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Structural Characterization of Arabian Crude Oils by ^{13}C N.M.R. Spectroscopy — A Comparative Study

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ABSTRACT

In this paper ^{13}C n.m.r. structural characterization of Saudi Arabian light and extra light (Berri) crudes is reported and results are compared with our previously reported results on Arab heavy and Arab medium crudes. It is found that ash, sulphur, carbon, vanadium, nickle and viscosity increases from Arab light to Arab heavy crudes. The yield of residue boiling above 454 °C also increases from Arab light to Arab heavy crudes. It appears from these results that the differences in structure and composition of the aliphatic portion of these crudes are mainly of quantitative nature. These crudes are basically a mixture of similar aliphatic compounds but they are present in different concentrations in each crude. It is also observed that the Arab heavy contains a higher percentage of aromatic carbons which have polycyclic aromatic rings in comparison to other crudes. This study has therefore, provided an important insight into the similarities and differences between the four commercial Saudi crude oils.

INTRODUCTION

The use of ^{13}C n.m.r. spectroscopy for the average structure analysis of crude oils is now well established (Clutter et al, 1972; Boduszynski, 1984; Young & Gayla, 1984; Greinke, 1984; Ali et al, 1985). We have previously reported the results of ^{13}C n.m.r. characterization of Saudi Arabian heavy (Hasan et al, 1983) and medium (Hasan et al, 1985) crude oils. In this paper the results of ^{13}C n.m.r. characterization of six distillate fractions of Arab light and extra light (Berri) crudes are reported. In addition a comparison of various structural parameters for all the four crudes is presented. The differences and similarities in their average structures are also described.

EXPERIMENTAL

The crude oils were obtained from the Arabian American Oil Company (ARAMCO). Five distillate fractions of 93, 93-204, 204-260, 260-343, 343-454 °C boiling ranges and one distillation residue 454 °C were collected, in accordance with method ASTM D-2892-78.

Solutions for the measurements of ^{13}C n.m.r. spectra were prepared by dissolving 1 ml of each of the first five cuts in 2 ml of d-chloroform containing 10 mg of Irontri-acetonylacetonate as the relaxation agent. Because of the lower solubility of the residue, a smaller amount (0.7 ml) of the F-6 cut was dissolved in 2 ml of solvent, and 15 mg relaxation reagent was added. Tetramethylsilane (TMS) was used as the internal standard.

Proton decoupled ^{13}C n.m.r. spectra were recorded on the XL-200 n.m.r. spectrometer operating at 50.3 MHz and using 10 mm sample tubes. The solvent d-chloroform also provided the internal field-frequency lock signal. The nuclear overhauser enhancement was suppressed by operating the spectrometer in the gated decoupling mode in which the protons were irradiated only during the processing of the free induction decay. The decoupler was off during pulse and delay time. The experimental parameters were: spectrum width, 10,000 Hz; data points, 24,000; pulse width, 12μs (45°); and pulse delay, 15 second. The number of transients required was 3,000 for the five distillation fractions and 20,000 for the residue.

RESULTS & DISCUSSION

Some general properties of the four Saudi crudes are reported in Table 1. As expected, the ash, sulphur, carbon, vanadium and nickle contents and viscosity increase from Arab Berri to Arab heavy crudes.

The percentage yields by volume of each of the six fractions of the Arab light and extra light crude oils. alongwith their specific gravities, C, H and S analyses and atomic C/H ratios are given in Table 2. It is noted that the yield of last fraction, F-6 is much lower for Arab light and Arab Berri crudes in comparison to Arab heavy and medium crudes. In addition the percentage of sulphur is also generally lower in Arab light and Arab Berri crudes.

^{13}C n.m.r. Characterization

A comparison of the average structural parameters for each of the six fractions of the four Saudi crudes is made on the basis of their ^{13}C n.m.r. data.

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Table 1. General properties of crude oil.

Test	Test Methods (ASTM)	Arabian Extra Light (BERRI)	Arabian Light	Arabian Medium	Arabian Heavy
1. Gravity, °API	D 287	38.50	33.80	30.40	28.03
2. Ash,. ppm	D 482	20	44	48	110
3. Pourpoint °F (°C)	D 97	0(-17.8)	+5(-15.0)	+10(-12.2)	-10(-23.3)
4. Hydrogen sulphide,ppm	LP 103T	60	40	50	Nil
5. Sediment & water	D 96	Trace	Trace	Trace	Trace
6. Sulphur, % Wt.	D 129	1.10	1.81	2.59	2.79
7. Viscosity SUS@100 °F (37.8 °C)	D 445	41	49	70.5	118
8. Carbon residue, Wt %	D 189	2.0	3.58	5.87	6.75
9. Nitrogen, Wt %	-	0.042	0.098	0.114	0.168

Table 2. Chemical & physical properties of Arab Light and Arab Berri crudes.

	F-1	F-2	F-3	F-4	F-5	F-6
Arab Light						
Boiling range(°C)	93	93-204	204-260	260-343	343.454	454
Yield (vol %)	10.4	19.6	10.4	15.7	21.2	22.7
Specific gravity (60/60°F)	0.6575	0.7535	0.8080	0.8470	0.9085	0.9885
Carbon (Wt.%)	84.35	85.39	85.68	85.51	85.09	84.40
Hydrogen (Wt.%)	15.50	14.46	13.92	13.10	11.96	11.29
Nitrogen (Wt.%)	0.03	0.03	0.03	0.03	0.03	0.16
Sulphur (Wt.%)	0.041	0.065	0.28	1.20	2.56	3.35
Atomic C/H ratio	0.45	0.49	0.51	0.54	0.59	0.62
Arab Berri						
Boiling range(°C)	93	93-204	204-260	260-343	343-454	454
Yield (Vol.%)	10.8	22.8	10.7	15.9	19.0	20.8
Specific gravity (60/60 °F)	0.6595	0.7545	0.8070	0.8430	0.8885	0.9592
Carbon (Wt.%)	84.38	85.02	85.24	85.02	85.32	84.41
Hydrogen (Wt.%)	15.46	14.61	13.60	13.04	12.13	11.61
Nitrogen (Wt.%)	0.03	0.03	0.03	0.03	0.03	0.14
Sulphur (Wt.%)	0.032	0.063	0.23	0.87	1.76	3.20
Atomic C/H ratio	0.45	0.48	0.52	0.54	0.59	0.61

Aliphatic Carbons

Some structural parameters for the aliphatic carbons of the four Saudi crudes are shown in Table 3. The percentage of saturated carbons, C_{sat}, does not vary a great deal between the crudes. In general the differences between the lowest and the highest C_{sat} values are of approximately 5% value. In the first fraction, Arab Berri is found to have the lowest percentage of saturated carbons while Arab heavy has the highest value. In the residue, F-6, this trend is reversed and the Arab Berri has the highest percentage of saturated carbons while Arab heavy and medium have much lower values. As expected, the value of C_{sat} is highest in F-1 and lowest in F-6. The other fractions are found to have mixed values. The percentage of normal straight chain alkanes is found to vary significantly between the crudes. Again, major

Table 3. A Comparison of the structural parameters for Aliphatic Carbons in Saudi Arabian crude oils.

Parameter	Crude	F-1	F-2	F-3	F-4	F-5	F-6
C_{sat}	Berri	93.8	86.8	85.7	83.1	79.8	73.0
	Light	95.4	86.3	84.9	82.1	75.9	69.4
	Medium	96.4	84.5	82.4	80.8	75.9	65.0
	Heavy	98.7	88.6	86.8	81.0	77.9	67.0
%n-alkane	Berri	56.9	52.2	47.6	50.8	41.9	34.2
	Light	56.6	50.5	46.2	43.5	39.8	31.3
	Medium	65.6	49.2	45.9	44.3	38.6	43.0
	Heavy	67.4	58.1	51.7	43.2	43.4	39.0
Chain length	Berri	6.85	8.3	9.9	12.5	16.4	20.1
	Light	6.5	8.4	11.3	13.8	15.3	20.2
	Medium	5.5	7.7	9.7	12.7	16.4	21.0
	Heavy	5.6	7.5	9.5	11.8	14.2	17.3

differences are observed only in first and last fraction. In the first fraction, F-1, Arab heavy and Arab medium crudes have a higher percentage of n-alkane (67, 66%) while Arab Berri and Arab light have a lower value (57%). The average chain length of paraffinic hydrocarbons in each of the six fractions of various Saudi crudes is also shown in Table 3. The differences in paraffinic chain length between various crudes are found to be rather small (1-2%). The paraffinic chain length is found to increase from F-1 to F-6 for each crude.

It thus appears from these results that differences in the structure and composition of the aliphatic portion of these crudes are mainly of quantitative nature. Qualitative differences between the crudes are rather small. Each crude is basically a mixture of similar compounds but they are present in different concentrations in each crude. In general the yields (% volumes) of various fractions obtained by the distillation of the four crudes show small differences for the first five fractions, F-1 to F-5, whereby Arab Berri and light have somewhat higher yield than Arab medium and heavy crudes. However for the residue, F-6, the yields for Arab medium and heavy are much higher than the other two crudes. These quantitative differences in the % yield of each fraction must be kept in view while interpreting the following structural characterization data obtained by quantitative analysis of each of these fractions.

Aromatic Carbons

Various structural parameters for the aromatic portion of each of the four Saudi crudes are shown in Table 4. The percentage of total aromatic carbon C_{ar}, in these crudes varies significantly in the first and last fraction only. In the first fraction, F-1, Arab heavy has the lowest percentage of aromatic carbons (1.3%) while Arab Berri has the highest value (6.2%). In residue, F-6, Arab medium and heavy have a higher percentage (35, 33%) in comparison to Arab Berri and light crudes (27, 30%). In other fractions, the differences between crudes are small. In general Arab medium is found to have highest percentage of aromatic carbon in all fractions. As expected the percentage of aromatic carbons increases from F-1 to F-6, for each crude. The percentage of hydrogen-bearing aromatic carbons, C_{ar-H}, in the first fraction is same as the total aromatic carbons C_{ar} in the fraction for all crudes. This is due to the fact that in this low boiling range, probably benzene is the only aromatic hydrocarbon present in the fraction. In the residue, F-6, we observe that the value of % C_{ar-H} is lower for Arab Berri and light crudes (8.3, 8.5%) in comparison to Arab medium and heavy crudes (12.2, 11.4%). The percentage of C_{ar-H} is also found to increase from F-1 to F-6 for each crude. The percentage of alkyl-bearing aromatic carbons is found to be generally higher for all fractions of Arab medium crude. It is observed that in general Arab heavy and Arab medium have a higher percentage of alkyl-bearing aromatic carbon than Arab Berri and Arab light for the fraction F-2 to F-5. In the residue, F-6, however, this percentage increases significantly for Arab light and only slightly for other crudes. The percentage of C_{ar-alk} also increases from F-1 to F-6 for each crude. The percentage of methyl-bearing aromatic carbons, C_{ar-CH3}, is found to be generally higher for all fractions of Arab Berri and light crudes in comparison to Arab medium and heavy crudes. This percentage is highest for all fractions of Arab light crude. The percentage of carbons which exist as bridgehead between two or more rings, C_{ar-b}, is found to be highest in general, for all fractions of Arab heavy crude. In the residue, F-6, it is clearly observed that Arab heavy and medium have a higher percentage of these types of carbons (13.1, 11.7%) in comparison to Arab Berri and light (9.8,

Table 4. The percentage carbon distribution under aromatic region of ^{13}C n.m.r. spectra of Saudi crudes.

Parameter	Crude	F-1	F-2	F-3	F-4	F-5	F-6
C_{ar}	Berri	6.2	13.2	14.3	16.9	20.2	27.0
	Light	4.6	13.7	15.1	17.9	24.1	30.1
	Medium	3.6	15.5	17.6	19.2	24.1	35.0
	Heavy	1.3	11.4	13.2	19.0	22.1	33.0
C_{ar-H}	Berri	6.2	8.7	8.8	8.6	8.7	8.3
	Light	4.6	7.1	7.4	9.5	10.5	8.5
	Medium	3.6	10.3	9.1	9.9	11.9	12.2
	Heavy	1.3	7.5	7.1	8.7	9.5	11.4
C_{ar-alk}	Berri	0	1.2	2.4	2.7	3.0	5.2
	Light	0	1.1	3.2	3.4	4.7	9.2
	Medium	0	1.5	4.8	5.4	8.2	9.8
	Heavy	0	1.0	2.7	4.5	6.2	6.4
C_{ar-CH3}	Berri	0	2.6	2.4	2.3	2.2	3.9
	Light	0	4.4	3.0	3.6	3.9	3.9
	Medium	0	2.6	2.0	1.3	1.0	1.3
	Heavy	0	2.5	1.6	2.1	2.0	2.1
C_{ar-b}	Berri	0	0.7	0.7	2.1	6.0	9.8
	Light	0	1.1	1.5	1.5	5.0	8.6
	Medium	0	1.1	1.7	2.6	3.0	11.7
	Heavy	0	0.4	1.8	3.7	4.4	13.1

Table 5. A Comparision of the structural parameters for the Aromatic Carbons in Saudi crudes.

Parameter	Crude	F-1	F-2	F-3	F-4	F-5	F-6
F_a	Berri	0.062	0.132	0.14	0.17	0.20	0.27
	Light	0.042	0.14	0.15	0.10	0.24	0.30
	Medium	0.032	0.15	0.10	0.19	0.24	0.35
	Heavy	0.013	0.11	0.13	0.19	0.22	0.33
F_{ar-H}	Berri	1.0	0.66	0.61	0.51	0.43	0.31
	Light	1.0	0.53	0.44	0.53	0.43	0.30
	Medium	1.0	0.67	0.52	0.51	0.49	0.39
	Heavy	1.0	0.66	0.54	0.46	0.43	0.34
F_{ar-CH3}	Berri	0	0.20	0.17	0.14	0.11	0.14
	Light	0	0.32	0.30	0.30	0.16	0.12
	Medium	0	0.17	0.11	0.07	0.04	0.03
	Heavy	0	0.22	0.12	0.11	0.09	0.06
F_{ar-b}	Berri	0	0.05	0.051	0.12	0.30	0.36
	Light	0	0.08	0.10	0.08	0.21	0.25
	Medium	0	0.073	0.10	0.14	0.12	0.33
	Heavy	0	0.03	0.14	0.14	0.20	0.40
F_{ar-alk}	Berri	0	0.09	0.17	0.14	0.15	0.22
	Light	0	0.08	0.21	0.19	0.19	0.30
	Medium	0	0.10	0.27	0.28	0.30	0.28
	Heavy	0	0.09	0.20	0.24	0.28	0.19

8.6%) crudes. The general picture, which therefore, emerges concerning the overall structure of these crudes is that all the four crudes are mainly paraffinic in nature. The Arab heavy contains a higher percentage of aromatic carbons which exist as polycyclic rings. In this crude, number and chain length of alkyl substituents attached to the aromatic carbons, is small in comparison to other crudes. In comparison, Arab medium contains a lower percentage of aromatic polycyclic rings but has a higher percentage alkyl chains attached to them which are longer in length. The Arab Berri and light contain an even lesser number of polycyclic rings and most of the substituents attached to them are hydrogens and methyl groups. Although the percentage of alkyl groups attached to the aromatic rings is lower for these two crudes, the average chain length of the alkyl groups is same as observed for Arab medium crude. In the residue, F-6, Arab medium and heavy have a higher value (43, 39%) in comparison to Arab light and Arab Berri (31, 34%). In other fractions, F-2 to F-5, only small differences are observed. The various structural parameters calculated for the aromatic carbon for Arab light and Arab Berri crudes are shown in Table 5. The parameter F_a is the aromaticity factor and is obtained by dividing the % of aromatic carbons by the % of total carbons. Similarly the fraction of aromatic carbons attached to a hydrogen, $F_{ar\text{-}H}$, the fraction of aromatic carbons attached to methyl groups, $F_{ar\text{-}CH3}$ and the fraction of aromatic carbons attached to alkyl groups $F_{ar\text{-}alk}$ are obtained by dividing the % of these types of carbons by the total number of aromatic carbon. The parameter $F_{ar\text{-}b}$ which indicates the % of aromatic bridged carbon is obtained by dividing the % of bridged carbons by the total numbers of aromatic carbons. This study has therefore, provided an important insight into the similarities and differences between the four commercial Saudi crude oils.

REFERENCES

Ali. M.F, M.U. Hasan, A. Bukhari and M. Saleem: Oil & Gas Journal, August 1985, p.71.

Boduszynski, M.M, 1984: Liquid Fuel Technology, v.2, p.221.

Clutter, D.R., L. Patrakis, R.L. Selenger and P.K. Jensen, 1972: Anal. Chem., v.44, p.1395.

Greinke, R.A, 1984: Fuel, v.63, p.1374.

Hasan, M.U., M.F. Ali, and A. Bukhari, 1983: Fuel, v.62, p.518.

Hasan, M.U, A. Bukhari and M.F. Ali, 1985: Fuel, v.64, p.839.

Young, D.C., and L.G. Gayla, 1984: Liquid Fuels Technology, v.2, p.307.