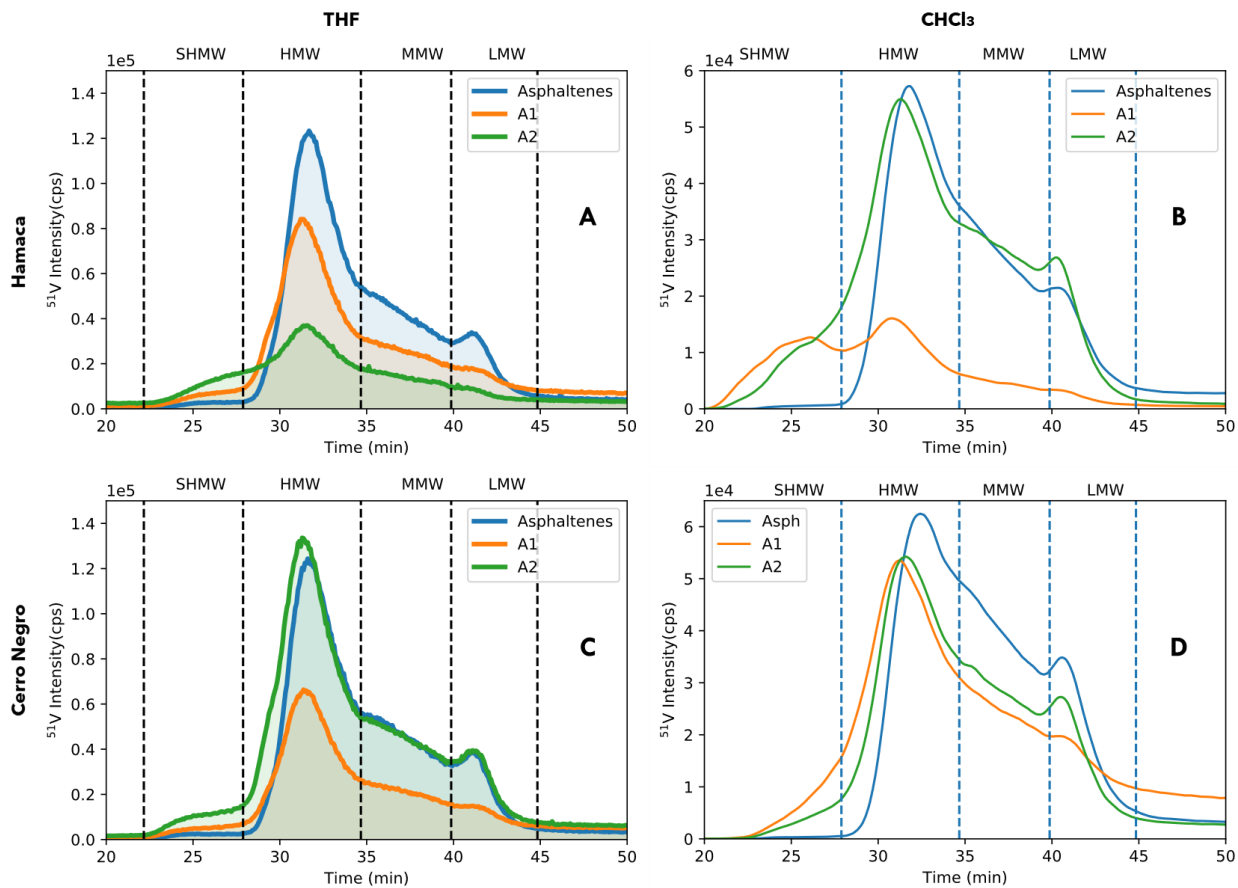
310 Fig. 3 shows the GPC-ICP HR MS profiles for asphaltene and subfractions A1 and A2 in
 311 chloroform from Cerro Negro (A) and Hamaca (B) crude oils. The plots show the signals for
 312 vanadium, in the case of nickel, and sulfur isotopes the behavior is similar. Chloroform is an
 313 aprotic solvent with higher polarity than toluene and lower polarity than THF and a small
 314 molecular size, which allows it to more easily diffuse into the aggregate. Fig. 3B show the results
 315 for Hamaca, where subfractions A1 and A2 show a tendency to form larger aggregates with a
 316 higher hydrodynamic volume than when they are mixed to form asphaltenes. This effect is much

317 more marked for the solutions in CHCl_3 than in THF. In the case of the Cerro Negro crude oil
318 (Fig. 4A-C), the differences are less noticeable, although the changes are still observed. These
319 changes are due to the difference in solubility of the asphaltenes in both solvents and the
320 solubility of the vanadyl compounds trapped in the asphaltene aggregate structure [32–34].



321
322 **Fig. 3.** GPC-ICP HR MS profiles of vanadium, for Hamaca (A) and Cerro Negro (B) asphaltenes
323 and subfractions A1 and A2 in CHCl_3 at 1000 mg L^{-1} .

324 Fig. 4 shows the comparison of vanadium profiles for asphaltenes and its subfractions A1
325 and A2 for Hamaca and Cerro Negro crude oils dissolved in THF and CHCl_3 at the same
326 concentration. This figure clearly shows the differences and the effect of the solvent on the size
327 distribution of the aggregates. There are variations in the vanadium signal in the A1 and A2
328 subfractions, probably because when the trapped vanadium is being liberated [11,36], the
329 asphaltene aggregates are redistributed, and this effect is more remarkable when a more polar
330 solvent chloroform is used. In the case of Cerro Negro, the differences are less noticeable,
331 although they persist, and the decrease in intensity for the subfractions is also present. The
332 changes using CHCl_3 as the solvent are more noticeable than those using THF, and a tailing
333 effect appears.



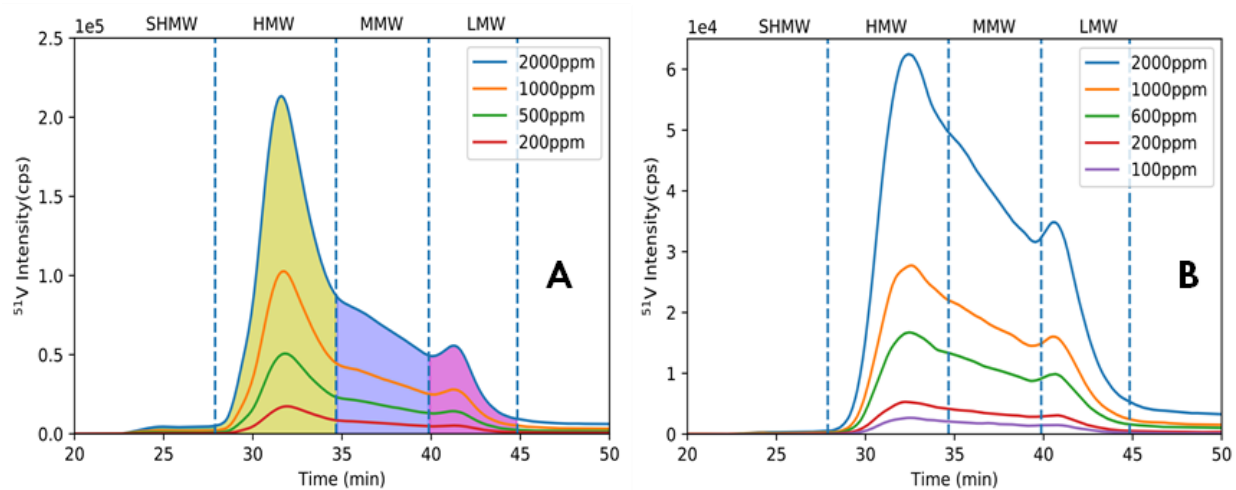
334

335 **Fig. 4.** Vanadium GPC-ICP HR MS profiles for asphaltenes and their subfractions A1 and A2
 336 dissolved in two solvents (THF and CHCl_3) at 1000 mg L^{-1} for Hamaca and Cerro Negro crude
 337 oils. Sulfur and nickel profiles are shown in Figs. S1 and S2, respectively, in the supporting
 338 information. Plots A and C were taken with permission from reference [28].

339 **3.2 Concentration Effects on the GPC-ICP HR MS Profiles**

340 Fig. 5 shows the change in vanadium chromatogram as a function of the concentration for Cerro
 341 Negro asphaltenes in THF (A) and CHCl_3 (B) solutions the behavior its similar for A1 and A2.
 342 In both cases, there is a linear decrease in the total area as a function of concentration, and the
 343 observed molecular mass distribution profile remains constant. This result shows that there are
 344 three distributions at equilibrium: $\text{HMW} = \text{MMW} = \text{LMW}$, and the dilution in the solvent only
 345 decreases the concentrations in all distributions without changing their proportions. This

346 behavior was previously observed by González et al. [28], who found that the behavior of
 347 asphaltene solutions and their subfractions in THF as a function of concentration does not follow
 348 the tendency of a micellar system; the behavior is similar to a dispersion of particles of different
 349 size distributions in a similar process to phase separation [12]. The most remarkable result is that
 350 in both solvents, the behavior is identical, and the redissolution of a determinate sample in THF
 351 for an injection in the GPC-ICP HR MS does not alter the aggregate characteristics.

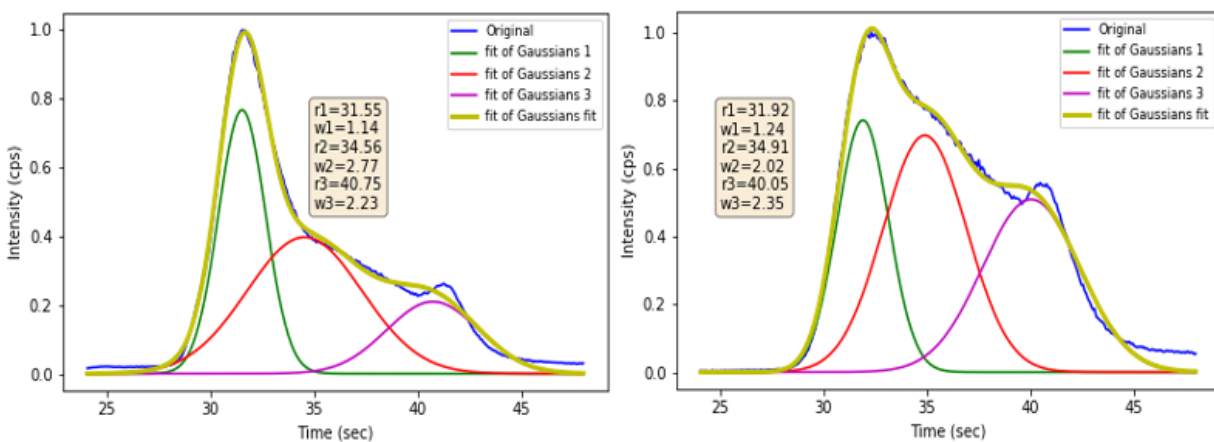


352
 353 **Fig. 5.** Vanadium GPC-ICP HR MS profiles for Cerro Negro asphaltenes in THF (A) and in
 354 CHCl_3 (B) by varying the concentration (50–2000 mg L^{-1}).

355
 356 **3.3 Free surface energy of the aggregates**

357 The fraction of asphaltene molecules is composed of multiple molecules of different molecular
 358 weights and composition, an approximation to understand their behavior and their interaction
 359 with nanoparticles can be made assuming an aggregate with average size and a size distribution
 360 of it[30]. The adsorption experiments could not be interpreted from a classical thermodynamic
 361 point of view so we introduce a first approximation based on the calculation of the surface
 362 energy[47-51] for the interaction of the species, the surface energy of nanoparticles, and

363 aggregate is the most important parameter because it provides information about the number of
364 active sites on the surface of the nanoparticle and the type of preferential interaction between
365 nanoparticle and aggregates. The free energy of the aggregate surface can be calculated from the
366 fit of each distribution that composes the sample. The intensity of the signal is proportional to the
367 mass fraction of the sample, and based on the experimental results, we propose the existence of
368 three distributions of different aggregates. The fitting of the experimental data was made with 3
369 Gaussian distributions with the maximum approximately in the mean value of the regions
370 defined as HMW, MMW and LMW. Small variations are observed in the maxima and semi-
371 widths of the curves of the fits with respect to the experimental signal depending on the solvent.
372 This is due to the ability of the medium to solvate and achieve a better definition of the
373 aggregates present. Using Equation 3, the value of α is obtained using approximate radii of 8, 16
374 and 21 nm taken from the literature [9]. For the asphaltene aggregates using Equation 3, the
375 interfacial tension γ is obtained. Fig. 6 shows the original curves for asphaltenes dissolved in
376 toluene and CHCl_3 and their respective fits taking 3 distributions in each case. Table 2 shows the
377 fit values: α is the fitting constant, γ is the surface free energy or the energy needed to transfer
378 one molecule from the aggregate surface to the solution, and r is the radius of the aggregate. As
379 observed in Table 2, the values of α grow with the size of the aggregate and γ , which indicates
380 that a larger aggregate is less likely to dissolve, which increases its stability.

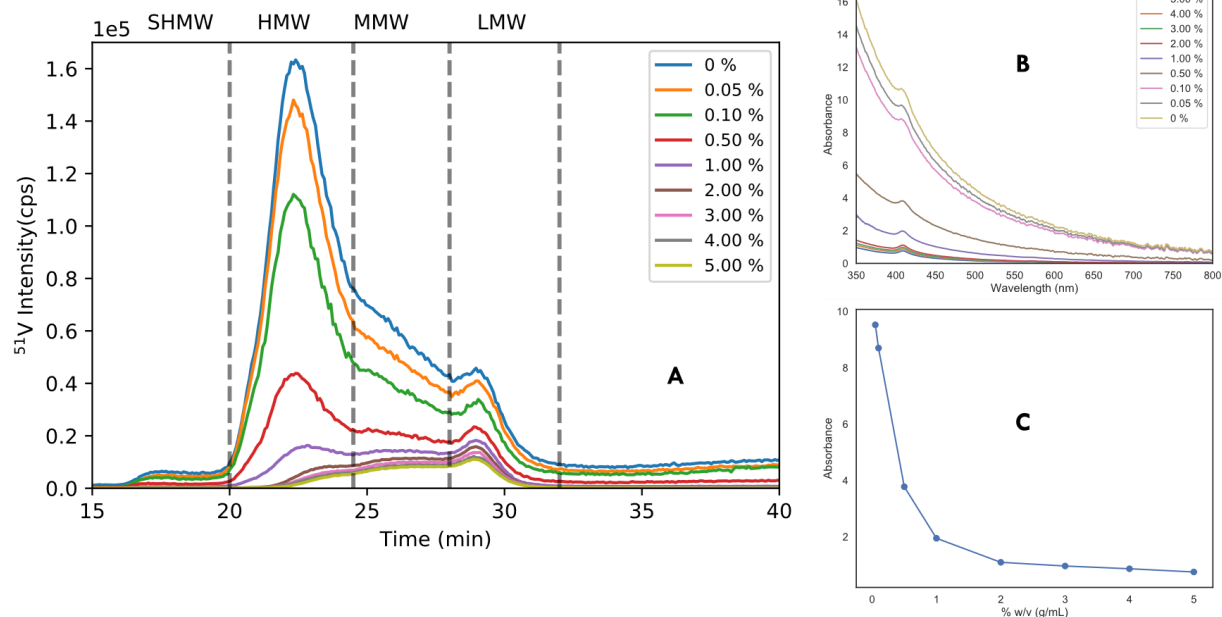


381
 382 **Fig. 6.** Vanadium GPC-ICP HR MS normalized profiles in THF (left) and CHCl₃ (right) and the
 383 Gaussians fit of the HMW, MMW and LMW regions. Sulfur GPC-ICP HR MS Gaussian fit for
 384 the chromatograms obtained in THF and in CHCl₃ are given in in supporting information Fig. S7
 385 and S8.
 386 **Table 2.** Fitting parameters for asphaltenes in both solvents, where α is the fitting parameter, γ is
 387 the surface energy or interfacial tension calculated from Equation 3 and using ratio r

Solvent		LMW	MMW	HMW
	α	2.7	13.88	60.52
<i>CHCl₃</i>	γ (mJ/m^2)	0.0124	0.0168	0.044
	r (nm)	8.52	16.49	21.14
	α	2.31	7.85	76.09
THF	γ (mJ/m^2)	0.0130	0.0089	0.0530
	r (nm)	7.44	17.04	21.71

389 ***3.4 Adsorption Experiment in Toluene***

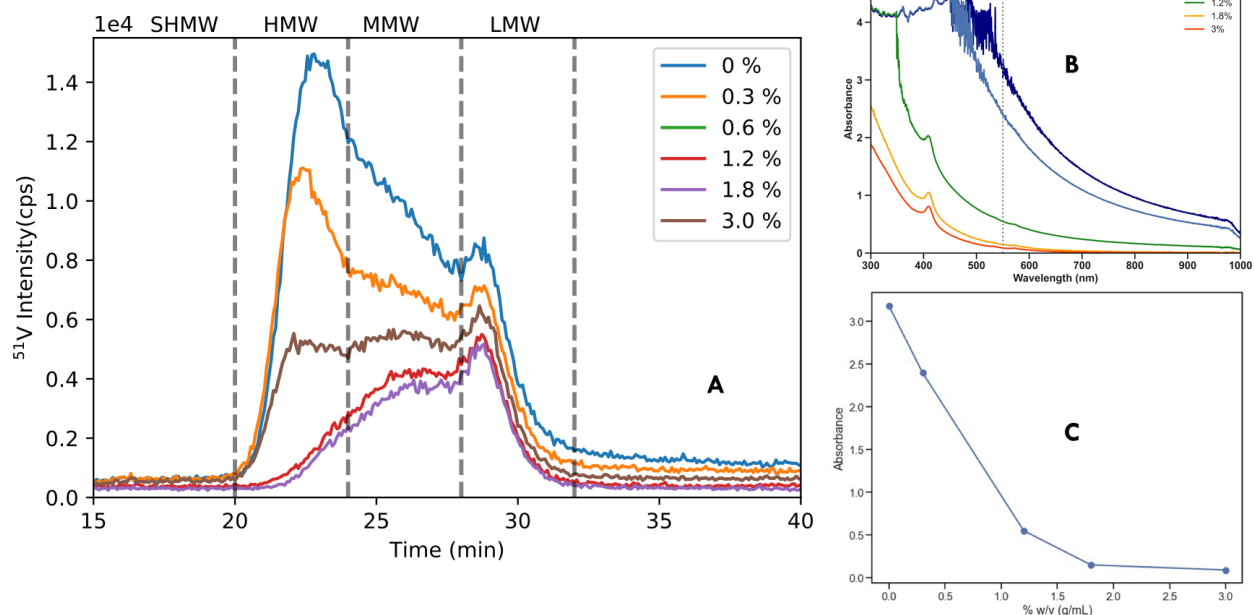
390 Asphaltene adsorption experiments are focused on determining the amount of asphaltenes
391 that are adsorbed onto nanoparticles. These experiments are usually performed to determine
392 the efficiency of these nanoparticles to be used as adsorbents, or many reports in the
393 literature focus on associating the efficiency with properties of the nanoparticles such as
394 their size and composition [17,37–42]. In our experiment, we focused on studying the
395 interaction of the nanoparticles with different aggregates that are in equilibrium in an
396 asphaltene dispersion [16]. Fig. 7A shows the vanadium GPC-ICP HR MS profiles of Hamaca
397 asphaltene solutions after being in contact with different percentages of silica nanoparticles. As
398 shown in plot A, for percentages below 0.5%, a homogeneous decrease in the signal is observed;
399 at higher percentages of nanoparticles, a significant decrease in the high-molecular-weight
400 fraction and a relative increase in the low-molecular-weight fraction are observed. Plot 7B
401 shows the UV–visible spectrum for each sample, where a decrease in magnitude of the spectrum
402 is observed when the amount of adsorbent increases. Plot 7C shows the variation in the
403 absorbance at 450 nm, which indicates a typical exponential decay for these systems. Both plots
404 7B and 7C show the typical adsorption behavior of asphaltenes, as presented in the literature.
405 This result is the average behavior of the system without considering the individual behavior of
406 different distributions that compose the sample. The curves in plot A show how the areas
407 corresponding to the high-molecular-weight zone decrease, while the low-molecular-weight zone
408 has a relative increase.



409
 410 **Fig. 7.** Hamaca asphaltene adsorption onto silica nanoparticles in toluene. Vanadium GPC-ICP
 411 HR MS chromatogram (A) and UV spectrum (B) for the asphaltene and the remaining asphaltene
 412 solution after contacting 0.05 to 5% NPs. Variation of the UV absorbance with w. S and Ni
 413 GPC-ICP HR MS chromatogram are given in supporting information Fig. S3 for CERRO
 414 NEGRO and Fig. S4 for Hamaca.

415
 416 **3.5 Adsorption Experiment in CHCl_3**

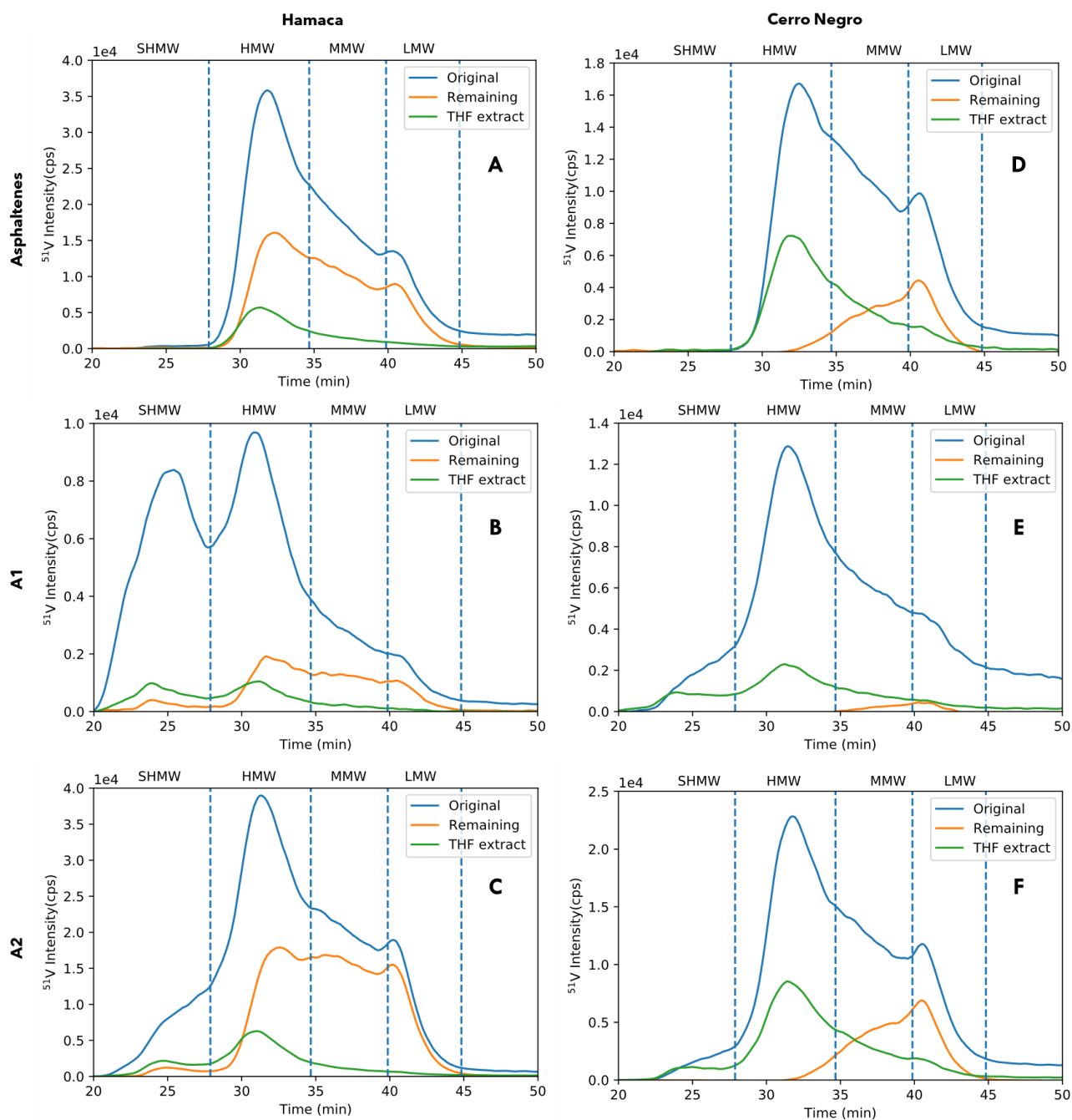
417 Fig. 8A shows the vanadium GPC-ICP HR MS chromatograms of Hamaca crude asphaltene
 418 solutions in chloroform after being in contact with different percentages of silica
 419 nanoparticles. As shown in plot 8A, for percentages below 0.5%, a homogeneous decrease
 420 in the signal is observed at higher percentages of nanoparticles, a significant decrease in the
 421 high-molecular-weight fraction and a relative increase in proportion of the low-molecular-
 422 weight fraction are observed. Plot B shows the UV-visible spectrum for each sample, where
 423 a decrease in magnitude of the spectrum is observed when the adsorbent amount increases.



424
 425 **Fig. 8.** Hamaca Asphaltene adsorption onto silica nanoparticles in chloroform. Vanadium GPC
 426 ICP HR MS chromatogram (A) and UV spectrum (B) for asphaltene and the remaining
 427 asphaltene solution after contacting 0.3 to 3% NPs. Variation of the UV absorbance w.

428 Fig. 9 shows the adsorption experiments of Hamaca and Cerro Negro asphaltenes and
 429 their subfractions A1 and A2 in CHCl_3 at concentrations of 600 mg L^{-1} and 300 (mg/L)
 430 nanoparticles. The first column shows the results for Hamaca, and the second column shows the
 431 results for Cerro Negro. For all cases, the signals of the original solution, solution after
 432 adsorption, and extracted fraction of nanoparticles after adsorption are plotted. In all cases, the
 433 behavior is similar; the fraction after adsorption shows a significant decrease in intensity in the
 434 section corresponding to the high-molecular-weight zone, and the fraction extracted from the
 435 nanoparticles shows a higher signal in the high-molecular-weight zone. This behavior is
 436 consistent with the hypotheses, where two important points have been emphasized: the fraction
 437 adsorbed on the nanoparticles is the high-molecular-weight nanoaggregate or larger-

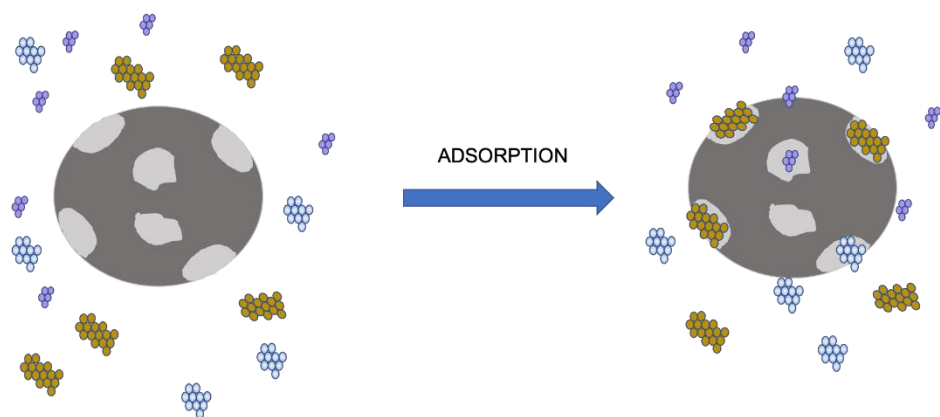
438 hydrodynamic-volume nanoaggregate, and the nanoaggregates remain unaltered even after
439 adsorption.



440
441 **Fig. 9.** Vanadium GPC-ICP HR MS chromatogram obtained during adsorption experiment in
442 CHCl_3 for Hamaca asphaltene and subfractions (left) and Cerro Negro asphaltene and

443 subfractions (right). The S GPC-ICP MS results are given in supplemental information Fig. S9.

444 In Fig. 10, a scheme of the adsorption model is presented, which is very close to the
445 observed results. Initially, different aggregates are dispersed in the solution with the highly
446 porous nanoparticles. After adsorption, the larger components occupy the pores of the
447 nanoparticle, and the remaining surface is left to small aggregates because the nanoparticles
448 have a porosity of 78%, and there are very few spaces for the small and medium aggregates.



449

450 **Fig. 10.** Adsorption model of asphaltenes aggregates on NPs.

451

452 **4 Conclusions and Final Comments**

453 The results in this work show that asphaltenes are present in the form of aggregates of different
454 hydrodynamic volumes in different solvents. The measurements with different solvents show
455 that there is no critical aggregation concentration, as formally defined, since different molecular
456 distributions proportionally dilute, which suggests that the interaction forces responsible for
457 stabilizing them in the medium are greater than solvation and solubilization. The results show
458 that for different solvents, there are different aggregate volume distributions. A shift to a larger
459 hydrodynamic volume is observed when the solvency power of the solvent is lower, which
460 indicates the increase in interaction forces between the aggregates. Our results demonstrate that

461 the nanoparticles preferentially adsorb the larger or heavier fractions of the asphaltenes. The
462 adsorption process is primarily mediated by interparticle (asphaltene nanoaggregate – silica
463 nanoparticle) interactions instead of being a typical adsorption process mediated by the active
464 center adsorption type. The adsorption experiments in different solvents for asphaltenes and their
465 subfractions A1 and A2 show that for polar solvents such as THF, the stabilization of the solvent
466 on the aggregates is more important than the interaction energies, while the same experiments in
467 toluene or CHCl_3 exhibit a different behavior. Toluene can dissolve them because it can enter the
468 structure of the aggregates and enhance the stabilization.

469

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474

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