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Energy Fuels, **Just Accepted Manuscript** • DOI: 10.1021/acs.energyfuels.8b03951 • Publication Date (Web): 22 Jan 2019

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Temperature dependence of the EPR spectrum of asphaltenes from Venezuelan crude oils and its vacuum residues

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Keywords: Electron Paramagnetic Resonance, Asphaltenes, Curie-Weiss like temperatures

ABSTRACT

The Electron Paramagnetic Resonance (EPR) technique is used to evaluate the temperature dependence of the aggregation processes in asphaltenes of heavy and extra heavy crude oils and its vacuum residues from Venezuelan Oil Belt. All the EPR spectra of the samples studied show an intense central signal assigned to Free radicals (FR) and a multiplet due to the presence of a V⁺⁴ porphyrin. From the analyses of the inverse of the normalized area as a function of the temperature for the FR signal and the most intense peak in the vanadium

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3 multiplet, we obtain a set of temperatures related to the transition of fast-to-slow motion
4 regions, the temperature of generation-recombination of FR and cracking temperature in all
5 the samples. On the other hand, applying a Curie-Weiss law we obtain the order-disorder
6 temperatures and correlated them with the API grade of the samples. A computational
7 simulation was performed in order to propose possible conformers based on the experimental
8 data to confirm our results, which can be used as a probe of the structural and conformational
9 changes in asphaltenes structure.
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20 INTRODUCTION

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23 The understanding of the mechanisms of interaction between the different constituents of
24 crude oil is one of the most desired goals by researchers in the area. A clear understanding of
25 these mechanisms would be a very important factor to comprehend the processes of
26 aggregation of asphaltenes in crude oils. Vacuum residues, extra-heavy and heavy crude oils
27 are very complex structures, mainly they are constituted by groups of chemical compounds
28 classified as SARA: Saturates, Aromatics, Resins, and Asphaltenes [1,2]. Asphaltenes are
29 defined as the heaviest constituents of crude oil insoluble in normal alkanes [3] and impact all
30 aspects of crude oil production and utilization. Asphaltenes structure contains many
31 aromatics fused rings with heteroatoms (N, S, and O) in different functional groups, metals
32 (Ni, Fe, and V) mostly in porphyrins form. Also, asphaltenes structure is characterized by the
33 presence of aliphatic chains with different lengths, free radicals (FR), and vanadyl ions.
34 Because of these characteristics, asphaltenes are the heaviest and most complex compounds
35 present in heavy crude oils. Martyanov et al. [4] and Gafurov et al. [5] state that a
36 fundamental condition for the development of effective processes for heavy oil production
37 and processing is the understanding of the key factors that determine the aggregative
38 behavior and stability of oil disperse systems (ODS), behavior and chemical transformations
39 of their components under various external conditions including elevated temperature.
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3 The crude oils are subjected to innumerable processes in the oil industry. Within these
4 processes, it is possible to mention two fundamental ones: atmospheric distillation and
5 vacuum distillation. Initially, crude oils are subjected to an atmospheric distillation, in which
6 the petroleum products are separated by means of the boiling temperatures according to each
7 dish of the atmospheric distillation tower. The residue of the distillation tower obtained at
8 temperatures less than 350 °C is known as atmospheric residue. This residue is used as a load
9 in the vacuum distillation tower where physical separations occur as a function of the boiling
10 point as in atmospheric distillation. The residue obtained from the vacuum distillation tower
11 (temperatures <350 ° C) is known as a vacuum residue [6,7].
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24 In spite of advances in analytical techniques, Electron Paramagnetic Resonance (EPR) is
25 still applied in studies of paramagnetic properties of crude oils and their fractions, mainly
26 asphaltenes [8,9], vacuum residues [10,11, 12,13], as well as, in determining the nature of the
27 metal complexes in this type of compounds. The majority of metals in oil have been located
28 in the polar fractions (resins and asphaltenes), most concentrated in the asphaltenes though a
29 part of vanadium (IV) complexes, which is not trapped there but remains in the crude oils
30 bulk fraction [14]. EPR is a non-destructive technique and a very useful tool for
31 characterizing paramagnetic species. It is used to detect and characterize free radicals among
32 others. EPR gives quantitative information about the magnetic behavior of materials [15].
33 EPR technique does not require the diluted samples and can sense the intrinsic paramagnetic
34 centers also in the unfractionated species, i.e., in the native environment [16,17].
35 Polyconjugated systems in asphaltenes molecules, where electrons are delocalized, have been
36 studied by EPR obtaining a paramagnetic species concentrations between 10^{18} to 10^{20} spin/g
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56 EPR experiments have been carried out on asphaltenes from different crude oils in order to
57 elucidate the relation between asphaltenes structure, morphology and their tendency to form
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3 aggregates [8]. Asphaltenes EPR spectra show the signals of paramagnetic VO^{+2} cations and
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5 of organic free radicals. The temperature effect on the EPR line intensity was investigated in
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7 argon and pure oxygen. The results show that radicals behave as paramagnetic molecules in
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9 all temperature range test in argon, there is a linear dependence of the reciprocal of the EPR
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11 intensity on the absolute temperature in accordance with the Curie-Weiss law. In oxygen, the
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13 temperature effect on the EPR line intensity is dramatically different and does not follow the
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15 Curie-Weiss law in all the temperature range [8]. The evolution of the EPR signal as a
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17 function of temperature is affected by multiple factors and various mechanisms are proposed
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19 to explain the behavior of the EPR intensity of the free radicals in asphaltenes. Acevedo et al.
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21 [19] state that free radicals are trapped in the internal structure of asphaltenes and when they
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23 are treated chemically or thermally, the radicals are exposed, thus increasing their
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25 concentration. Dolomatov et al. [20,21] propose that the increase in the intensity of the EPR
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27 signal when increasing the temperature is related to several mechanisms, among others
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29 breakdown of bonds by thermal decomposition, radical recombination, and the triplet-singlet
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31 transition. The magnetic susceptibility is evaluated from the normalized area (A_N) under the
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33 absorption curve in the EPR spectra for all the studied samples. In accordance with the Curie-
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35 Weiss law, from the curve $1/A_N$ vs T , we obtain the order-disorder transition temperature in
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37 the paramagnetic centers, something like the Curie-Weiss temperature. In this work, we study
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39 the temperature dependence of the EPR line intensity from free radicals and vanadium
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41 (VO^{+2}) signals of asphaltenes of different Venezuelan heavy crude oils and for the vacuum
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43 residues of some of them. Temperatures obtained from this analysis could be used to
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45 characterize asphaltenes, generating information about a possible magnetic order-disorder
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47 transition at very low temperatures in free radicals and vanadium species and the correlation
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49 between the magnetic properties and the intrinsic characteristics of the crudes and vacuum
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51 residues that contains the asphaltenes.
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MATERIALS AND METHODS

Asphaltenes and vacuum residues (Carabobo, Hamaca and Zuata) were obtained from crudes of the Orinoco Oil Belt, a territory in the southern strip of the eastern Orinoco River Basin in Venezuela which overlies the world's largest deposits of petroleum. Also, we study samples coming from the western coast of the Maracaibo's Lake (Merey and Boscan). API gravity and asphaltenes content for each sample are listed in Table 1. Asphaltenes precipitation was conducted by heating extra-heavy crude oils (heavy crude oils and/or vacuum residues), and then by adding a ratio of 40 volumes of heptane per gram of sample. The mixture was continuously stirred for 4 hours and then left to settle for 24 hours. Subsequently, the vacuum filtration process was carried out and the asphaltenes + resins fractions were obtained. Asphaltenes were cleaned by Soxhlet extraction with heptane over 4 days or more. Asphaltenes were dried in an oven at 60 °C, and then 0.50 mg of each sample was introduced in an EPR tube.

The EPR experiments were carried out in an air atmosphere using a Bruker EMX spectrometer operating at X-band ($\nu = 9.33$ GHz) with a rectangular cavity equipped with an N₂ BRUKER temperature controller. The normalized area values for free radicals were determined using 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical as an external standard, and for the most intense signal in the multiplet of V⁺⁴ were determined employing 5,10,15,20-tetraphenyl-21H,23H-porphine vanadium (IV) oxide as a standard. All the measurements were performed in the $90 \leq T \leq 670$ K temperature range in stages of 15 K, each of the measured EPR spectra represents a point in the graph of the reciprocal of the normalized area ($1/A_N$) as a function of temperature.

DFT calculations were carried out using DMol3 code included in Materials Studio with the PW91 functional, the core treatment including all electrons and the DNP basis set. The

physicochemical characterization was used as feed for the establishment of the models of the average chemical structures of asphaltenes from heavy crude oils and vacuum residues.

Table 1. API gravity, asphaltenes content and its FR and V⁺⁴ concentration and linewidths.

Sample	Label	API gravity	Asphaltene Content (%)	Concentration of FR in asphaltenes, spin/g (x 10 ¹⁷)	Concentration of V ⁺⁴ in asphaltenes, spin/g (x 10 ¹⁹)	ΔH_{pp} [G] of FR	ΔH_{pp} [G] of V ⁺⁴
Carabobo Crude Oil (Extra-Heavy)	ASCC	8.1	13.6	23.2	8.4	6.9	12.9
Hamaca Crude Oil (Extra-Heavy)	ASCH	8.9	12.9	41.8	6.8	6.8	12.6
Merey Crude Oil (Heavy)	ASCM	16.0	8.2	131.1	6.9	6.3	12.7
Boscan Crude Oil (Heavy)	ASCB	10.5	17.2	2.4	10.2	7.8	14.1
Carabobo Vacuum Residues	ARVC	1.7	23.1	1372.4	24.6	6.7	12.5
Hamaca Vacuum Residues	ARVH	2.8	17.6	1163.1	13.8	6.6	11.9
Zuata Vacuum Residues	ARVZ	2.4	18.1	1257.6	41.3	6.9	12.5
Merey Vacuum Residues	ARVM	3.3	18.2	912.7	15.8	6.3	12.1

RESULTS AND DISCUSSION

In Figure 1 we show the EPR spectrum for ASCM asphaltenes at room temperature. A typical spectrum for crude oils [19,22,23] is shown in which a very intense and symmetrical signal around $g = 2.0052 \pm 0.0005$, attributed to stable carbon-centered "free" radicals (FR) in the sample is observed. It is noteworthy that this averaged signal includes all free radical

contributions in the sample and a less intense set of signals corresponding to V^{+4} in accord with a nuclear spin $I = 7/2$ for ^{51}V (in the inset of Figure 1 an extension of this line octet is shown). In Table 1 the ΔH_{pp} and the spin/g concentrations for the FR and V^{+4} in all the samples studied are shown.

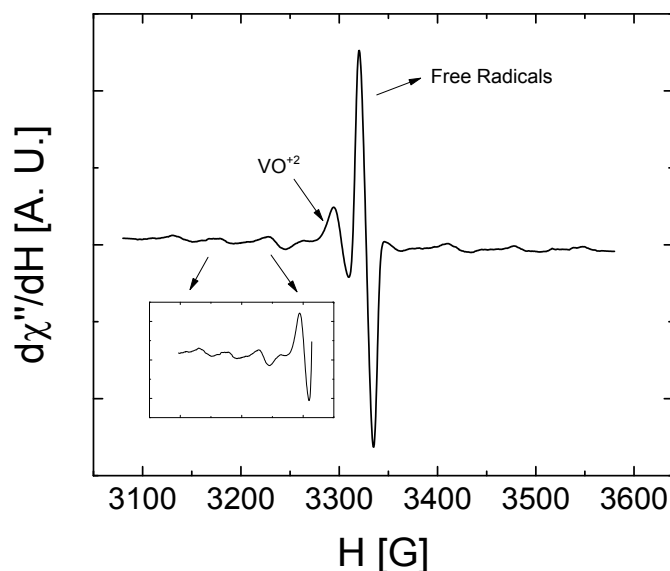


Figure 1. EPR spectrum of ASCM asphaltenes at room temperature.

EPR STUDY OF FREE RADICALS

Figure 2 shows the temperature dependence of the inverse of the normalized area of the EPR spectrum ($1/A_N$) for free radicals in asphaltenes from heavy and extra-heavy crude oils and its respective vacuum residues. Only results for ASCC, ARVC, and ASCM asphaltenes are shown, the rest of the samples are presented in the Appendix section. Each normalized EPR spectrum represents a point in graphs.

In Figure 2a, a linear behavior of the $1/A_N$ vs. T curve for the ASCC asphaltenes, in the temperature range $90 \leq T \leq 510$ K, in accordance with the Curie-Weiss law is observed:

$$\frac{1}{\chi} = \frac{T}{C} + \frac{\theta}{C} \propto \frac{1}{A_N} \quad (1)$$

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3 A sharp cusp appears at $T = 510$ K when the slope of the curve changes drastically from
4 positive to the negative one. The change from positive to the negative slope may be
5 associated with an increase in the concentration of the free radical number generated by
6 changes in the samples due to temperature effects. The behavior of the FR concentration has
7 several and complex origins. It is known that the thermal treatment leads to the destruction of
8 the asphaltene complexes onto the 4–5 small pieces [5] and mechanisms such as generation,
9 recombination and singlet-triplet transitions of state can occur [20,21]; by the other way, the
10 majority of the organic free radicals are concentrated in the structure of a condensed
11 polyaromatic core of asphaltenes molecules [14]; the changes in the structure, caused by
12 thermal treatment, *can peel the onion* and strip the radicals causing an increase in the free
13 radicals concentration observed by EPR [19]. We named this temperature as *cusp*
14 *temperature 1* (T_{c1}). We observe an increment in the count of free radical concentration up to
15 630 K where an abrupt change in slope occurred. Above $T = 630$ K a decrease in free radical
16 concentration was observed; maybe due to fast recombination of FR to form new chemical
17 bonds or because of the FR follows a Curie-Weiss law beyond the cracking temperature;
18 experiments at highest temperatures must be done. This temperature can be associated with
19 the *cracking temperature* of the sample, which is, in our case around 650 K [6,7]. In most of
20 the samples, a valley at sufficiently high temperatures, associated with the cracking
21 temperature of the same ones is obtained.

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47 From $1/A_N$ vs T curves, it follows that all the samples showed a linear behavior in the
48 temperature range $90 \leq T \leq T_{c1}$. ASCM asphaltenes (Figure 2c) and ARVM, ARVH, ASCB
49 and ARVMM asphaltenes (Appendix A.1) have additional changes in the slope at different
50 temperatures. The increase in the free radicals concentration occurs up to a temperature
51 named T_{v1} (valley temperature 1) where the recombination of free radicals starts to lower its
52 concentration. This phenomenon takes place until a cusp temperature named T_{c2} in which
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3 mass losses or structural changes may occur. It must be considered that ARVC (Figure 2b)
4 and ASCH (Figure A.1.b) did neither show temperatures T_{v1} , T_{c2} nor cracking temperature
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6 in the range of temperatures studied. Cusp and valley temperatures T_{c2} and T_{v1} (540 and 480
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8 K , respectively) obtained for ASCM asphaltenes (Figure 2c) are higher than those obtained
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10 for asphaltenes of its vacuum residue ARVM (Figure A.1.a, 510 and 450 K , respectively).
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12 Taking into account that T_{v1} is associated to recombination of paramagnetic species, could be
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14 considered that free radicals in ASCM are more stable than those in ARVM due to the last
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16 one requires higher temperatures to initiate its recombination. We regard those organic free
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18 radicals in ASCM are tertiary or are forming resonant structures, also higher temperatures are
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20 required for possible mass losses in ASCM, because of its free radicals are in aromatic
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22 structures, and it is necessary to supply more energy for the breakage of bonds.
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29 Meanwhile, ARVH asphaltenes (Figure A.1.c) show the temperatures: $T_{c1} = 440 K$, $T_{v1} =$
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31 $530 K$, $T_{c2} = 560 K$, and cracking temperatures = $650 K$ as long as ASCH asphaltenes only
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33 have a critical temperature T_{c1} . This behavior could be related to atmospheric distillation
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35 process (atmospheric residue) and subsequent vacuum distillations (vacuum residue) at which
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37 heavy crude oils are subjected, inducing structural changes in asphaltenes. It should be noted
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39 that this behavior not followed by free radicals in asphaltenes from Carabobo extra-heavy
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41 crude oils ASCC (Figure 2.a) and its respective vacuum residue ARVC (Figure 2.b). The
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43 ASCH sample (Figure A.1.b) does not show cracking temperature, may because the cracking
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45 temperature in this sample is out of the temperature range of the measurements. Free radicals
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47 in asphaltenes from different vacuum residues have similar behavior as its counterparts in
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49 heavy crude oils; i.e. these radicals exhibit a linear behavior from $90 K$ to T_{c1} in accordance
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51 with the Curie-Weiss law for paramagnetic systems at low temperatures.
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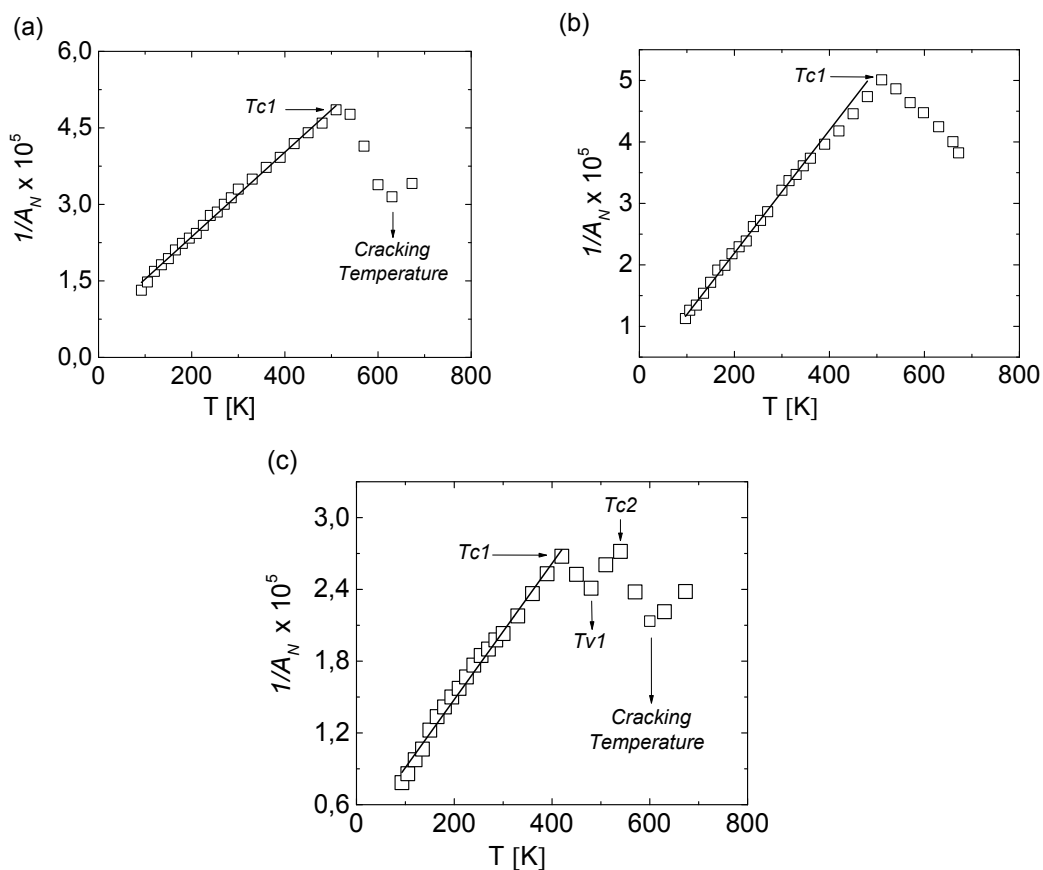


Figure 2. Reciprocal of the normalized area for free radicals vs. Temperature: (a) ASCC; (b) ARVC; (c) ASCM.

In Figure 3, the behavior of the linewidth as a function of the temperature of the FR for all the samples under study is shown. An almost constant trend of linewidth over the entire temperature range is observed, which is indicative that the behavior of the inverse of the normalized area for free radicals is essentially due to the increase or decrease of free radicals concentration and not to conformational changes in the sample.

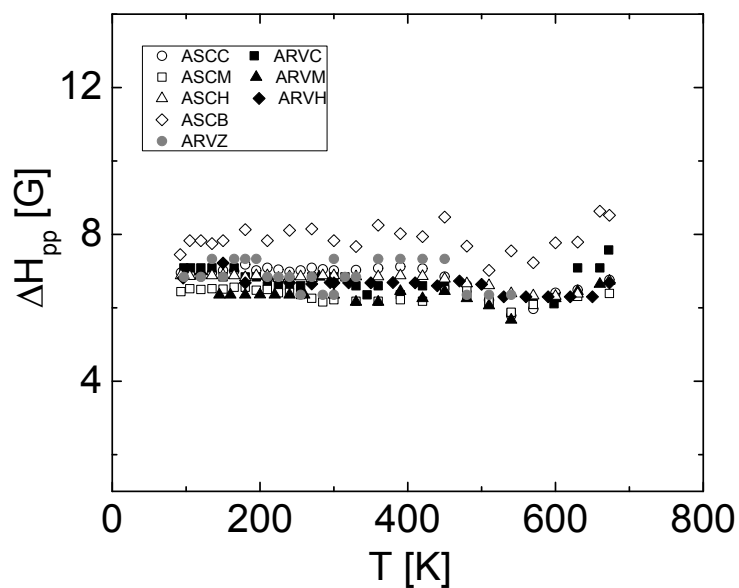


Figure 3. Temperature dependence of the ΔH_{pp} of the FR for all the samples studied.

In Table 2 we show the temperatures obtained by fitting the inverse of the normalized area for free radicals in all the samples studied. From the best fit, we obtain a Curie-Weiss-like (T_{CW1}) temperature, for free radicals, which we can name order-disorder temperature, indicative of a possible weak antiferromagnetic ordering of the spins at low temperatures. These order-disorder temperatures are lower for free radicals in asphaltenes of vacuum residues than those of its counterparts heavy and extra-heavy crude oils in accordance with the increase of spin concentration in the former ones (Table 1).

In Figure 4 the dependence of T_{CW1} temperature with its API gravity for free radicals in asphaltenes from heavy crude oils is shown. The Curie-Weiss-like temperature linearly increases in modulus with the decrease of the API gravity. An increase in the T_{CW1} temperature modulus is related to an increase in the interactions between spins or paramagnetic species due to the decrease in the mobility of these species because of the increase in the viscosity of the sample.

Table 2. Temperatures obtained by fitting the inverse of the normalized area for free radicals.

Asphaltene	T_{c1} (K)	T_{v1} (K)	T_{c2} (K)	Cracking Temperature (K)	T_{CWI} (K)
ASCC	510	----	----	630	-85
ARVC	510	----	----	----	-12
ASCM	420	480	540	600	-60
ARVM	420	450	510	600	-200
ASCH	450	----	----	----	-83
ARVH	440	530	560	650	-128
ASCB	390	420	510	600	-77
ARVZ	510	----	----	600	-70

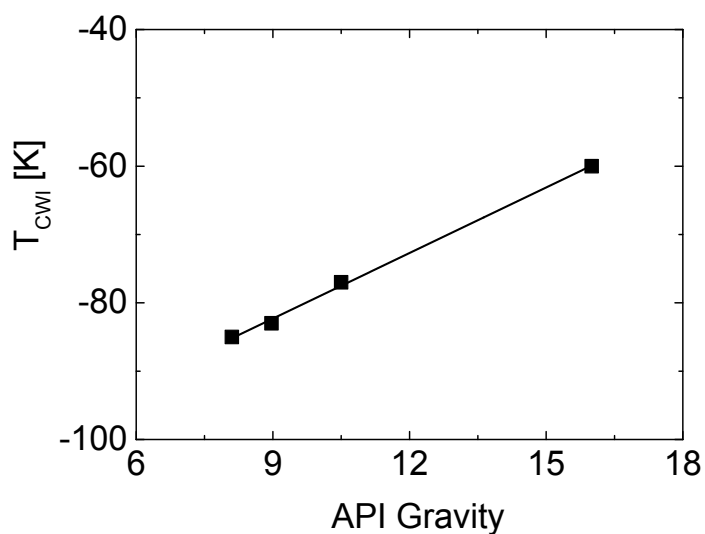
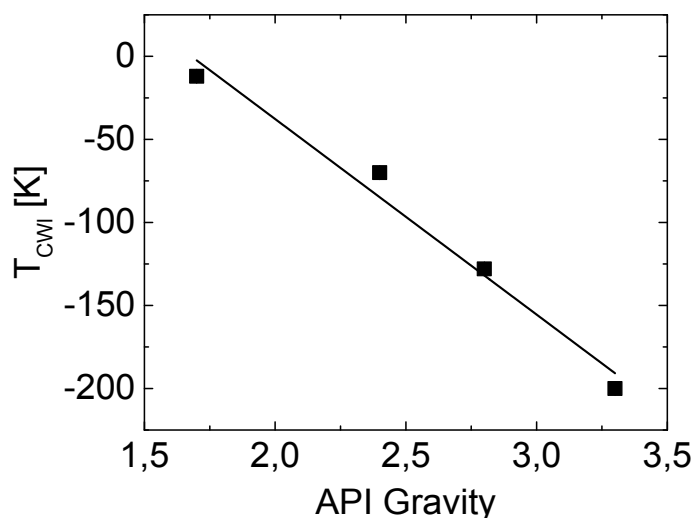


Figure 4. T_{CWI} temperatures for free radicals vs. API gravity of heavy crude oils.

The dependence of T_{CWI} temperature with API gravity of free radicals from asphaltenes of vacuum residues of heavy crude oils is presented in Figure 5. Linear decreasing behavior of the modulus of the T_{CWI} temperature with the API gravity increasing is observed, in accordance with a rise in the interaction between FR when increasing in the API gravity. In

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3 Table 1, we observe that the spin/g for the FR in vacuum residues have values greatest than
4 one order of magnitude than those for the heavy crude oils, such increment is accompanied
5 with an increment in the exchange interaction, increasing the T_{CWI} temperature. The spin
6 concentration follows a similar behavior than that followed by the graph in Figure 5
7 indicating a close correlation between these two behaviors. The highest concentration is
8 obtained for the lowest API gravity because of the lack of mobility of the FR.
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36 **Figure 5.** T_{CWI} Temperatures for free radicals vs. API gravity from vacuum residue of heavy
37 crude oils.
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41 EPR STUDY OF VO^{2+} SIGNAL

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43 Vanadium species in asphaltenes are generally in porphyrin structures with an oxidation
44 state V^{+4} ($\text{V}=\text{O}$) $^{+2}$. The V^{+4} ions are detectable by EPR due to the $3d^1$ electron configuration
45 (see Figure 1). Results obtained for the reciprocal of the normalized area vs temperature for
46 the most intense vanadium multiplet signal of the ASCC, ARVC, and ASCM are shown in
47 Figure 6, rest of all samples are shown in the Appendix section.
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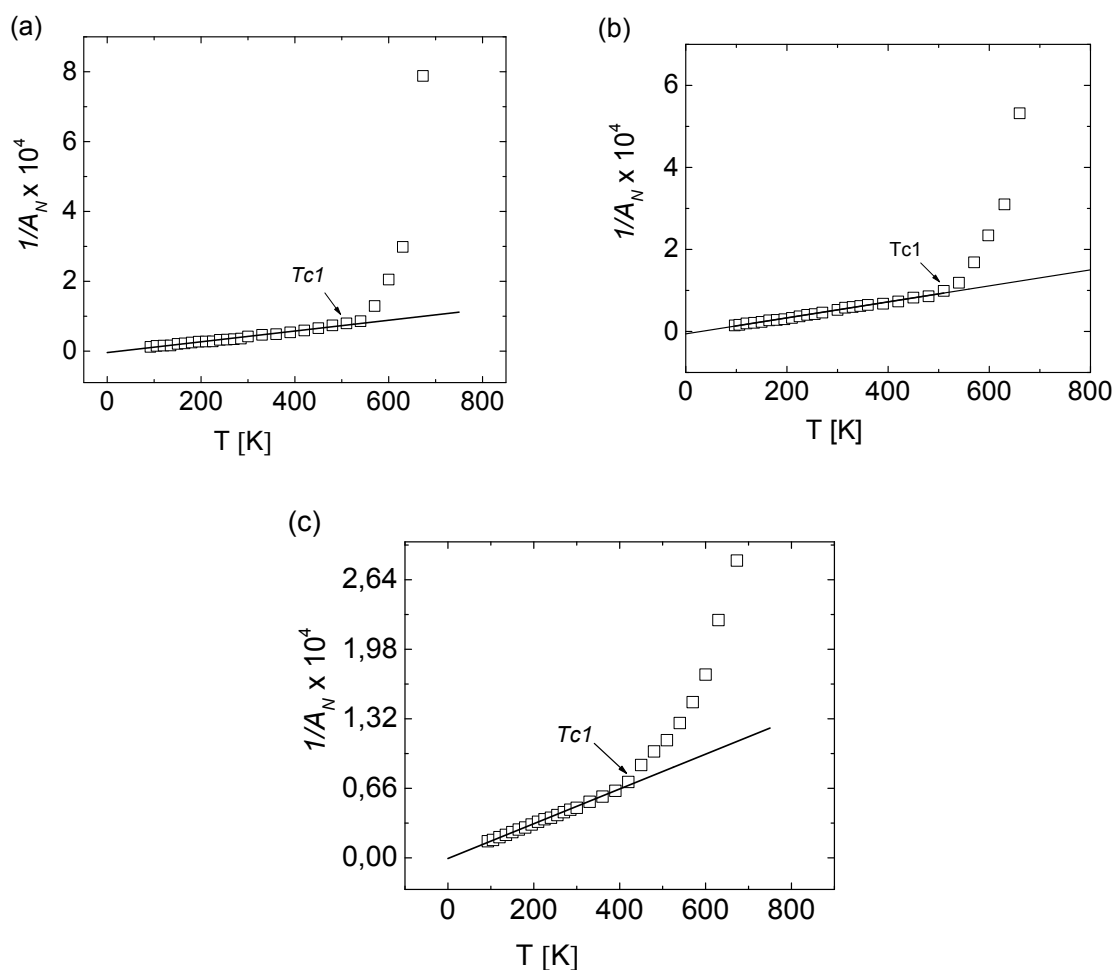
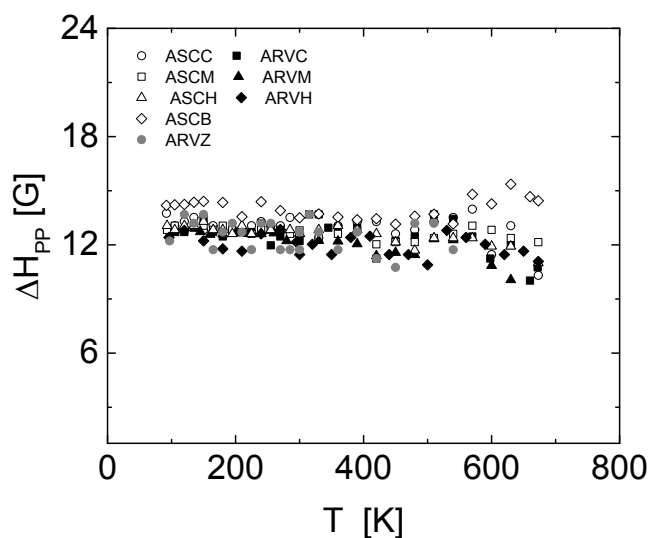


Figure 6. Reciprocal of the normalized area for the most intense signal in the multiplet of V^{+4} vs. temperature: (a) ASCC; (b) ARVC; (c) ASCM.

The straight line is a linear fit in the low-temperature region (linear region). Two zones are observed in Figure 6 (high and low-temperature regions). In the low temperatures region ($90 \text{ K} \leq T \leq T_{c1}$), a linear behavior in the $1/A_N$ vs T curve is observed in accordance with the Curie-Weiss law for paramagnetic systems. T_{c1} is the temperature at which the experimental data departs from this linear behavior and is the same one as obtained for FR. In the high temperatures range ($T_{c1} \leq T \leq 670 \text{ K}$), a sharp increase in the reciprocal of the normalized area is observed. Probably this behavior in the reciprocal area of the most intense signal of the vanadium spectra may be due to a change in the mobility of the vanadium ion, we explore this option in the next section. The reciprocal of the normalized area for the most intense

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3 peak of the vanadium EPR spectrum don't show the temperatures T_{c2} , T_{v1} , and cracking
4 observed for the FR, which indicates that free radicals are a good probe for detecting
5 structural changes in the samples. The plots for ARVC, ARVH, and ARVM show similar
6 behavior as those for ASCC, ASCH, and ASCM. In Table 3 we show the results of T_{c1} for
7 all studied samples.
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11 Figure 7 shows the Temperature dependence of the linewidth for the V^{+4} signal in all the
12 samples studied. An almost constant behavior of the linewidth in the whole temperature range
13 for all the samples studied is observed, so it can be said that the behavior of the inverse of the
14 normalized area as a function of temperature is not clearly linked to conformational changes
15 in the studied samples.
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Figure 7. Temperature dependence of the linewidth for the V^{+4} in all the samples studied.

Curie-Weiss-like temperatures obtained from the most intense signal in the vanadium multiplet are listed in Table 3. These T_{CW1} temperatures indicate that there are two types of magnetic interactions at low temperatures: an antiferromagnetic type interaction and ferromagnetic type interactions in which the magnetic moments align quasi-antiparallel ($\theta < 0$) and quasi-parallel ($\theta > 0$), respectively. The vanadium in asphaltenes ARVM, ARVH, and ARVZ display an antiferromagnetic-like order while the vanadium in the other

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3 asphaltenes samples shows a ferromagnetic-like order at low temperatures. These results are
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5 consistent with previous work for the vanadyl octaethylporphyrinate derivative [24].
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10 **Table 3.** Temperatures obtained for the most intense signal in the V^{+4} multiplet.
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Asphaltenes	T_{Cl} (K)	T_{CWI} (K)
ASCC	510	26
ARVC	510	30
ASCM	420	4
ARVM	420	-19
ASCH	450	11
ARVH	440	-34
ASCB	390	-6
ARVZ	510	-4

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36 In Figure 8 we show the dependence of T_{CWI} temperature with API gravity for heavy crude
37 oils. With exception of ASCM asphaltenes, obtained from Merey heavy crude oil (16 ° API),
38 the most intense line for the vanadium of asphaltenes of the other three samples shows that
39 the modulus of the T_{CWI} temperatures has a linear decreasing behavior with API gravity, as is
40 expected, due to the increase of the mobility of the paramagnetic species. Merey heavy crude
41 oil is the result of the mixture of three crude oils denominated: Mesa 30 (light crude),
42 Carabobo and Hamaca (both heavy crudes oils). This mixture of crude oils could be the
43 reason of the non-alignment in the straight line of ASTM asphaltenes.
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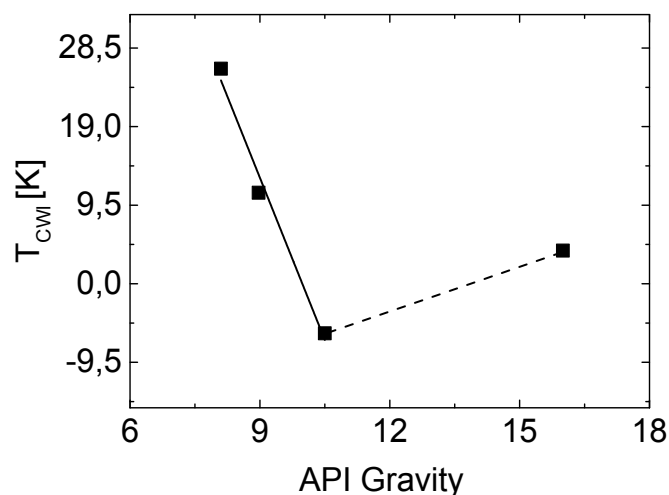
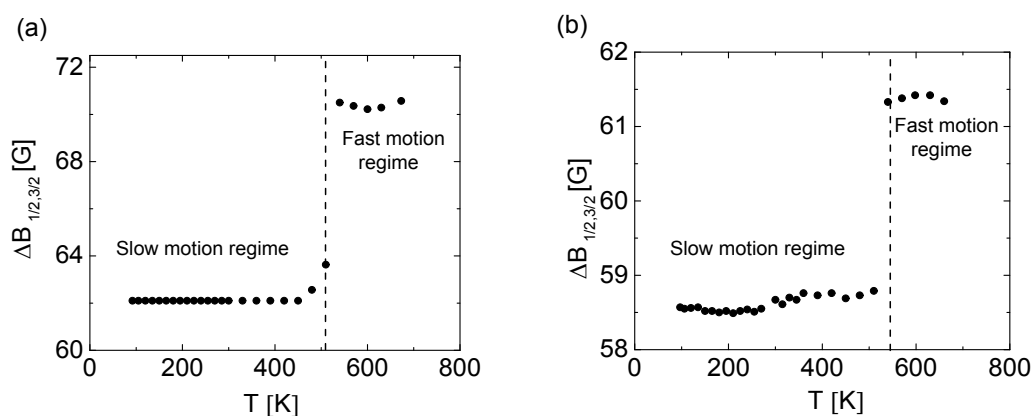


Figure 8. T_{CWI} temperature for the most intense signal of V^{+4} multiplet vs. API gravity of heavy crude oils.

In order to evaluate the effect of the temperature in the mobility of the paramagnetic ions, we measure the distance between the $m_l = \frac{1}{2}$ to $m_l = \frac{3}{2}$ transition in the EPR spectra of the vanadium as a scaling of mobility. Being diffusion a random process characterized by a correlation time τ we evaluate the $\Delta B_{1/2,3/2}$ as mobility parameter, which is the distance (in field) between hyperfine position 1/2 and the same one at position 3/2. The local magnetic fields induced by this type of motion initiate transitions with particular frequencies. This, in turn, influences the line shape of EPR spectra [14]. In addition, the analysis of the temperature dependencies of $\Delta B_{1/2,3/2}$ and EPR spectra suggests a discontinuous change of the rotational correlation time in the region close to the phase transition (only the values of $\Delta B_{1/2,3/2}$ related to a rigid regime and fast motion are observed; Figure 9) [14].

In Figure 9 we show the temperature dependence of the experimental values of $\Delta B_{1/2,3/2}$ obtained for $m_l = \frac{1}{2}$ to $m_l = \frac{3}{2}$ transition in the EPR spectra of vanadium for the heavy crude oil ASCC (Figure 9.a) and its vacuum residue ARVC (Figure 9.b), an abruptly jump in the $\Delta B_{1/2,3/2}$ parameter just in the temperature T_{c1} is observed, no coexistence of the slow

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3 motion and fast motion regimes, as has been noticed by other authors [5], is observed in our
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5 results, possibly due to the lack of resolution in the spectra; simulations to corroborate these
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7 results must be done. On the other hand, the change in the mobility parameter $\Delta B_{1/2,3/2}$ is
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9 smallest for the ARVC sample than that for the crude oil, maybe due to the ARVC sample is
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11 cleanest than the crude oil. The temperature T_{c1} can be associated with a change in the state
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13 of the sample from a slow-motion regime to a fast motion regime and the temperature T_{c1} is
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15 the same temperature than that obtained from the I/A_N when the curve moves away from
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17 linearity, so we can associate that behavior with a change in the motion regime of the
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19 samples. All the samples showed similar behavior, as we can see in the Appendix section, an
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21 abruptly jump at temperature T_{c1} associated with a change in the mobility regime.
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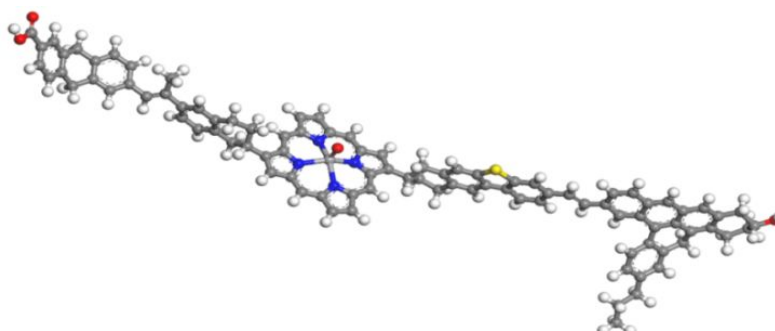
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41 **Figure 9.** Temperature dependencies of the experimental values of $\Delta B_{1/2,3/2}$ obtained for m_I
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43 $= \frac{1}{2}$ to $m_I = \frac{3}{2}$ transition in the EPR spectra of vanadium: a) ASCC; b) ARVC.
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46 COMPUTATIONAL SIMULATION

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49 With the aim of explaining our EPR results, we made a computational simulation of the
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51 possible structure of our asphaltenes. Different conformers were proposed from the physical-
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53 chemical characterization of each sample: NMR- ^{13}C , NMR- ^1H , SEC, and elemental analysis
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55 (C, H, N, and S) (these results will be published as soon as possible). Structural assignments
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57 of NMR- ^{13}C and NMR- ^1H are based on Poveda et al. work [25]. These assignments include:
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3 non-protonated aromatic carbons; benzo and dibenzo aromatic carbons type alpha to oxygen
4 atom; methyl carbons in the alpha position to aromatic rings; aromatic hydrogen linked to
5 aromatic carbons in di or polyaromatic rings; and aromatic hydrogen linked to monoaromatic
6 rings. Following structural assignments, geometrical optimizations were carried out that
7 allowed choosing one conformer as an average chemical structure representative for each
8 asphaltene. As it follows from Figure 10 that ASCM asphaltenes structure include linear and
9 branched aliphatic chains of different length (methyl, ethyl, and iso-butyl groups),
10 cycloalkanes and benzene rings. It is well known, that free radicals formation reactions from
11 n-alkanes and cycloalkanes are even more effective than those with an involved aromatic
12 structure [26]. It may arise that the cycloalkanes allow the formation of free radicals, and
13 through the aromatic rings, these radicals remain stable being able to justify that the
14 temperature $T_{v1} = 480$ K obtained for this type of asphaltenes is higher than the temperature
15 $T_{v1} = 450$ K (Table 2) presented by the ARVM asphaltenes, that is, free radicals in ASCM
16 asphaltenes must be supplied with more energy to promote the recombination of their free
17 radicals. This behavior can be reinforced by the fact that the temperature T_{c2} is higher for
18 ASCM asphaltenes (540 K) compared to the ARVM asphaltenes (510 K). The aliphatic
19 structures could justify the presence of the cracking temperature in 600 K.

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42 Molecular Formula $C_{94}H_{74}N_4O_4SV$ Molecular Weight = 1406,65 a.m.u
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3 **Figure 10.** Representative average chemical structure of ASCM asphaltenes obtained from its
4 physical-chemical characterization.
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8 SUMMARY 9

10 The inverse of the normalized area of absorption curve shows four temperatures, T_{c1}
11 associated to free radicals generation, T_{v1} associated with free radicals recombination, T_{c2}
12 related to possible mass losses; and cracking temperature associated with cracking processes
13 of resins and asphaltenes. T_{c1} temperatures for FR are in concordance with those
14 temperatures for vacuum residues of heavy crude oils indicating a thermal stability of the
15 system. T_{CWI} temperatures obtained for free radicals linearly increase with the API gravity of
16 crude oils. Results of inverse of the normalized area of the absorption curve of the EPR
17 spectrum of vanadium as a function of temperature indicate that vanadium in asphaltenes
18 from heavy crude oils has a ferromagnetic-like order at low temperatures with exception of
19 ASCB while vanadium of asphaltenes from vacuum residues of heavy crude oils shown an
20 antiferromagnetic like order at low temperatures with exception of ARVC and ARVMM.
21 Curie-Weiss-like temperatures obtained for the most intense signal of vanadium multiplet in
22 asphaltenes from heavy crude oils decreases with increases of the API gravity. Curie-Weiss-
23 like temperatures obtained for free radicals indicates an antiferromagnetic order at low
24 temperatures for all samples studied by EPR. Our results can be used as a probe for the
25 structural and conformational changes in asphaltenes and may be used as a method for
26 determined the API gravity in heavy crude oils.
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52 ACKNOWLEDGMENT AND DEDICATORY 53

54 The authors wish to thank the Institute of Venezuelan Technology for Petroleum
55 (INTEVEP), through the IVIC-INTEVEP agreement for providing all the samples in this
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3 study. On the other hand, this work is especially dedicated to the memory of Olga Castellano,
4
5 who in life was a fundamental member of this teamwork and promoter of this research work.
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