NMR used for Saudi crude asphaltenes

Misbah Ul Hasan
Fuel Research Center
Karachi, Pakistan

M. Naheed Siddiqui
M. Arab
University of Petroleum and Minerals
Dhahran, Saudi Arabia

Nuclear magnetic resonance (NMR) spectroscopy with proton (^1H) and carbon 13 (^{13}C) has been used to determine the structural characteristics of asphaltenes from four commercial Saudi Arabian crude oils. These characteristics are important to refiners that have deep conversion processes to determine yields from the residual fractions of the Saudi crudes, and to determine the operating parameters of the process units.

The spectra obtained give some structural similarities among the crude oils, as well as some differences. Values of various structural parameters have been tabulated from the spectra.

The use of ^1H and ^{13}C NMR spectroscopy for analysis of crude oils and fractions was suggested only a few years ago.[1-3]

The narrow range of chemical shifts in ^1H NMR poses serious limitations on the quantitative estimates of hydrogens. In contrast, ^{13}C NMR offers a direct observation of the basic carbon skeleton with signals of good resolution. Previous test problems associated with ^{13}C NMR have been solved.

The combination of ^{13}C and ^1H NMR spectroscopy is useful in assessing the average molecular composition of asphaltenes. We have, therefore, used these analytical techniques for the analysis of asphaltenes from the four commercial Saudi crude oils.

The procedure for isolation of asphaltenes and measurement of their ^1H and ^{13}C NMR spectra have been previously reported.[1]

Findings. The average structural parameters for Arab Heavy, Arab Medium, Arab Light, and Arab Berri asphaltenes have been calculated from their NMR spectra. Table 1 shows the parameters obtained from the peak intensities of their ^1H NMR spectra. Details were published previously[1]

The Arab Berri asphaltenes are found to possess highest aromatic hydrogen content (15.4%) followed by Arab Light (14.2%), Arab Medium

Table 1

Distribution of hydrogen*

Type of proton	Chemical shift, ppm	% Arab Heavy	Arab Medium	Arab Light	Arab Berri
H_{sat}†	0.0-4.0	94.7	88.8	85.8	84.6
H_α	1.9-4.0	17.3	13.6	17.9	19.8
H_η	1.6-1.9	16.0	18.4	20.9	19.1
H_β	1.0-1.6	34.7	40.0	32.1	31.5
Total H_β	1.0-1.9	50.7	58.4	53.0	50.6
H_γ	0.5-1.0	26.7	16.8	14.9	14.2
H_{ar}†	6.0-9.0	5.30	11.2	14.2	15.4
$H_{\alpha\text{-alk}}$†		22.3	13.8	18.01	26.7
$H_{\alpha\text{-Me}}$†		0.0	0.0	0.0	0.0
C/H ratio		0.84	0.85	0.91	0.99

* Obtain by ^1H NMR.
† Aromatic hydrogen (H_{ar}), alkyl bearing H_α ($H_{\alpha\text{-alk}}$), methyl bearing H_α ($H_{\alpha\text{-Me}}$), saturated hydrogens (H_{sat}).

Table 2

Distribution of aliphatic carbons*

Type of carbons	Chemical shift, ppm	% Arab Heavy	Arab Medium	Arab Light	Arab Berri
C_{sat}†	0-70	45.3	39.3	35.6	25.4
C_α†	14.1	2.0	2.1	2.0	1.6
$C_{Me\text{-}b}$§	19.7	2.0	1.8	1.7	0.9
C_β†	22.9	2.0	2.1	1.7	1.6
C_γ†	29.7	13.2	14.8	7.9	8.3
C_η†	32.2	2.0	2.0	2.0	1.6
% straight chain		19.2	21.0	13.6	13.1
Average chain length		19.2	20.0	13.6	16.3

* By ^{13}C NMR.
† Characteristic resonances due to long chain alkyl substituents on the aromatic rings.
§ Bridgehead carbons between methyls.

Table 3

Distribution of aromatic carbons and some structural parameters*

Parameters	Arab Heavy	Arab Medium	Arab Light	Arab Berri
C_{ar}†	54.7	60.7	64.4	74.6
$C_{ar\text{-}H}$†	6.3	13.2	15.6	15.6
$C_{ar\text{-}Me}$†	0.0	0.0	0.0	0.0
$C_{ar\text{-}alk}$†	13.3	8.1	9.9	13.5
$C_{ar\text{-}J}$†	19.6	21.3	25.5	29.1
$C_{ar\text{-}b}$†	35.1	39.5	38.9	45.5
f_a§	0.55	0.60	0.64	0.74
$f_{ar\text{-}H}$§	0.12	0.22	0.24	0.34
$f_{ar\text{-}alk}$§	0.24	0.13	0.15	0.18
f_c§	0.65	0.65	0.60	0.60
f_p§	0.36	0.35	0.40	0.39

* By ^{13}C NMR.
† Total aromatic carbons (C_{ar}); hydrogen bearing aromatic carbons ($C_{ar\text{-}H}$); methyl bearing aromatic carbons ($C_{ar\text{-}Me}$); alkyl bearing aromatic carbons ($C_{ar\text{-}alk}$); sum of $C_{ar\text{-}H}$, $C_{ar\text{-}Me}$, $C_{ar\text{-}alk}$ ($C_{ar\text{-}J}$). § Aromaticity factor (f_a); ratios of $C_{ar\text{-}alk}$, $C_{ar\text{-}H}$, $C_{ar\text{-}Me}$ to the total C_{ar} ($f_{ar\text{-}alk}$, $f_{ar\text{-}H}$, $f_{ar\text{-}Me}$); compactness factor (f_c); ratio of $C_{ar\text{-}J}$ to C_{ar} (f_p).

(11.2%) and Arab Heavy asphaltenes (5.3%). The relative depletion of aromatic protons in Arab Heavy asphaltenes indicates that in this crude the aromatic structures are highly condensed and are more highly substituted than the Arab Light asphaltenes.

Among the H_α, H_β, and H_γ protons, the H_β constitute a major portion of the paraffinic protons in all four asphaltenes. H_α are the protons attached to a saturated carbon in the α position with respect to an aromatic ring; H_β are the protons attached to paraffinic methylenes, and methyl or methylene, and are further removed from an aromatic ring; and H_γ are protons of paraffinic methyls, further removed from an aromatic ring.

The Arab Light asphaltenes have the highest content of cyclohexyl protons, H_η (20.9%), while the Arab Heavy has lowest value of H_η (16.0%).

The higher vaue of H_η is a good indication of a high content of polymeric cyclohexyl structures in Arab Light asphaltenes (26.7%). The highest content of H_γ is found in Arab Heavy asphaltenes (26.7%) which indicates that Arab Heavy has mostly long paraffinic chains as substituents on condensed aromatic structures.

The percent distribution of aliphatic carbons obtained from the peak intensities of ^{13}C NMR spectra is shown in Table 2. The saturated carbon content is found to be highest in Arab Heavy asphaltenes (45.4%), followed by Arab Medium (39.3%), Arab Light (35.6%), and Arab Berri (25.4%).

The percent distribution of straight chain alkanes is lowest in Arab Berri asphaltenes (13.1%), highest in Arab Medium (21.0%), while Arab Heavy (19.2%) and Arab Light asphaltenes

The authors. . .

Hasan

Siddiqui

Misbah Ul Hasan is a principal scientific officer in the Fuel Research Center of the Pakistan Council of Scientific & Industrial Research in Karachi, Pakistan. His main interests are the application of high resolution nuclear magnetic resonance spectroscopy to identify organic compounds.

Hasan received a PhD from the University of Massachusetts, and he has worked as a professor of chemistry at the King Fahd University of Petroleum and Minerals in Saudi Arabia.

M. Naheed Siddiqui is a scientist-II in the water resources and environment division of the Research Institute at the King Fahd University of Petroleum and Minerals in Dhahran, Saudi Arabia. His research interests are mainly in the use of NMR spectroscopy for analytical purposes.

Siddiqui received an MS degree in chemistry from the King Fahd University of Petroleum and Minerals under professor Hasan. He also received an MSc degree in chemistry from Aligarth Muslim University in India.

Arab

Mohammad Arab is a chemist at the King Fahd University of Petroleum and Minerals in Dhahran, Saudi Arabia. His main research interests are in carbon 13 and proton NMR characterization of various organic compounds. Arab previously worked for Aramco in the oil operation division in Ras Tanura, Saudi Arabia, and at M/S Dilon Ltd.'s polymerization plant in Karachi, Pakistan. He received an MSc degree in physical chemistry from the University of Karachi.

(13.6%) show intermediate values. The Arab Medium asphaltenes have the longest average chain length followed by Arab Heavy asphaltenes. The shortest chain length is found in Arab Light asphaltenes.

The distribution of aromatic carbons and some structural parameters from the ^{13}C NMR spectra of asphaltenes are given in Table 3. The aromatic carbon content is highest in Arab Berri (74.6%) and lowest in Arab Heavy asphaltenes (54.7%). The Arab Medium and Arab Light asphaltenes show intermediate values.

The percentage of aromatic carbons bearing alkyl groups (except methyl) is highest in Arab Berri asphaltenes (13.6%) while Arab Heavy, Arab Medium, and Arab Light asphaltenes have values of 13.3%, 8.1%, and 9.9% respectively. A major portion of the aromatic carbons is present in the ring junctions, and is highest in Arab Berri asphaltenes (45.5%), and lowest in Arab Heavy asphaltenes (35.1%).

The Arab Medium and Arab Light asphaltenes show almost equal percentages of ring junction carbons. The percentage of aromatic carbons, substituted by methyl groups, is almost negligible in all four asphaltenes.

The aromaticity factor, f_a, is highest in Arab Berri asphaltenes (0.74) and lowest in Arab Heavy (0.55) asphaltenes. The ratio of aromatic carbons bearing hydrogen atoms to the total aromatic carbons, $f_{ar\text{-}H}$, a useful parameter, is found to increase from Arab Heavy asphaltenes to Arab Medium, Arab Light, and Arab Berri asphaltenes, thus indicating that the greatest percentage of aromatic carbons are substituted in Arab Heavy asphaltenes. The ratio of aromatic carbons bearing alkyl groups (except methyl) to the total aromatic carbons of the asphaltenes, $f_{ar\text{-}alk}$, is found to be highest in Arab Heavy asphaltenes.

The ratio of bridgehead carbons to total aromatic carbons, f_c, indicates the extent of compactness and ring condensation in asphaltenes. This parameter decreases from Arab Heavy (0.65) to Arab Berri (0.60).

Thus, the Arab Heavy asphaltenes possess the highest percentage of bridgehead carbons in their skeleton. The conclusion drawn is that these asphaltenes consist of mostly polynuclear hydrocarbons polysubstituted by long chain paraffinic alkyl groups.

References

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