

# Articles

## Observations about the Structure and Dispersion of Petroleum Asphaltenes Aggregates Obtained from Dialysis Fractionation and Characterization<sup>†</sup>

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A sample of asphaltenes (ACN) precipitated from Cerro Negro crude oil had been divided into 14 fractions using a dialysis procedure employing THF–acetone mixtures as the extracting solvent. Seven extracts (F<sub>1</sub>–F<sub>7</sub>) and the corresponding residues R<sub>1</sub>–R<sub>7</sub> were obtained as the mixture composition changed from 40 to 100% THF. These materials were characterized by elemental analyses, VPO, solubility, C-13 NMR, and electron paramagnetic resonance (EPR). As the last fractions are approached, the following trends were observed: H/C decreases, aromaticity increases, solubility decreases, and S<sub>d</sub>, the spin density, increases. Removal of the first fraction (F<sub>1</sub>, 15% of ACN, acetone–THF (40%)) afforded a residue (R<sub>1</sub>) insoluble in toluene, indicating that 85% of ACN is present as colloidal particles (R<sub>1</sub>) dispersed in this solvent by F<sub>1</sub>. More than 12% of ACN found in the last residues (R<sub>6</sub> and R<sub>7</sub>) were found to be insoluble in organic solvents, suggesting that these fractions are formed by aggregates of molecules held in place by strong intermolecular forces. In an asphaltene micelle they would be at the core and its solubility in organic solvents is due to dispersion by the other components of the micelle. Although other effects are not disregarded, it is suggested that transannular electron delocalization in free radicals could play an important role in aggregate formation.

### Introduction

There is some direct and indirect evidence of the presence of asphaltene in crude as colloidal dispersion. Activities in this direction started at the beginning of this century with the work of Mack,<sup>1</sup> Pfeiffer,<sup>2</sup> Nellensteyn,<sup>3</sup> and others.<sup>4,5</sup> Among other things these researchers proposed that asphaltenes are colloids dispersed in asphalt and bitumen by resins. Kats,<sup>5</sup> on the basis of electron microscope measurements, suggested that asphaltene colloids, if present, should have diameters less than 65 Å. Pollack and Yen,<sup>6</sup> using X-ray small angle scattering proposed diameters between 30 and 50 Å for spherical particles of asphaltenes. Leon-

taritis and Mansoori<sup>7</sup> have proposed that flocculation of asphaltenes after the addition of pentane or hexane is due to desorption of resins from the asphaltene colloids. Similar propositions were made earlier by Van Kerkvoort et al.<sup>8</sup> and Heithaus.<sup>9</sup>

Andersen and Birdi<sup>10</sup> and Sheu et al.<sup>11</sup> have reported cmc for asphaltenes using calorimetric and surface tension measurements, respectively. Sheu and Storm,<sup>12</sup> using SANS, have reported that asphaltenes are poly-disperse spheres with a radius around 32 Å when measured in toluene–pyridine mixtures.

Asphaltenes samples had been the subject of some

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EPR studies in the past.<sup>13,14</sup> Usually, a relative low concentration of radicals is found in these samples, and hence, their role in asphaltene aggregation could be minor.

In this article we present the results of an asphaltene fractionation using a dialysis procedure. As shown below, these results give strong support to the presence of asphaltenes as colloidal particles in both organic solvents and crude oils. Also, this fractionation has proved to be useful in the EPR studies of the core of asphaltene aggregates.

### Experimental Section

**Materials.** Cerro Negro extra heavy crude oil (8° API) containing 13% asphaltene (ACN) was used.

**Asphaltenes.** These were obtained from a 1:1 mixture of toluene and crude oil after the addition of 60 volumes of *n*-heptane as described earlier.<sup>15</sup> When "pure" asphaltene were required, the precipitate was stripped of resins and other components by Soxhlet extraction with *n*-heptane for 30 h. Elemental analyses of pure asphaltene showed the following: C, 81.2; H, 7.7; N, 2.1; S, 4.5; H/C, 1.16.

**Octylated Asphaltene (OA).** These OA samples were synthesized using the described method.<sup>16</sup> In brief, asphaltene are treated with potassium naphthalide (**I**) prepared in situ by the reaction between naphthalene and potassium in dry THF under argon. Reaction between **I** and pure asphaltene involves reduction of asphaltene by electron transfer, leading to sulfide and carbanion, which are then quenched by the addition of octyl iodide.<sup>16</sup> About 4 *n*-octyl groups per 100 carbons atoms are incorporated in the asphaltene.<sup>17</sup>

**Methods. SARA Analysis.** The precipitated asphaltene obtained above was placed in a Soxhlet and extracted with *n*-heptane, and six liquid fractions were collected during a period of 30 h. The first two fractions were collected within the first 2 h of extraction. Longer periods were employed for the other fractions. After evaporation of the solvent the saturated, aromatic resins and asphaltene content of these fractions (SARA analysis) were determined by an automatic thin layer equipment provided with a flame ionization detector. Silica rods (0.9 mm diameter) were used. These are sold by the manufacturer in a rack containing 10 rods. A 1  $\mu$ L of a toluene solution (ca. 2%) of the sample was applied to the rods, and after drying, the rack was placed in a tank containing hexane. The tank was stoppered, and the chromatography was performed until the solvent reached a mark placed at the top of the rods. This procedure was repeated with a second tank containing toluene and then with a third containing a dichloromethane (60%)–methanol mixture.

**Asphaltene Fractionation.** A simple flask device, constructed with two cylindrical glass tubes of different diameters and lengths, was used in this experiment. The device is similar to a cylindrical funnel (diameter of 3 cm) with a long stem. About 1.3 g of pure asphaltene (see above) was placed in a Teflon membrane (pore size of 0.2  $\mu$ m). The membrane was attached to the device, placed in a Soxhlet apparatus, and the sample was extracted with boiling mixtures of acetone and tetrahydrofuran (THF) for 24 h for each mixture (seven in total; see Table 2). The temperature range from the first solvent mixture (40% THF) to the last (100% THF) was 57.6–62 °C. After each extraction, samples of both the extracted

solution (F) and the residue asphaltene (R) were prepared for analyses.

**EPR Experiments.** The EPR experiments were carried out at room temperature in a Varian E-line spectrometer working in the X-band ( $\nu = 9.3$  GHz) with a cylindrical cavity and a homemade coaxial microwave coupler for the X-band. The spin densities  $S_d$  or number of spin per gram of sample values were determined using the 4-(2-iodoacetamide)-2,2,6,6-tetramethylpiperidinoxyl radical as an external standard.

Experimental conditions (microwave power and modulation field) were adjusted to avoid saturation of signal intensity. Quantities between 17 and 9 mg of sample were employed. Intensities of samples ( $I_s$ ) were obtained from the spectrum by the usual procedure,<sup>18,19</sup> where the peak to peak high ( $Y_{pp}$ ) is multiplied by the square of the peak to peak bandwidth  $\Delta H_{pp}$ ; that is

$$I_s = Y_{pp}(\Delta H_{pp})^2$$

The spin density  $S_d$  of the samples were then calculated by referring this intensity to  $I_0$ , the one for the standard; that is

$$S_d^s = \frac{N_A}{M_0}$$

and

$$S_d = \frac{N_A I_s}{M_0 I_0}$$

where  $S_d^s$  and  $S_d$  are the spin densities for the standard and samples,  $N_A$  is Avogadro's number, and  $M_0$  is the molecular weight of the standard equal to 339.07 g/mol.

**Magnetic Resonance Spectra.** Solid-state C-13 spectra were taken in a high-resolution MSL-300 Bruker spectrometer, using the long recycling technique that allows for appropriate relaxation. HP/MAS was employed with a  $\pi/2$  pulse of 4  $\mu$ s and a recycling delay of 15 s. Samples (about 50 mg) were packed in a 4 mm rotor, and adamantane was used as an indirect chemical shift reference standard.

### Results and Discussion

**SARA Analysis.** On Table 1 we have collected the SARA results for the hexane extraction of "impure" asphaltene. As shown here, the precipitate usually is a SARA mixture of compounds. Thus, this precipitated material should be called asphalt rather than asphaltene.

The number average molecular weight values ( $M_n$ ) collected at the bottom of the Table 1 were estimated as follows.  $M_n$  for asphaltene is an experimental value taken from the literature, measured in pyridine by VPO.<sup>15</sup> Assuming ideal behavior, the other  $M_n$  could be obtained using eq 1 below:

$$M_n = \frac{100}{\sum_i \frac{w_i}{M_i}} \quad (1)$$

where  $w_i$  and  $M_i$  are the weights and molecular weight of the mixture components.

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**Table 1. SARA Results for *n*-Heptane Extracts of Asphaltenes Precipitated from Cerro Negro Crude Oil**

fraction	extraction time (h)	percentages				$M_n^a$
		saturates	aromatics	resins	asphaltenes	
1	0.5	4.6	8.5	66.2	20.7	1220
2	1		7.2	68.5	24.3	1230
3	2			75.2	24.8	1250
4	4			67.9	32.1	1180
5	24			62.2	37.8	1310
6	72			58.9	41.1	1320
$M_n$		1209 <sup>b</sup>	1569 <sup>b</sup>	1061 <sup>b</sup> (800) <sup>c</sup>	2000 <sup>d</sup>	

<sup>a</sup> GPC values (THF). <sup>b</sup> Calculated; see text. <sup>c</sup> Measured (VPO, benzene), ref 15. <sup>d</sup> Measured (VPO, pyridine), ref 15.

**Table 2. Properties of Asphaltenes Fractions (F<sub>*i*</sub>) and Residue (R<sub>*i*</sub>) Obtained by Extraction with Acetone-THF<sup>a</sup>**

	F <sub>1</sub>	F <sub>2</sub>	F <sub>3</sub>	F <sub>4</sub>	F <sub>5</sub>	F <sub>6</sub>	F <sub>7</sub>	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	R <sub>7</sub>
% <sup>b</sup>	15	4.6	10.3	21.9	13.4	11.6	6.31	85.0	80.0	69.8	47.9	34.8	23.2	13.0
$M_n$ (GPC)	1800	4500	4600	5300	5700	5700	5500	2900		3260	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>
H/C	1.21		1.33				1.15	1.2						1.05
solubility (g L <sup>-1</sup> , toluene)	91	72	123	58	3.2	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>
$f_a^e$	0.47	0.46		0.53	0.57		0.57	0.51		0.50		0.56		0.57

<sup>a</sup> Solvent sequence: % acetone 1:60, 2:50, 3:40, 4:30, 5:20, 6:10, 7:0. <sup>b</sup> Between 1.6 and 1.3 g of asphaltenes in the membrane. Average of three runs. <sup>c</sup> Owing to very low solubility in THF, no molecular weight could be measured. <sup>d</sup> Solubility too low (<0.5) to be measured (see Experimental Section). <sup>e</sup>  $f_a = C_{Ar}/(C_{Ar} + C_{AR})$ .

This equation can be written in the form

$$\frac{1}{M_k} = \frac{1}{w_k} \left( \frac{100}{M_n} - \sum_{j \neq k} \frac{w_j}{M_j} \right) \quad (2)$$

where the summation is over components other than *k*.

The value for the resins is an average of the four entries in Table 1, calculated using eq 2. By use of this average, the others could be estimated. For example, for the aromatics (A<sub>r</sub>),

$$\frac{1}{M_{A_r}} = \frac{1}{w_{AR}} \left( \frac{100}{M_n} - \frac{w_A}{M_A} - \frac{w_R}{M_R} \right) \quad (3)$$

by the reading of the values of  $w_{AR}$ ,  $w_A$ , and  $w_R$ , the percentage weights of aromatics, asphaltenes and resins, respectively, and the molecular weights of asphaltenes ( $M_A$ ) and resins ( $M_R$ ) from row 2 in Table 1, eq 4 is obtained after substitution:

$$\frac{1}{M_{A_r}} = \frac{1}{7.2} \left( \frac{100}{1230} - \frac{20.7}{2000} - \frac{68.5}{1061} \right) \quad (4)$$

and

$$M_{A_r} = 1569$$

The value for the resins, an average of the four entries in this table, is in fair agreement with the other reported previously for this sample<sup>15</sup> (see Table 1).

Even though the  $M_n$  values for saturates and aromatics may be in error, there is no doubt that these values should be high. This could be deduced from the small change experimented by  $M_n$  in going from fraction 3 to fraction 2 or to fraction 1. It is well-known that  $M_n$  averages are quite sensitive to low molecular weight values.

Although several mechanisms, such as dipole-dipole, electron transfer, etc., could be envisaged to account for the presence of soluble aromatics and resins in the precipitate, they are not useful for soluble saturates. Also, owing to the high  $M_n$  of these saturated compounds, they are not good candidates to fit in presumed

empty spaces of the colloidal structure of the precipitates. Rather, we suggest that during the precipitation procedure they get adsorbed at the colloidal surface in order to reduce the interfacial energy of the system (see below and Figure 2).

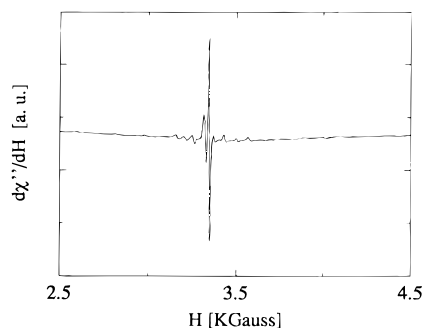
**Asphaltene Fractionation.** The results of the experiments are summarized in Table 2. Here, the specimens represented by F<sub>*i*</sub> and R<sub>*i*</sub> are, respectively, the materials extracted from the solvent mixture and the residue corresponding to that extraction. For the glass device employed, only small quantities of asphaltenes could be extracted. Because of low solubility, C-13 spectra were taken using solid asphaltene samples.

Perhaps the most interesting results in Table 2 are from the solubility test. About 85% of the sample (R<sub>1</sub>) is insoluble in toluene, although the whole sample (i.e., pure asphaltene) has a large solubility in this solvent (100 g L<sup>-1</sup>). Thus, the F<sub>*i*</sub> fraction acts as a surfactant for dispersing the colloidal particles in toluene.

In general crude oils are poorer solvents than toluene. Thus, it is expected that the solubility of fractions R<sub>*i*</sub> would be lower in the crude. Therefore, these results provide strong evidence that asphaltenes form colloidal particles dispersed in the crude by resins and other components.

In general, a decrease in solubility is observed in going from F<sub>1</sub> to F<sub>7</sub> with the exception of F<sub>3</sub>. Also, the solubility of R<sub>1</sub> in toluene was recovered when it was remixed with F<sub>1</sub>. However, when a similar test was performed with other specimens (for example, R<sub>2</sub> with F<sub>1</sub> plus F<sub>2</sub>, etc.), no dissolution or dispersion occurred. Thus, although removal of F<sub>1</sub> appears to be a reversible process, this behavior is exceptional.

The residues R<sub>1</sub>–R<sub>3</sub> were soluble (>10 g L<sup>-1</sup>) in THF. However, the solubility of R<sub>4</sub>–R<sub>7</sub> in this and other common solvents that dissolve asphaltenes (pyridine, nitrobenzene, chloroform, carbon tetrachloride, etc.) was very low (<0.5 mg/mL). The soluble fraction F<sub>1</sub>–F<sub>7</sub> amounted to 76.8% of asphaltenes. Thus, in this case the solvation energy of the THF-acetone mixture is enough to break any bond between these fractions and the rest. On the other hand, residue R<sub>7</sub> was insoluble in THF and in the other solvent mentioned above.



**Figure 1.** EPR spectrum of Cerro Negro asphaltenes.

**Table 3. Spin Densities  $S_d$  Measured for Several Samples**

	ACN <sup>b</sup>	ACNR <sup>c</sup>	OA <sup>d</sup>	R <sub>1</sub>	R <sub>3</sub>	R <sub>5</sub>	R <sub>7</sub>
$S_d \times 10^{-18}$ <sup>a</sup>	9.16	2.89	0.79	0.8	3.21	4.1	8.78

<sup>a</sup> Number of spins per gram of sample. <sup>b</sup> Asphaltenes for Cerro Negro. <sup>c</sup> ACN recovered from THF (see text). <sup>d</sup> Octylated asphaltenes.

Thus, it is doubtful that this solubility behavior is due only to strong intermolecular forces such as hydrogen bonding, permanent dipole–dipole, charge interactions, etc.

Solvents such as chloroform, acetone–THF, THF, and particularly pyridine are likely to break any polar interaction in organic compounds. In fact THF–acetone dissolves more than 70% of the sample in the way described above. Although the above polar interactions cannot be disregarded, we suggest that the low solubility discussed above for fraction R<sub>7</sub> is due to the formation of aggregates promoted by the presence of free radicals (see below).

Both H/C and C-13 results indicate that aromaticity ( $f_a$ ) increases when going from F<sub>1</sub> to F<sub>7</sub> or from R<sub>1</sub> to R<sub>7</sub> (see Table 2). However, these  $f_a$  changes are somewhat low in view of the H/C result for R<sub>7</sub>. A sample calculation will show that in passing from a H/C of 1.21 (the one for F<sub>1</sub>) to 1.05 for R<sub>7</sub>, eight double bond equivalents or insaturations will be required per 100 carbon atoms. Assuming these insaturations to be aromatic,  $f_a$  values around 63% should be expected. With these results, we believe that as the last fractions or residues are approached, there is an increase in  $f_a$ , favoring the stacking of aromatic structures and the appearance of strong and specific interactions between the molecules, which leads to the formation of insoluble aggregates (see below).

**Electron Paramagnetic Resonance (EPR) Experiments.** In Figure 1 the EPR spectra for Cerro Negro asphaltenes are shown. In this, as well as the other measured spectra the resonance lines for the free radical and vanadium are clearly distinguished and easily resolved. In Table 3 we present the results for the samples studied.

To assess the possible role of the solvent, the asphaltenes were dissolved in THF and boiled for 24 h, and the sample (ACNR) was recovered after evaporation. As shown in Table 3, a significant reduction in spin density was observed. This suggests that the solvent actually reacts with the radicals, which in some way is expected (see below). Since the residues R<sub>1</sub>–R<sub>7</sub> in Table 3 were isolated using THF (see Methods), their spin density should be 3.17-fold higher (9.16/2.89; see Table 3).

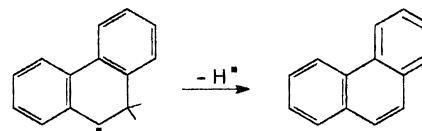
During the synthesis of OA, the asphaltenes are treated with potassium naphthalide (I) in THF (see

Experimental Section). Under these strong reducing conditions it is expected that any radicals present will be reduced immediately after the contact with I. Although reduction was in fact observed (see Table 3), it occurred in a somewhat less extended manner than expected.

In general, the results of the R<sub>i</sub> residues show the expected trend; that is, the spin density should increase with aromaticity.<sup>13</sup> After the solvent effect is corrected, the R<sub>7</sub> residue contains the highest spin density, amounting to about  $2.8 \times 10^{19}$  spin g<sup>-1</sup>. This is equivalent to 1 radical every 11 asphaltene molecules for a molecular weight of 2000 Da.

The presence of free radicals in asphaltene samples is a well-known and interesting phenomena.<sup>13,14</sup> These radicals are very reactive species. Thus, strict requirements are needed in order to keep them in the radical form.

First, there should be no reactive hydrogen; otherwise, aromatization will take place. The example below illustrates this point:



It can be easily proved that this should always be the case for radicals with an even number of carbons in the polycyclic system. Therefore, these arguments suggest that radicals likely have the structural feature of perynaphtil (**II**); that is, they should have an odd number of conjugated aromatic carbons such as structure **III**. Besides, to a first approximation the electron must be delocalized between the starred carbon atoms<sup>20,21</sup> (see Figure 3).

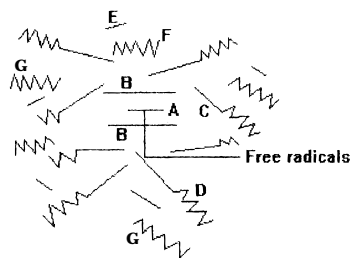
Second, the presence of alkyl substituents in these radicals and in aromatic compounds nearby should be very low. Otherwise, they would eventually disappear as a consequence of reactions such as hydrogen exchange,  $\pi$  bond formation, etc. The increase in both the aromaticity  $f_a$  and spin density as well as the decrease in H/C observed when the residue R<sub>7</sub> is approached (see above and Tables 2 and 3) are consistent with these requirements.

Finally, to avoid intermolecular reactions, these radicals should be “caged” by other even polycyclic aromatic hydrocarbons. In view of the high tendency of asphaltenes to form aggregates, these caging effects should be expected. It is possible that the presence of an unpaired electron in such aggregates could increase intermolecular associations through transannular electron delocalization. This possibility is under investigation in our labs by means of computer programs and model compounds. Preliminary results, using the ZINDO programs,<sup>22</sup> are encouraging. Taking the corrected number of spin density quoted above for R<sub>7</sub>, the fraction of asphaltene molecules involved in the aggregation would be about 27% when two asphaltene molecules surround

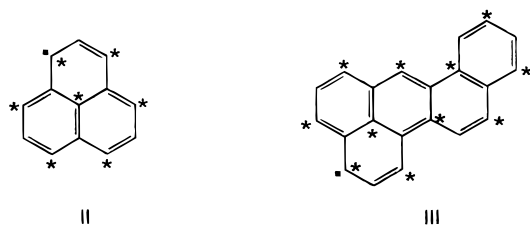
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**Figure 2.** Schematic transversal cut of an asphaltene micelle: (A) free radicals; (B) even aromatic structures. (A) and (B) would be  $R_5$ – $R_7$  aggregates, and (C) would be type f and  $R_1$ – $R_4$  asphaltene molecules. D, E, and G stand for resins, aromatics, and saturates, respectively.



**Figure 3.** Structures showing the perynaphthyl radical **II** and the odd aromatic polycyclic system **III**. The electron is delocalized between the starred carbons.

the radical. This could be compared with the percentages of  $R_6$  and  $R_7$  in Table 2.

Placing aromatic compounds around the radical (caging effect) would avoid its reaction with other components and will produce an aggregate with characteristics similar to the ones found for  $R_7$ . In fact these radicals are very stable and its stability could be accounted for with the caging effect above, which prevents the reactive compound from reaching the high electron densities inside the aggregate (see below).

Using the electron–nuclear double resonance technique (ENDOR), Galtsev et al.<sup>23</sup> have reported that paramagnetic centers (PC) are present in stacks of condensed aromatic sheets and form the core of asphaltene micelles. According to their data, no protons could be found near the PC, in agreement with the above chemical arguments.

**Micelle Structure.** From the results discussed above the following micelle structure, depicted schematically in Figure 2, could be proposed. The center or core of the micelle would be occupied by aromatic molecules of the type found in  $R_7$ – $R_5$ . Thus, the residues  $R_7$ – $R_5$  are formed mainly by aggregates of aromatic components similar to the EAH, which cage the free radicals. In turn, these aggregates are surrounded by other more soluble molecules such as those found in  $F_1$ – $F_7$ . According to the solubility results (see above), these fraction are likely to be responsible for the solubility of the colloid of pure asphaltene in toluene, probably by reducing the interfacial tension between this solvent and the particles or colloids formed by the above aggregates.<sup>24</sup>

Finally, there is a diffuse peripheral region containing resins and quantities of other compounds such as asphaltene ( $F_1$  type) and aromatic and saturated compounds. Since they could be removed from the precipitated material with *n*-heptane (see Methods), it is reasonable to suggest that they are loosely bonded to the pure asphaltene in the crude oil by interfacial tension forces.<sup>24</sup>

It is worth mentioning that the above micelles or aggregates would be porous materials. When dispersed, they would be penetrated by the solvent to some extent. If this reaches deep enough, a reaction with the free radicals could occur, as was the case for THF (see above). Apparently, the OA results suggest that some radicals are so well caged that even strong reducing agents cannot get to them.

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### List of Symbols and Acronyms

ACN	asphaltene from Cerro Negro Crude
API	American Petroleum Institute
ACNR	Cerro Negro asphaltene recovered from tetrahydrofuran
cmc	critical micelle concentration
C-13	carbon-13 NMR spectra
EPR	electron paramagnetic resonance
EAH	even aromatic hydrocarbon
ENDOR	electron–nuclear double resonance technique
F	soluble asphaltene fraction
$f_a$	aromaticity or percentage of aromatic carbons
$\Delta H_{pp}$	peak to peak field bandwidth in EPR spectra
H/C	hydrogen to carbon atomic ratio
HP/MAS	high-power/magic angle
$I_0$ and $I_s$	band intensities of the standard and samples, respectively, in EPR spectra
$M$	molecular weight
$M_n$	number average molecular weight
$M_0$	molecular weight of standard in EPR experiments
$N_A$	Avogadro's number
OA	odd aromatic hydrocarbon
OA	octylated asphaltene
PC	paramagnetic center
R	asphaltene fraction of low solubility
SARA	saturated, aromatic, resins, asphaltene
SANS	small angle nuclear scattering
$S_d$	spin density
THF	tetrahydrofuran
VPO	vapor pressure osmometry
$w$	weight of materials
$Y_{pp}$	peak to peak bond high in EPR spectra

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