

Mobility of Asphaltene Samples Studied by ^{13}C NMR Spectroscopy

Sara Pekerar and Teresa Lehmann

Laboratorio de Análisis Instrumental, Centro de Química, Instituto de Investigaciones Científicas, IVIC, Apartado 21827, Altos de Pipe, Edo. Miranda, Venezuela

Bernardo Méndez and Sócrates Acevedo^{*,†}

Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela, Apartado 47102, Caracas, 1041-A, Venezuela

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Cerro Negro (CN) and Furrial asphaltenes have been analyzed using both liquid and solid-state ^{13}C NMR spectroscopy. The spin–lattice relaxation times exhibited by the carbons in the resin containing CN asphaltene samples indicate that these carbons relax more slowly than the equivalent carbons in the resin-free samples. This fact suggests a higher mobility of the molecules in the sample in the presence of resins. CP/MAS experiments showed that, in general, all asphaltene samples have rigid alicyclic structures. This fact is consistent with the presence of condensed aliphatic rings. The results of the measurements of the cross-polarization relaxation times obtained from the variable contact-time CP/MAS experiments indicate that Cerro Negro samples are more “mobile” than Furrial. These findings point toward the presence of a larger number of CH_2 chains bonding different ring clusters in the Cerro Negro samples.

Introduction

Asphaltenes are materials with a self-assembling capacity in nonpolar organic solvents as well as in crude oils. The formation of colloids and flocs in organic solvents such as toluene have been detected both by the SANS and SAXS techniques.¹ Besides the usual structural considerations such as aromaticity, aliphatic ring content, and the presence of heteroatoms, the way in which these structural units are assembled in the asphaltene molecule is important when the solubility and other properties of these materials are analyzed. For instance, the globular structure proposed by Strausz et al. for Athabasca asphaltenes,² would allow the penetration of smaller molecules within the structure. This favors the solubility in view of the anticipated changes in the entropy and enthalpy of mixing. Any aggregates formed by these asphaltenes are expected to be “loose” and easy to disperse. With compact structures, the aforementioned solvent effects would be less important and the formation of large aggregates or flocs should be considered.

Globular structures are likely to occur when different ring clusters are joined by aliphatic chains. If so, the molecule would have many internal rotational degrees of freedom when the ring clusters mentioned before rotate with respect to each other. It could be anticipated

that the “mobility” referred to above would be less for compact structures.

NMR spectroscopy has proved to be a good technique for the structural characterization of liquid petroleum products. The introduction of magic-angle spinning (MAS)^{3–5} and ^1H – ^{13}C cross-polarization (CP)⁶ with high-power ^1H decoupling, in the past decade, has made the ^{13}C NMR analysis of solid materials a nearly routine experiment.⁷ However, not many studies on the mobility of asphaltenes through the use of NMR spectroscopy have been reported so far. Vucelic et al. used solid-state ^{13}C NMR spectroscopy to calculate relaxation parameters to estimate differences in the relative “mobility” of various structural units in kerogens.⁸ In this paper, we used liquid as well as solid-state ^{13}C NMR spectroscopy to obtain information regarding the molecular mobility in Cerro Negro (CN) and Furrial (F) asphaltene samples. As shown below, the ^{13}C NMR techniques employed were useful to find important differences in mobility between these samples.

Experimental Section

Cerro Negro crude oil (8.3° API) is an extra heavy crude from the Orinoco Valley in Venezuela. Furrial (21° API) is a heavy oil produced in Monagas State in the eastern part of

* To whom correspondence should be addressed.

† Current address: c/o Pakmail No. 1068, PO Box 02 5304, Miami, Florida 33102-5304.

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Table 1. Properties of Samples Studied Deduced from Elemental and ^{13}C NMR Analysis

sample ^a	wt % ^b	H/C	f_a^c	D		
				DBE ^e	A _r DBE ^f	A _l DBE ^g
A1CN	11	1.170	39.5	43	28	15
A2CN		1.140	42.8	44	30.5	13.5
RCN ⁱ	7	1.450	29 ^h	29	20.5	8.5
A3CN		1.050	57.3	49	41	8
A1F	10	1.105	49.1	46	35	11
A2F		0.993	54.1	51	39	12
RF ^j	2	1.470		28		

^a See text. ^b Relative to crude oil. ^c Percent of aromatic carbons determined by CP/MAS unless stated otherwise. ^d All DBE values are related to 100 carbon atoms. ^e Double-bond equivalents = 101 - 50(H/C). ^f Aromatic double-bond equivalents. ^g Aliphatic double-bond equivalents. ^h In CDCl_3 from ref 9. ⁱ Cerro Negro resins. ^j Furrial resins.

the country. CN asphaltenes were obtained by addition of 40 volumes of *n*-heptane to a 1:1 v/v mixture of crude and toluene, as reported earlier.⁹ F asphaltenes were derived from the crude oil after addition of 40 volumes of *n*-heptane to it. In each case, the precipitate was filtered and a portion of it (A1CN and A1F for asphaltenes with resins derived from CN and F crude oils, respectively) was studied as such. The rest of the precipitate for both CN and F asphaltenes was Soxhlet extracted with *n*-heptane for 4 days to remove the coprecipitated resins.⁹ These asphaltenes without resins are called A2CN or A2F in this work. Some properties of these asphaltenes and resins are collected in Table 1.

Sample A3CN was obtained from A2CN by Soxhlet extraction with an acetone-tetrahydrofuran (THF) solvent mixture (40:60) as described elsewhere.¹⁰ This sample amounts to ca. 12% of the A2CN sample and is insoluble in all common organic solvents.¹¹

Double-Bond Equivalent (DBE). In general, the DBE is obtained from eq 1 where C, H, and N are the number of carbon, hydrogen, and nitrogen atoms, respectively.

$$\text{DBE} = \frac{2\text{C} + \text{N} - \text{H} + 2}{2} \quad (1)$$

Since the number of nitrogens is usually small, a good approximation for DBE per 100 carbon atoms is obtained from eq 2, which was used to obtain the DBE values listed in Table 1.

$$\text{DBE} = 101 - 50(\text{H/C}) \quad (2)$$

For pericondensed aromatic rings, the aromatic double bond (A_rDB) could be obtained from eq 3, where C_{Ar} is the number of aromatic carbons:

$$\text{A}_r\text{DB} = -\frac{1}{2} + 0.75\text{C}_{\text{Ar}} \quad (3)$$

For benzene and phenantrene, with C_{Ar} = 6 and 14, the A_rDB values are 4 and 10, respectively. In fossil hydrocarbons, one should consider the presence of an undetermined number of aromatic ring systems. By considering a large number of possible combinations, the following equation was obtained:

$$\text{A}_r\text{DB} = -0.392 + 0.721\text{C}_{\text{Ar}} \quad (4)$$

The slope of the curve obtained from eq 4 (0.721) is similar to

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Table 2. Spin-Lattice Relaxation Time, T_1 , Values for the Different Carbon Types in the Asphaltene Samples^a

sample	chemical shift (ppm) T_1 (s)						
	15	19	23	29	32	126	133
A1CN	2.18	0.69	1.14	0.48	0.70	0.52	1.80
A2CN	1.64	0.52	0.98	0.46	0.39	0.36	1.36

^a Measured in CDCl_3 solution using the inversion-recovery pulse sequence.

the value (0.72) used earlier by Strausz et al.¹² Equation 4 was employed to calculate the aromatic double-bond equivalent (A_rDBE) values collected in Table 1. Subtraction from the total DBE values yielded the corresponding aliphatic double-bond equivalent (A_lDBE).

^{13}C NMR Experiments. All of the NMR experiments were carried out on a Bruker AM-300 spectrometer at 75.47 MHz at room temperature. All the ^{13}C chemical shifts are referenced to TMS. For liquid-state NMR experiments, 150 mg of the asphaltene samples were dissolved in 0.5 mL of CDCl_3 . An inversion-recovery pulse sequence ($180^\circ - \tau - 90^\circ - \text{AQ}$) was used to obtain spin-lattice relaxation times, T_1 .^{13,14} Eight experiments with 1600 transients were run for each determination. For the solid-state NMR experiment, the magic angle was adjusted with KBr and the rotor was spun at 3900 kHz. High-power ^1H decoupling (HPD) experiments were performed with a 45° pulse and a repetition delay of 4 s. Standard CP/MAS experiments with variable contact time were carried out. Series of seven spectra were obtained with contact times ranging between 10 μs and 2 ms and 1024 or 2048 scans depending on the sample. The repetition delay was 4 s. Signal-to-noise ratios were improved by using a line-broadening factor of 100 in the Fourier transformation. The cross-polarization relaxation time, T_{CH} , for each carbon type in the analyzed samples were derived from the slopes of the intensity vs contact-time plots as described by Yu and Guo.¹⁵

Results and Discussion

Some relevant properties of the materials studied in this work are shown in Table 1. When compared with A2, the high H/C and low f_a values obtained for A1 can be attributed to the presence of resins in this type of sample. Resins have been shown to exhibit a very high content of aliphatic residues.⁹

As a result of the low H/C values, the asphaltene samples listed in Table 1 have a large number of DBE, that is, actual aromatic double bonds plus aromatic and aliphatic rings. Using the procedure described in the Experimental Section, the total DBE was divided into aromatic and alicyclic. As shown in Table 1, a number larger than expected of aliphatic rings can be found in these asphaltenes. This finding suggests that a large percentage of alicyclic chains could be anticipated, indicating the presence of rigid or low mobile structures. As shown below, this fact was confirmed by the ^{13}C NMR CP/MAS experiments.

Spin-Lattice Relaxation Time, T_1 , Values. The results of the measurements of spin-lattice relaxation times, T_1 , are shown in Table 2. It is well-known that

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Table 3. Percentages of Aliphatic Carbons Measured through ^{13}C NMR CP/MAS and HPD Experiments

	percentage			
	CP/MAS		HPD	
	<i>a</i>	<i>b</i>	Δ^c	
A1CN	60.5	71.3	66	9.1
A2CN	57.2	68.3	59	3.1
A3CN	42.7	68.5	54.3	27
A1F	50.9	61.5	60.4	19
A2F	45.8	55.7	54.7	19

^a Measured with a contact time of 0.5 ms. These values were used to obtain the f_a values listed in Table 1. ^b Measured with a contact time of 10 μs . ^c Relative difference (%) between HPD and CP/MAS values.

Table 4. Cross-Polarization Relaxation Time, T_{CH} , Values for the Different Carbon Types in the Asphaltene Samples^a

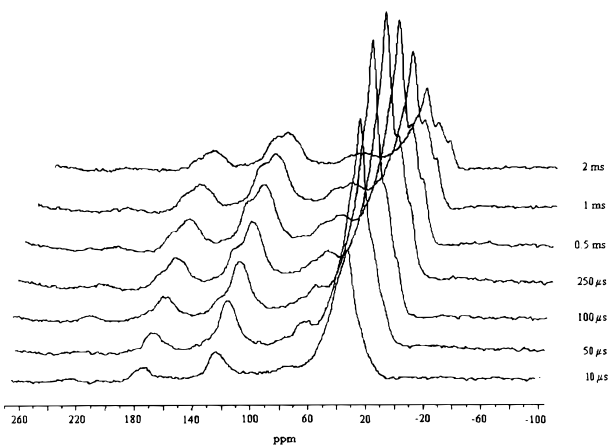
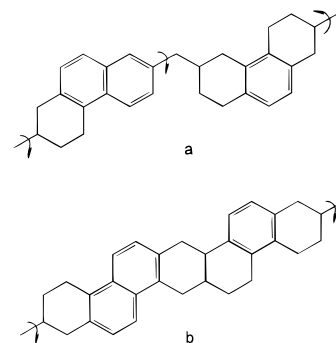
sample/chemical shift (ppm)	T_{CH} (μs)				
	15	23	30	126	133
A1CN	110	70	40	55	350
A2CN	70	50	35	100	190
A3CN	95	55	30	110	250
A1F	230	60	40	<i>b</i>	<i>b</i>
A2F	35	15	7	<i>b</i>	<i>b</i>

^a Derived from the CP/MAS experiments with variable contact times as described in the Experimental Section. ^b These values could not be determined in this work due to the interference of the spinning side bands in the aromatic region of the spectra.

when plotted against the correlation time in solution, τ_c , the T_1 values go through a minimum.¹⁶ In turn, τ_c could be related to the mobility of molecules in the sample: short and long corresponding to high and low mobility, respectively. Thus, for highly as well as low mobile structures, the T_1 's are long with short T_1 's exhibited by molecules with τ_c 's in between. As expected, the longest T_1 's in Table 2 correspond to the methyl groups ($\delta = 15$ ppm) being the most mobile groups. Also, the T_1 value corresponding to the aromatic signal at 133 ppm, assignable to nonprotonated aromatic carbons, is long since these carbons cannot relax through bonded hydrogens.

As shown in Table 2, the T_1 values are longer for the sample with resins (A1CN). This could be predicted in view of the expected higher mobility of this material when compared to A2CN samples.

CP/MAS Experiments. The percentage of aliphatic carbons obtained by both CP/MAS and HPD are shown in Table 3. The values obtained through the CP/MAS experiments with optimum contact time (0.5 ms) are showed in the first column. These values were used to calculate the f_a 's listed in Table 1. The transfer of magnetization from hydrogen to carbon depends on the number of hydrogens available, as well as on the rigidity of the structure. The second column in Table 3 shows that the percentages of intensities acquired under minimal contact-time conditions (10 μs) are higher. These values reveal very clearly that the aliphatic sectors of all the samples listed in Table 3 have a very important rigid component. These results can be anticipated in view of the high content of aliphatic unsaturations or rings (see Table 1). The results of the HPD

**Figure 1.** Stack plot of variable contact-time CP/MAS spectra of Cerro Negro asphaltene with resins (A1CN) sample.**Figure 2.** Structures to illustrate the differences in mobility in hypothetical asphaltene models. Structure b is more rigid than structure a.

experiments also show the existence of mobile groups in the aliphatic region.

The results discussed above are evidence for the presence of rigid substructures associated with the aliphatic residues in the analyzed samples. So far, the rigidity of asphaltenes has been attributed almost exclusively to the aromatic core. Our results add new insight to the comprehension of these very complex materials.

Cross-Polarization Relaxation Time, T_{CH} . The results of the measurements of the cross-polarization relaxation time, T_{CH} , for the different carbon types in the analyzed samples are shown in Table 4. These were obtained from the variable contact-time CP/MAS experiments described in the Experimental Section. They are a measure of the efficiency in magnetization transfer and are related to the mobility. Thus, low mobile or rigid structures are related to small T_{CH} values, whereas highly mobile structures should exhibit longer T_{CH} 's. The variable contact-time CP/MAS spectra recorded for the A1CN sample are shown in Figure 1 as an example. It can be seen from this figure that for short contact times, only the band at 30 ppm can be observed in the aliphatic region of the spectra. This signal is assigned to CH_2 groups in aliphatic or alicyclic chains. The signals around 15 and 23 ppm, attributed to CH_3 and CH_2 terminal groups, are resolved only when long contact times are used. These graphical results are enough evidence of the differences in mobility found by us in asphaltene structures. It is noteworthy that samples with resins (A1CN and A1F) have the longest

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T_{CH} for the aliphatic carbons, in agreement with the T_1 's (Table 2). Perhaps the most interesting results in this table are the very short T_{CH} 's for the A2F sample. They suggest very strongly that this sample is more rigid than the rest. This "stiffness" is not due to a larger number of rings but rather to the way these rings are assembled (see Table 1, column 7). We suggest that in the CN asphaltene samples, relatively small ring clusters (aromatic and/or aliphatic) are joined mainly by aliphatic chains. This allows rotation around C–C bonds. In the A2F samples, the ring clusters would be larger and the number of the chains referred to above would be

smaller, resulting in more rigid structures (see Figure 2).

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