

Improvement in the Determination of Aromatic Carbons in Petroleum Fractions by Proton Nuclear Magnetic Resonance Spectroscopy

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The accuracy of the aromatic carbons values, calculated by proton nuclear magnetic resonance spectroscopy, in middle distillates and lube oils, is improved using the average number of aromatic rings per molecule, determined by ultraviolet spectrophotometry.

Keywords: Aromatic carbons; petroleum fractions; proton nuclear magnetic resonance spectroscopy

Introduction

Pulsed Fourier transform nuclear magnetic resonance (PFT-NMR) spectroscopy is an attractive technique for the analysis of petroleum and its fractions, basically because (1) the boiling-point ranges, viscosity, elemental composition, average molecular mass, *etc.*, have no influence on the procedure of recording the spectra; (2) the integrated intensities of specific groups of signals are proportional to the content of the corresponding structural fragments in the molecule and this assignment is unambiguous owing to the specificity of the chemical shifts; (3) it is possible to determine the presence of independent structural fragments by comparison with model compounds enclosing them regardless of the remainder of the molecule. These facts explain the many studies concerning the characterization of petroleum fractions and other complex hydrocarbon mixtures by NMR spectroscopy,¹ including the prediction of chemical and physical properties.²⁻⁴

The characterization of petroleum fractions is becoming routine owing to the advances in instrumentation (including software for data processing), pulse sequence design and progress in chemometrics, *e.g.*, multivariate analysis.⁵⁻⁹ Standard methods for the determination of aromatic hydrogen and carbon contents by high-resolution NMR spectroscopy are already available.¹⁰ However, the determination of structural groups is difficult and time consuming because of the experimental conditions required,¹¹ which has led to studies to improve the application of proton (¹H) NMR in the characterization of hydrocarbon fractions because of its sensitivity, accessibility and low time consumption.¹²

This paper reports improved results obtained in the calculation of aromatic structural units in middle distillates and base lube oils by ¹H NMR using the average number of aromatic rings per molecule, determined by ultraviolet (UV) spectrophotometry.

Experimental

Seven petroleum fractions from Cuban crude oils, Lago Medio crude oil (Venezuela) and Romashkino crude oil (Russia) were obtained by fractional distillation. Ten lube oils were supplied by the Santiago de Cuba refinery, including both imported and domestic lube oils.

The distilled fractions had distillation ranges from 50 to 100 °C within a range between 300 and 450 °C and were from

paraffinic to naphthenic types. The lube oils were of different types (light spindle oil to SAE-140) and with kinematic viscosities at 100 °C between 3 and 32 mm² s⁻¹.

Representative aromatic fractions of all samples were obtained by elution chromatography by a procedure similar to the American Society for Testing and Materials method D 2549.¹³

UV spectra were obtained with a PU 8700 UV spectrophotometer (Philips Scientific). Details of recording the spectra and calculations have been described elsewhere.¹⁴

¹H and ¹³C NMR spectra were recorded on a Tesla BS 567A spectrometer operating at 100 and 25.1 MHz, respectively. For ¹H NMR experiments, samples were dissolved in deuteriochloroform and placed in 5 mm sample tubes. Using a pulse width of 9 μs (90°), between 40 and 50 scans were collected. For ¹³C NMR analysis, 1 ml of sample was dissolved in 2 ml of deuteriochloroform containing 30 mg of Fe(acac) [tris(acetylacetonato)iron(III)] as relaxation agent. The spectrometer was operated in the gated decoupling mode and spectra were obtained using 10 mm sample tubes under the following experimental conditions: pulse width, 4 μs (flip angle about 45°); pulse delay, 5 s; power of the decoupler, 7 W; noise bandwidth, 800 Hz; word length for data processing, 16K; and number of transients, about 2500. In all cases tetramethylsilane (TMS) was used as an internal standard. The experimental parameters were selected taking into account the recommended conditions to obtain quantifiable spectra^{15,16} and were optimized using a model mixture of pure hydrocarbons with different structures. The aromatic carbon content of this mixture was 35.81% and the experimental value obtained under the selected conditions was 35.39%. The ¹³C NMR spectrum of this mixture is shown in Fig. 1. The over-all performance of the spectrometer was checked following the manufacturer's instructions with the standard samples supplied with the instrument for these purposes. All parameters (signal-to-noise ratio, resolution, *etc.*) were in acceptable ranges.

A signal-processing scheme similar to those usual in this type of analysis was used. The ¹H NMR spectra were divided into five regions (P₁–P₅) corresponding to the following proton types: aromatics (P₁, 9.5–6.0 ppm); α-CH, CH₂ to aromatic ring (P₂, 3.7–2.4 ppm); α-CH₃ to aromatic ring (P₃, 2.4–2.1 ppm); β,γ-CH, CH₂ to aromatic ring and paraffinic CH, CH₂ (P₄, 2.1–1.0 ppm); and β,γ-CH₃ to aromatic ring and paraffinic CH₃ (P₅, 1.0–0.5 ppm). The area equivalent to the total carbon (C_t) was calculated with the equation

$$C_t = AP_1 + AP_6 + AP_2 + 2AP_3/3 + AP_4/2 + AP_5/3$$

where: AP_i = area obtained by integration of the signals in region i and AP_6 = contribution of bridgehead aromatic carbons, calculated with the equation

$$AP_6 = (R_A - 1)(AP_1 + AP_2 + AP_3)/(R_A + 2)$$

where R_A , the average number of aromatic rings per molecule, is calculated from the percentages of mono- (M), di-

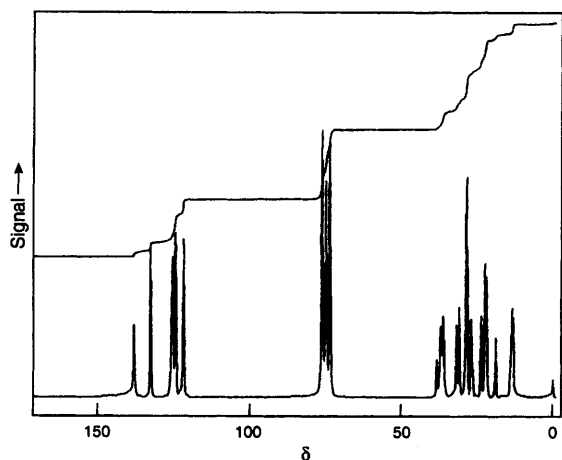


Fig. 1 ^{13}C NMR spectrum of a model mixture of pure hydrocarbons

(D) and triaromatics (T) obtained by UV spectrophotometry, by the equation

$$R_A = (M + 2D + 3T)/(M + D + T)$$

The mass percentage of aromatic carbon (C_a) is then given by

$$C_a = 100 (AP_1 + AP_6 + AP_2/2 + AP_3/3)/C_t$$

The percentages of aromatic carbon obtained from ^{13}C NMR by integration of the signals of the aromatic (160–110 ppm) and aliphatic (70–5 ppm) regions were used as reference values.

Results and Discussion

Fig. 2 shows typical ^1H and ^{13}C NMR spectra obtained from two oils with differences in their boiling ranges and aromatics content: a high-aromatic spindle oil ($C_a = 17.08\%$, aromatics by elution chromatography = 41.7%) and a low-aromatic SAE-20 oil ($C_a = 6.92\%$, aromatics by elution chromatography = 25.7%). Despite the differences between the two

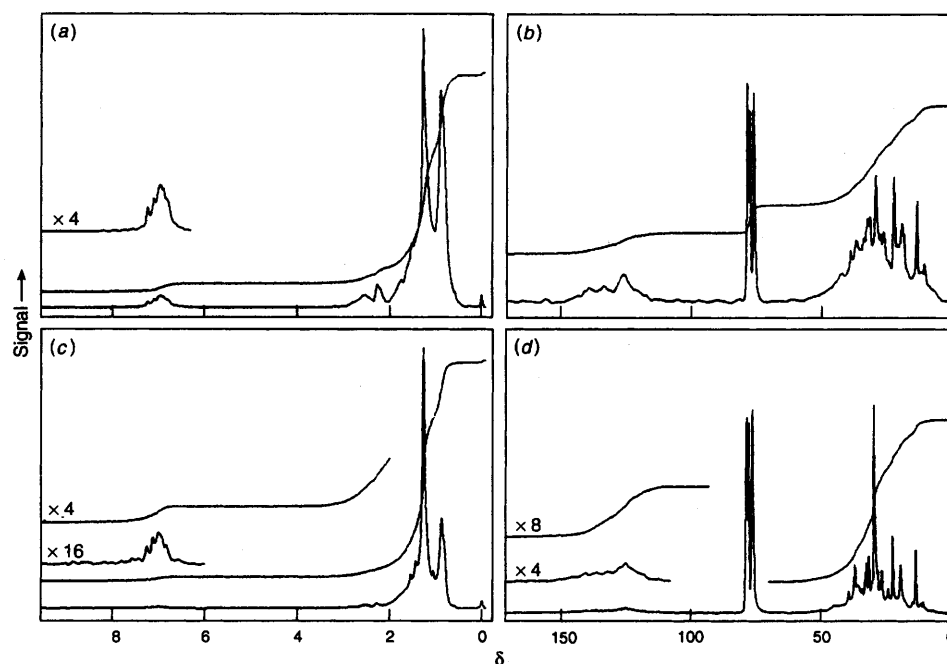


Fig. 2 NMR spectra of a high aromatic spindle oil, (a) ^1H and (b) ^{13}C , and an SAE-20 oil, (c) ^1H and (d) ^{13}C

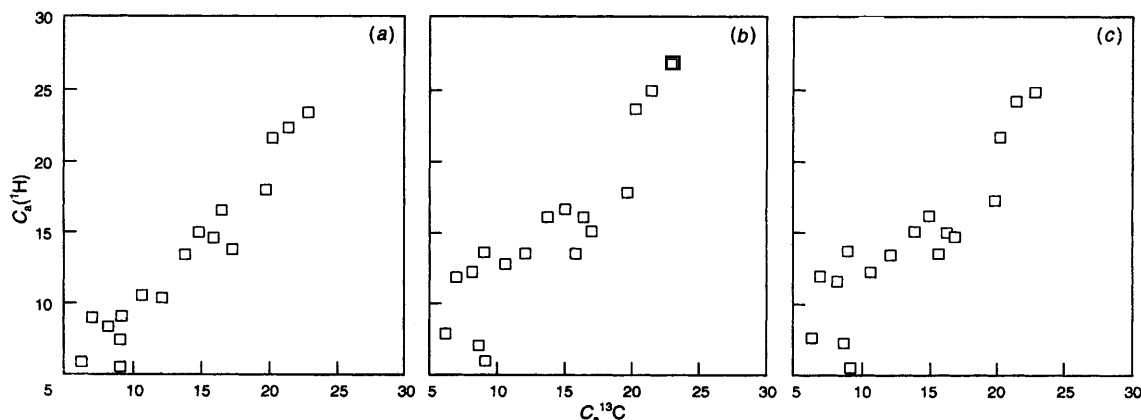


Fig. 3 Plots of $C_a(^1\text{H})$ versus $C_a(^{13}\text{C})$. (a) $s = 1.59$, $D = -0.46$, $A_0 = -0.78$, $A = 1.02$, $R = 0.964$, (b) $s = 2.96$, $D = 1.28$, $A_0 = 1.78$, $A = 0.96$, $R = 0.891$. (c) $s = 2.64$, $D = 0.75$, $A_0 = 2.21$, $A = 0.89$, $R = 0.886$

oils, the principal features concerning the signal splitting in the aliphatic hydrogen range are similar.

The exact limits of integration of the aliphatic hydrogen signals for each sample were selected according to the valleys in the peak system. It should be pointed out that a statistical evaluation of the minima located near 2.4 and 2.1 ppm using the 17 samples and the corresponding aromatics fractions gave mean values of 2.38 and 2.10 ppm with a standard deviation of 0.03 ppm.

Fig. 3(a) shows the values of C_a obtained by ^1H NMR following the procedure described in this paper versus the values of C_a obtained by the reference method. Fig. 3(b) shows the results obtained from Muhl *et al.*'s method,¹⁷ where the contribution of the bridgehead aromatic carbons is considered to be a constant fraction of the integrated area of the signals of the aromatic protons between 9 and 7.05 ppm, and Fig. 3(c) shows the values obtained by Deutsch's method,¹⁸ in which the percentages of mono-, di- and triaromatics for the calculation of R_A are obtained from the intensities of the ^1H NMR spectrum at 6.85, 7.40 and 8.50 ppm. Fig. 3 also shows the values of some statistical parameters, *i.e.*, s , the standard deviation, D , the difference of the average, calculated as

$$s = \frac{\left\{ \sum_{i=1}^n [C_{ai}(^1\text{H}) - C_{ai}(^{13}\text{C})]^2 \right\}^{1/2}}{n-1}$$

$$D = \frac{\sum_{i=1}^n C_{ai}(^1\text{H}) - C_{ai}(^{13}\text{C})}{n}$$

the independent term A_0 , the slope A and the regression coefficient R , obtained by simple linear regression of the $C_a(^1\text{H})$ values, $C_a(^{13}\text{C})$ being the independent variable. The plots and the statistical parameters demonstrate that the best results were obtained with the procedure described in this paper because of the smaller dispersion and more exact values

obtained, together with the smallest value of A_0 , a value of A closer to 1 and the best correlation coefficient.

Taking into account that in the ^{13}C NMR spectrum of petroleum cuts the signals of aromatic carbons attached to alkyl groups (except methyl) lie between 160 and 137.5 ppm and are not interfered with by other aromatic carbons,¹⁹ Fig. 4(a) shows a comparison of the plots and the s and D values of C_{alk} obtained from the integrated signals of region P_2 versus the corresponding values of C_{alk} obtained from the integration of the ^{13}C NMR spectrum over the range 160–137.5 ppm. Fig. 4(b) shows the same parameters but obtained by Deutsch's method.¹⁸ It can be observed that although there are no significant differences between the D values, the results obtained in this work have a smaller dispersion.

Conclusions

The percentages of mono-, di- and triaromatics obtained by UV spectrophotometry in the calculation of the average number of rings per molecule, R_A , used in the calculation of the percentage of aromatic carbons by ^1H NMR spectroscopy, improve the accuracy of the C_a values when they are compared with those obtained by ^{13}C NMR.

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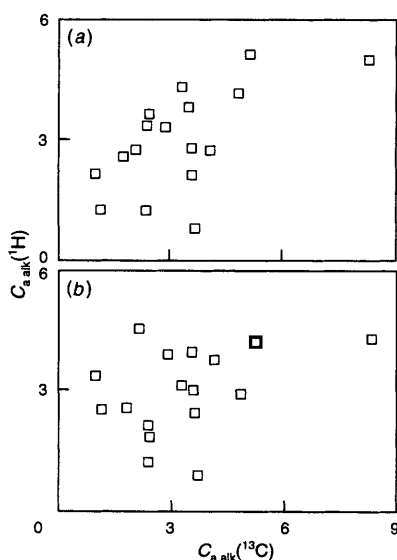


Fig. 4 Plots of $C_{a\text{ alk}}(^1\text{H})$ versus $C_{a\text{ alk}}(^{13}\text{C})$. (a) $s = 1.39$, $D = -0.32$. (b) $s = 1.70$, $D = -0.27$

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