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Distribution of Ni and V in A1 and A2 Asphaltene Fractions in Stable and Unstable Venezuelan Crude Oils

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ABSTRACT: Asphaltenes are a complex mixture of compounds grouped as the colloidal phase in crude oils. Two fractions, A1 and A2, have been isolated from them. A1 is defined as the mayor and practically insoluble fraction, while A2 has a similar solubility to the original asphaltenes in toluene. The studies on the molecular structure, organic compound distribution, and metal content can help to better understand the chemical behavior of these two fractions. In this sense, the concentration of Ni and V and elemental analysis (C, H, N, and S) were determined in asphaltenes and their fractions. The samples were analyzed using inductively coupled plasma atomic emission spectrometry and elemental combustion analysis. Results show that A1 presents higher Ni and V concentrations than A2, in both stable and unstable crude oils. These results can be explained by strong interactions, such as covalent bonds between the petroporphyrins and the asphaltene molecules. V/V + Ni ratios suggest differences in the distribution of metallo compounds between A1 and A2. Finally, organic elemental analysis ratios suggest variations in the aromatic character of both asphaltene fractions.

INTRODUCTION

The tendency of asphaltenes to flocculate from the crude oils represents a major concern because of its negative impact in exploration, production, transportation, and oil-refining processes. Studies clearly demonstrate that asphaltene precipitation can alter the flow phase of the reservoir, wellbore plugging, and precipitate, eventually clog up the pipelines, and hinder the refining yield, causing a reduction in capacity and productivity.^{1–4}

Asphaltenes are defined in terms of their solubility as the fraction that precipitates when an excess of low-molecular-weight paraffin, such as *n*-heptane, is added.⁵ Asphaltenes presents a really complex molecular composition. They correspond to the heaviest, polar, and aromatic portion of the crude oil. Asphaltenes are a mixture of polycyclic systems joined by flexible aliphatic chains, such as rosary- or archipelago-type molecules and condensed polycyclic structures, and bridging aliphatic rings or continental-type structure.^{6–8} Additionally, heterocyclic compounds of N, S, O, and metals can be found.^{9,10} The later are also a major concern because approximately 80% of these elements are co-precipitated with this polar crude oil fraction and they are well-recognized to have some negative effects, such as catalyst deactivation and fouling, corrosion of the equipment, and particulate emissions into the environment.¹¹ Ni and V are the most abundant elements, at concentration levels of mg kg^{−1}, and they are mainly present as mixed-ligand tetradantate, humate complex, and tetrapyrrole metallo-organic complex species.¹²

Recently, it was proposed that metalloporphyrin compounds together with paraffins, free radicals, and resins-like compounds can be trapped into the asphaltene colloids in a structure formed by clusters of two asphaltene fractions.^{10,14} Acevedo et al. have presented evidence of two asphaltene fractions using the *para*-nitrophenol (PNP) method.¹⁶ The first fraction, called A1, has a low solubility in toluene at room temperature (≤ 0.1 g L^{−1}) and molar mass of around 2600 g mol^{−1}.^{15,16} The second one,

called A2, shows a similar asphaltene solubility in toluene (≥ 50 g L^{−1}) and molar mass close to 1000 g mol^{−1}.^{16,19} A1 and A2 molecules form the asphaltene colloids in crude oils, where stacks of A1 are the colloidal core and A2 molecules are the periphery.^{15,16} According to this model, trapped compounds can be very difficult to remove from asphaltenes when they are separated from the crude oil.^{14,17}

This work focused on the determination of Ni and V in asphaltenes and A1 and A2 fractions from stable and unstable crude oils. H, C, N, and S were also included. The goal is to obtain information of the distribution and variety of Ni and V compounds trapped in A1 and A2 fractions using the elemental mass balance and V/Ni. This information can be useful to explain the interactions (van der Waals or covalent bonds) presented by the Ni and V porphyrins with the asphaltenes in the crude oil.

EXPERIMENTAL SECTION

Instrumentation. Asphaltene samples and their A1 and A2 fractions were digested in a microwave digestion system CEM model MDS 2000 (Mathews, NC). Ni and V were determined using the inductively coupled plasma optical emission spectrometer (ICP–OES), Thermo Jarrel Ash, model IRIS HR (Franklin, MA), with the instrument and the operating conditions listed in Table 1. C, H, N, and S content was obtained by combustion using an elemental analyzer, Thermo Scientific, model Flash EA 1112 (Milan, Italy).

Reagents. The following solvents, reactants, and standards were used to obtain asphaltenes from the crude oil samples: *n*-heptane and toluene. Chloroform, cumene, PNP, and sodium hydroxide were used to obtain A1 and A2 asphaltene fractions, with all of them provided by Riedel de Haën (Seelze, Germany). Nitric acid and hydrogen peroxide, used in the digestions of the samples, were also provided by

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Table 1. Instrumental and Experimental Parameters of the ICP–OES for Ni and V Determination

RF generator	IRIS HR (Thermo Jarrel Ash, Franklin, MA)
RF power (W)	1350
dispersive system	Echelle cross-dispersion spectrometer; focal length, 381 mm
detection system	charge injection device (CID) solid-state sensor; low-temperature operation; array size, 512 × 512
outer and intermediate gas flow rate (L min ⁻¹)	15 and 1.5, respectively
injector (mm)	1.5
nebulization system	crossflow nebulizer and Scott-type spray chamber
solution flow mode (mL min ⁻¹)	1.0 continuous
observation height (mm)	8 (above the last turn of the load coil)
working wavelengths (nm)	Ni ^{II} , 221.6; V ^{II} , 311.0

Table 2. Physical and Chemical Properties of the Crude Oil Samples Used in This Work

crude oil	Shell <i>P</i> value ^a	API gravity	SARA (%)			
			saturates	aromatics	resins	asphaltenes
Hamaca	2.3	9.0	19	25	43	13
Boscan	2.9	10.3	12	36	38	14
Furrial	1.5	23.7	55	28	13	4
Carabobo	1.8	8.0	19	28	42	11
Monagas	<1.6	24.3	60	14	24	2
Ceuta	<1.6	30.3	52	26	16	6

^a Shell *P* value <1.6 for unstable crude oil and >1.6 for stable crude oil.

Riedel de Haën (Seelze, Germany). Ni and V solutions were prepared by diluting in 1000 µg mL⁻¹ distilled water stock solutions from Merck (Darmstadt, Germany).

Samples. Asphaltenes from six Venezuelan crude oils were used in this work. Table 2 shows some properties of the crude oil samples. The Shell *P* value was used as stability criteria and was determined using hexadecane as a precipitant agent in accordance with the literature.^{18,19} Asphaltene samples were obtained by precipitation with *n*-heptane.²⁰ A1 and A2 fractions were obtained from 8 g L⁻¹ asphaltene solution in cumene saturated with PNP, using a previous reported method.^{15,21} In brief, precipitated solid, composed of A1 and PNP, was collected after 5 days, filtered by a microporous membrane (0.25 µm), washed with cumene, dried, and dissolved in chloroform, and the PNP was extracted repeatedly with 5% aqueous solution of NaOH. Extraction was monitored using ultraviolet–visible (UV–vis) absorption spectroscopy. The filtrate having the A2 fraction was evaporated to dryness under vacuum to remove cumene. The solid was dissolved in chloroform and treated as described for A1 to remove PNP. The content of A1 and A2 fractions for the asphaltene samples were the same as reported by Acevedo et al.^{6,14,15,21,22}

RESULTS AND DISCUSSION

Digestion of Asphaltenes and Their A1 and A2 Fractions. Metals in crude oil and in their products are usually determined in ICP–OES by direct nebulization of the samples dissolved in organic solvents. These methods are simple and less time-consuming,

Table 3. Microwave Digestion Method Used for Asphaltenes and Their A1 and A2 Fractions

step	1	2	3
power (W)	300	300	300
pressure (psi)	100	150	200
time (min)	15	15	15
tap (min)	5	5	10

Table 4. Concentration of Ni and V in Asphaltene Samples Using Two Digestion Treatments in ICP–OES^a

crude oil sample	microwave digestion		ashing method	
	Ni (mg kg ⁻¹)	V (mg kg ⁻¹)	Ni (mg kg ⁻¹)	V (mg kg ⁻¹)
Boscan	406	4958	425	4798
Carabobo	442	2057	576	2221
Ceuta	100	862	105	808
Hamaca	423	1934	462	1843
Monagas	253	1124	269	1154

^a Results are the mean of three replicates with a 4% relative standard deviation.

but the solvent load may affect the plasma discharge. Besides, asphaltene fractions have different solubility behavior. A1 is partially soluble in chloroform and insoluble in toluene, and A2 is soluble in these solvents;²¹ therefore, it is difficult to select one solvent to ensure the total dissolution of both fractions. Heating of the sample using a microwave digestion system with a high-pressure closed vessel is an excellent alternative to avoid the differences in the solubility of these fractions without consuming excessive time for the analysis and with the benefits that inorganic standard solutions can be used to elaborate the calibration curve.²³ In this sense, it was applied to the microwave heating program presented in Table 3. This digestion method was previously optimized in the laboratory. Portions of 0.2000 g of the sample were weighted into PTFE digestion vessels with 10 mL of concentrated HNO₃. After cooling, the digest was treated with 2 mL of 30% (v/v) H₂O₂ and diluted with water to 50 mL in a volumetric flask. Finally, Ni and V were determined using the ICP–OES technique. Results were contrasted with those obtained with the conventional ashing method using nitric acid to test the reliability of the microwave digestion method.

Table 4 presents the results of Ni and V determined in asphaltene samples using the microwave digestion and the traditional calcination methods.²⁴ Significant test (*t* test) at a confidence level of 95% indicates that the results obtained by both methods were in a good agreement; therefore, this procedure can be used for analysis of asphaltenes and their fractions.

Ni and V Concentration in Asphaltenes and Their A1 and A2 Fractions. It has been reported that solubility differences between A1 and A2 are not only related to the differences in molecular mass, aromaticity, and heteroatom and organic elemental content, exhibited by these asphaltene fractions. The nature of the molecular structure must be considered.^{6,22} It has been proposed that A1 contains molecules having condensed aromatic and naphthenic rings (continental-type structure^{7,8,25}). These structures are rigid and allow for efficient intermolecular interactions. The interaction occurs in a large molecular extension (packing effect) that enables the penetration of the solvent making this fraction insoluble.²² On the other hand, A2 is mainly

Table 5. Determination of Ni and V in Asphaltenes and Their A1 and A2 Fractions^a

crude oil sample	entire asphaltene fraction			A1 fraction			A2 fraction		
	Ni (mg/kg)	V (mg/kg)	V/V + Ni	Ni (mg/kg)	V (mg/kg)	V/V + Ni	Ni (mg/kg)	V (mg/kg)	V/V + Ni
Carabobo	442	2057	0.823	478	2190	0.821	310	1585	0.836
Hamaca	423	1934	0.821	447	2013	0.818	408	1917	0.824
Furrial	236	1220	0.838	292	1370	0.824	115	776	0.871
Monagas	253	1124	0.816	277	1200	0.813	156	802	0.837

^a Results are the mean of three replicates with a 4% relative standard deviation.

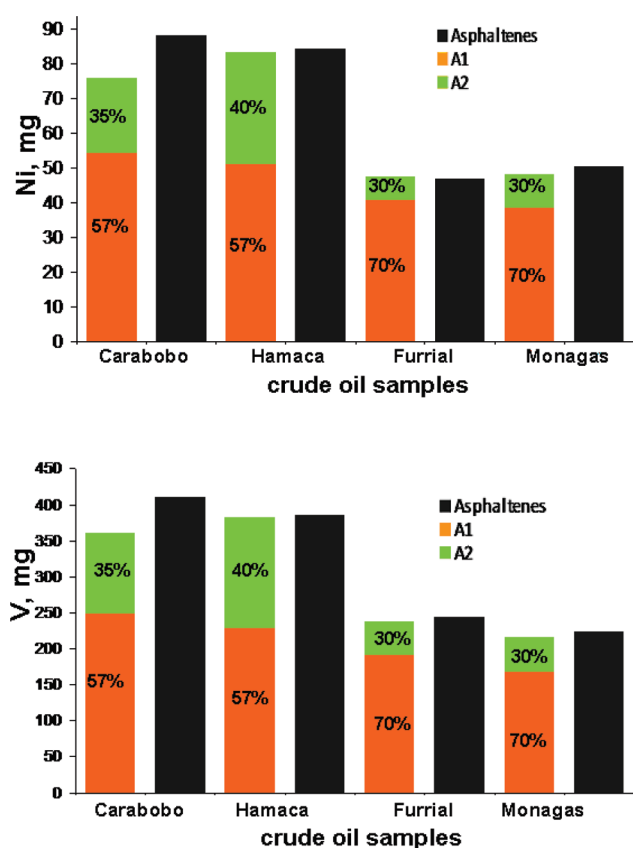


Figure 1. Ni and V distribution in asphaltene samples and their fractions.

composed of molecules with great flexibility that permits the internal rotation (archipelago-type structure^{7,8,25}) and is easily solvated or soluble.

It is well-known that metals, such as Ni and V, are linked to porphyrin compounds in the asphaltenes.^{11,12,26,27} A possible distribution of these metals in A1 and A2 fractions can be also associated with the molecular characteristics and colloidal behavior of the asphaltenes. In this connection, PNP complexes were used to fractionate the asphaltenes and determine Ni and V in each fraction to obtain the metal distributions.

Table 5 lists Ni and V concentrations in asphaltenes and their A1 and A2 fractions. It can be appreciated that A1 shows higher Ni and V concentrations than A2, in both stable (Hamaca and Boscan) and unstable (Furrial and Monagas) crude oils. It is important to state that V and Ni values are expressed in concentration units (mg/kg); therefore, the absolute amount of the metals in each fraction can be obtained by multiplying a sample

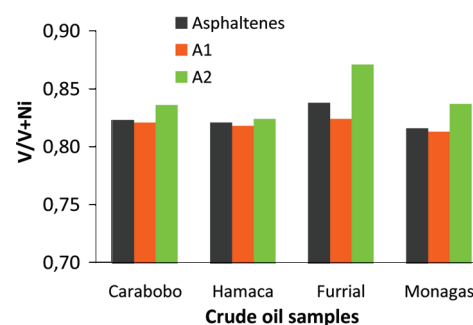


Figure 2. V/V + Ni ratios for asphaltenes and their fractions.

mass of 0.2000 g. Figure 1 presents the mass balance of Ni and V obtained by using the concentration in each asphaltene fraction (A1 and A2). The percentage content of A1 and A2 corresponds for each asphaltene sample, and these data were taken from the literature.^{15,21,22} The sum of the masses of Ni or V from A1 and A2 when compared to the amount obtained with our analysis of the original asphaltene samples (also presented in Figure 1) does not present significant differences. The little divergences can be attributed to the experimental error associated with the PNP method.¹⁵ However, the biggest variation found in Carabobo crude oil can be explained by the remotion of natural surfactants (around 6–10%) using alkaline solutions during the fractionation process. This fact was previously reported by Acevedo et al.²²

This almost perfect mass balance indicates that V and Ni compounds (porphyrin and non-porphyrin) are strongly linked to asphaltenes and are not easily removed by the fractioning process. This behavior can be explained by the existence of strong covalent interactions with asphaltenes. This fact was visually tested by using acetonitrile extraction (solvent commonly used to extract the porphyrin compounds at room temperature for 24 h). The extraction of these compounds can be assured by the presence a purple-colored dissolution (typical of porphyrin compounds). A1 did not show a purple color, and A2 presented a slightly colored dissolution.

It can also be noticed from the calculated mass of Ni and V shown in Figure 1 that A1 presents the higher metal content, specifically in unstable crude oils (Furrial and Monagas). This result clearly demonstrates a preferential metal distribution in the insoluble asphaltene fraction. This difference is independent of the A1/A2 ratio of the original sample (also shown in this figure), and it can be attributed to the rigid and flat structural core of their aromatic and naphthenic rings of A1 molecules, when compared to the rosary- or archipelago-type structure of the A2 fraction.

V/Ni and V/V + Ni ratios are used in geochemistry as a classification or genetic association (oil-to-oil and oil-to-source rock correlations) parameter with the origin and formation of oil

Table 6. Organic Elemental Analysis of C, H, N, and S in Asphaltenes and Their A1 and A2 Fractions^a

crude oil sample	entire asphaltene fraction					A1 fraction					A2 fraction				
	C	H	N	S	H/C	C	H	N	S	H/C	C	H	N	S	H/C
Carabobo	83.2	7.9	2.0	5.9	1.14	82.0	6.9	1.0	3.9	1.02	82.2	6.7	1.4	2.7	0.98
Hamaca	82.6	7.9	1.4	4.6	1.15	85.9	6.1	1.4	3.2	0.85	81.5	7.5	1.0	3.1	1.10
Furrial	87.4	7.1	1.3	2.1	0.98	89.3	6.3	0.7	1.1	0.85	83.7	6.9	1.4	1.0	0.99
Monagas	87.6	6.9	1.6	2.7	0.96	88.6	6.3	1.3	1.8	0.85	83.8	6.8	1.4	1.0	0.97

^aResults are the mean of three replicates with <1% relative standard deviation.

and with the history of migration and accumulation in oil fields.^{28–30} Some researchers consider that the V/V + Ni ratio can be used as fingerprint of the source rock or can be used to evaluate biodegradation processes.^{26,27,29,30} In this sense, this ratio in A1 and A2 was used to compare the type of metallo compounds presents; that is, a similar V/V + Ni ratio means the same type of metallo compounds presented in both fractions.

Figure 2 presents the V/V + Ni ratios of the asphaltenes and the A1 and A2 fractions (see Table 5 for values). It can be appreciated that the A2 fraction presents the higher ratios, mainly for Furrial and Monagas samples (the unstable crude oils). It is evident that, not only is the metal distribution in A1 and A2 preferential, the structure of metal is also different; this is, A1 and A2 may present different metallo compound composition (porphyrins or non-porphyrins). The latter comment indicates the importance of the speciation analysis of A1 and A2.^{29,31} Also, these results could explain the solubility behavior of these fractions and their possible participation in the colloidal behavior of asphaltenes in the crude oil.

Elemental H, C, N, and S Composition in Asphaltenes and Their A1 and A2 Fractions. The organic elemental analyses were also obtained to obtain more information regarding the elemental composition of A1 and A2. Table 6 presents the C, H, N, and S content and H/C ratio used to compare the aromatic character of the fractions. Results show that stable crude oils present bigger H/C values or lower aromatic contents, and these results are similar to other studies.^{14,20,26,27} A1 presents lower H/C and N values than A2. This is in agreement with a higher aromatic condensation and, therefore, more capacity to interact and trap metalloporphyrins. Finally, S presents the same Ni and V behavior in the asphaltenes and A1 and A2 samples; it is higher in A1 than A2, which indicates a strong association with Ni and V metallo compounds.^{13,17,32}

CONCLUSION

The existence of Ni and V in A1 and A2 asphaltene fractions demonstrates the presence of trapped porphyrin and non-porphyrin compounds in the asphaltenes that are not easily removed in the PNP fractionation method. The A1 fraction presents higher Ni and V content and high aromatic character than the A2 fraction. This can be associated with differences in the metal compound distribution; therefore, the speciation analysis of these compounds in asphaltenes and their A1 and A2 fractions would be important. The knowledge of these structures associated with Ni and V can help to understand the kind of molecular interactions and can demonstrate any possible participation of the metalloporphyrins in the aggregation mechanisms of asphaltenes, the differences in the solubility between A1 and A2 fractions, and their influence in the crude oil stability.

Finally, digestion and analysis of asphaltenes and their A1 and A2 fractions can be easily accomplished using a microwave digestion system and ICP–OES techniques, respectively.

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