^{1}H and ^{13}C NMR for Determining Average Molecular Parameters of Asphaltenes from Vacuum Residue Distillation

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Abstract: The aim of this work was to obtain average molecular parameters by using some analytical techniques, namely NMR (^{1}H and ^{13}C NMR), vapor pressure osmometry (VPO), and elemental analysis. NMR provided particular information on important molecular parameters such as aromatic carbon fraction, aliphatic carbons fraction, alkyl-substituted aromatic carbons, unsubstituted aromatic carbons, among others. Molecular modeling was employed to build the structure of asphaltenes using the experimental data.

Resumo: O objetivo deste trabalho foi obter parâmetros moleculares médios, utilizando algumas técnicas analíticas. As técnicas utilizadas foram: RMN (^{1}H and ^{13}C), osmometria de pressão de vapor (VPO) e análise elementar. A RMN em particular proporcionou a obtenção de importantes parâmetros moleculares tais como a fração de carbonos aromáticos, fração de carbonos alifáticos, carbono aromático ligado à cadeia alquila e carbono aromático não substituído. A modelagem molecular foi utilizada na construção da estrutura do asfalteno a partir dos dados experimentais.

Introduction

The deposition of asphaltenes is a well known problem in the petroleum industry, as it seriously affects oil production and refining, involving large costs in the prevention and removal of such deposition.[1] During the past years, studies on petroleum asphaltenes have increased significantly, which can be attributed to the high production of heavier crude oils. Asphaltenes are considered a problem for the industry because they may flocculate and precipitate during several stages of petroleum processing. As the heavier crude oil is refined, processing the residuum becomes increasingly difficult, resulting in many unit operation problems. The main problems for the oil industry caused by deposition of asphaltenes are as follows: reduction in oil flow, blocking of production pipes and serious drawbacks during the processing of heavy ends such as coke formation, catalyst deactivation and poisioning. [1,2,3]

The average molecular structures of asphaltene consist of condensed polynuclear aromatic ring systems bearing alkyl side chains, and some heteroatoms such as sulfur, oxygen and nitrogen. Traces of metals such as nickel and vanadium can be also present. In addition, asphaltenes are defined as the polar fractions of oil that are insoluble in n-alkane liquids, e.g. pentane or heptane, and soluble in aromatic solvents, like toluene and benzene.[2,4,5] Thus, many authors have focused on the molecular structure of asphaltenes, especially because such knowledge can broaden the understanding of their behavior in many processes involved in the petroleum industry.[1,2]

Several analytical techniques have been used to investigate asphaltene molecular structures. Among these, NMR should be highlighted, as it provides important and

reliable average molecular parameters. NMR data together with molecular weight and elemental analyses make it possible to determine the average molecular structure of asphaltene.[2,4,6]

Experimental

The asphaltenes used in this work were obtained from different vacuum residues according to the IP-143/96 method.[7] Elemental composition was determined on a Perkin Elmer CHNO Analyzer 2400. Average molecular weight measurements were determined by vapor pressure osmometry (VPO) in toluene at 50ºC on a Wescan, model 233. NMR (^{1}H and ^{13}C) spectra were obtained on a Varian Gemini-300 spectrometer, at resonance frequencies of 300 MHz and 75.4 MHz respectively and using 5mm o.d. NMR tubes. Acquisition conditions were as follows: For ^{1}H a flip angle of 30°

(pulse width of 5.0μs) was used, a repetition rate of 1s, spectral width of 4500 Hz and 128 transients. For ^{13}C a 90º pulse was used with a 10s delay between them, and a spectral width of 18700 Hz. The decoupler was in the gated mode, and more than 1000 transients were accumulated. The chemical shifts were referenced to tetramethysilane (TMS) for both spectra, and the asphaltene samples were dissolved (5% p/v) in a mixture of $CDCl_3$ and C_2Cl_4 (1:1) for the ^{1}H NMR acquisitions, and 40% p/v in a solution of $CDCl_3$ containing 0,05M of $Cr(acac)_3$ as relaxation reagent for the ^{13}C experiments.

Results and discussion

The elemental data of asphaltene samples are shown in Table 1. These asphaltenes were obtained from different vacuum residues.

Table 1. Analytical Data for Asphaltenes from Different Origins.

Asphaltenes	C (%w/w)	H (%w/w)	N (%w/w)	S (%w/w)	O (%w/w)	AC*
Residue A	86.4	8.1	1.8	2.1	1.5	6.50
Residue B	86.9	8.2	1.8	1.6	1.5	6.95
Residue C	86.5	10.9	1.0	1.3	1.3	11.37
Residue D	81.4	8.1	1.9	7.4	1.2	16.90

AC* = Asphaltene Contents

The elemental analysis results in Table 1 reveal that asphaltenes from residue D have higher sulphur and lower carbon content. Nitrogen and oxygen content appear very similar for all asphaltenes extracted, with sliglitly lower nitrogen for residue C. The

oxygen content is calculated by difference. Residue D has the higher asphaltene content.

The NMR spectrum of asphaltene is shown in Figure 1 for ^{1}H and in Figure 2 for ^{13}C. According to Hassam et al.[5], the following regions of chemical shift are of interest in a ^{1}H NMR spectrum: aromatic hydrogens (9 to 6

ppm), aliphatic hydrogens (4.5- 0.5 ppm) divided into Hα (4 to 2 ppm); Hβ (2 to 1 ppm); and Hγ (1 to 0,5 ppm). The ^{13}C NMR spectrum has been divided into different integration domains: aliphatic carbons (10-65 ppm) and aromatic carbons (100-170 ppm).[6]

Tables 2 and 3 show average molecular parameters for the asphaltene samples. The asphaltenes from residue C show a higher aromatic carbons content, a higher number of aromatic carbons bonded to alkyl chains and also a higher C/H ratio.
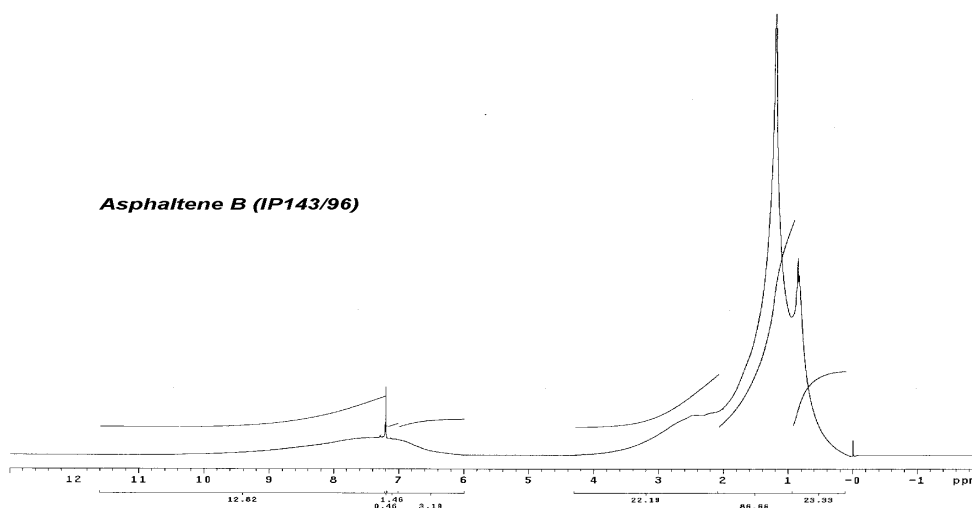

Figure 1. [1]H spectrum of asphaltenes for which different integration domains are shown.
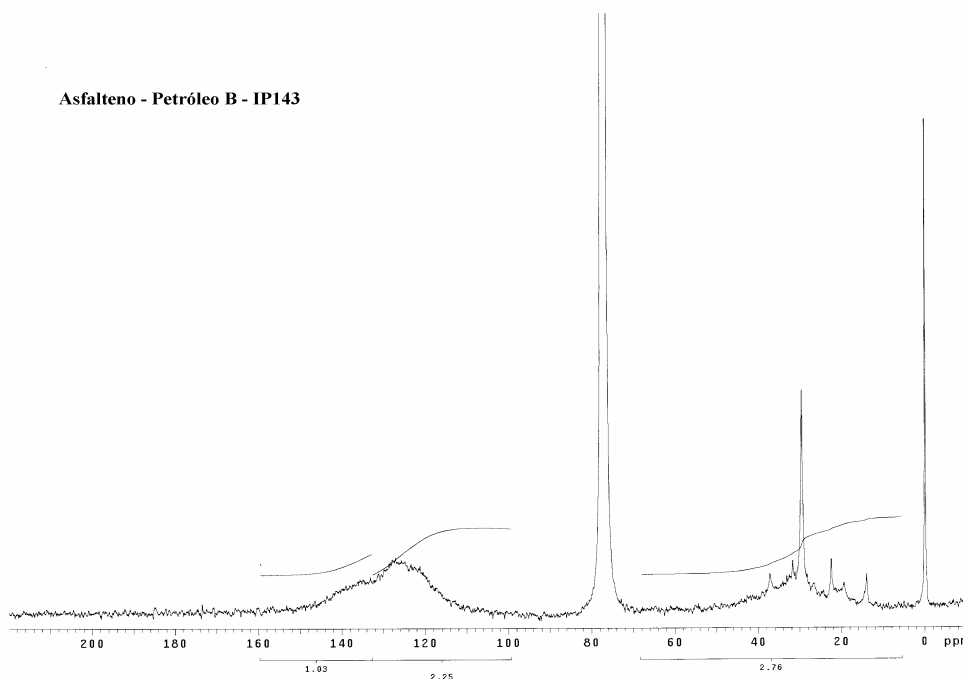

Figure 2. [13]C spectrum of asphaltenes for which different Integration domains are shown.

The asphaltenes from residue B show the lowest aromatic carbons content and the highest length of alkyl side chains, as can be verified from hydrogen β content.

According to Speight[4], the apparent molecular weight of asphaltenes by VPO is in the range of 3000-10000,[3,4] higher than that found by other techniques such as size exclusion chromatography (SEC) and mass spectrometry.

Table 2. Average Molecular Parameters Obtained by ^{1}H and ^{13}C NMR.

Molecular Parameters	Asphaltenes Residue A	Asphaltenes Residue B
% of aromatic carbons	58.8	58.6
% of saturated carbons	41.2	41.4
% of aromatic carbons bonded to alkyl branches	10.4	9.5
% of aromatic carbons bonded to hydrogen	15.4	14.7
Fa (aromatic carbon fraction)	0.59	0.59
% aromatic hydrogens	10.9	10.4
% hydrogen (α)	17.7	9.6
% hydrogen(β)	52.9	65.6
% hydrogen(γ)	18.2	14.5
% saturated hydrogens	88.7	89.6
C/H ratio	0.71	0.71

Table 3. Average Molecular Parameters Obtained by ^{1}H and ^{13}C NMR

Molecular Parameters	Asphaltenes Residue C	Asphaltenes Residue D
% of aromatic carbons	64.1	60.8
% of saturated carbons	35.9	39.2
% of aromatic carbons bonded to alkyl branches	27.2	10.4
% of aromatic carbons bonded to hydrogen	16.3	12.5
Fa (aromatic carbon fraction)	0.64	0.61
% aromatic hydrogens	12.0	9.0
% hydrogen (α)	12.7	16.4
% hydrogen (β)	58.6	57.3
% hydrogen (γ)	16.6	18.7
% saturated hydrogens	88.0	91.0
C/H ratio	0.74	0.72

Table 4 presents the average molecular weight for asphaltene samples, which are similar to Speight's results.

Table 4. Average molecular weights of asphaltenes from different vacuum residues

Asphaltenes	Molecular Weight (Mn)
Residue A	6727
Residue B	8080
Residue C	8320
Residue D	NA*

NA* = Not Available

The rather high VPO molecular weights are due to strong intermolecular attractions among asphaltene molecules, which results in large, colloidal aggregates in solution.

Conclusions

The results of this work indicate that the use of several techniques, particularly ^{1}H and ^{13}C NMR to analyze asphaltene can broaden the understanding of its molecular structure. The asphaltenes from different vacuum residues

show some significant trends in terms of molecular structure: when the heteroatom content decreases, the average molecular weights become smaller.

As aromaticity increases, the % of aromatic carbons bonded to alkyl branches increases. Also, as aromaticity increases, molecular weight becomes higher due to strong intermolecular attractions among asphaltene molecules, resulting in colloidal aggregates in solution. This effect can be explained by the formation of lamellar stacks of aromatic sheets. The lowest the aromatic carbons content, the higher the length of alkyl side chains observed.

Therefore, NMR can provide valuable information about the chemical structure of asphaltenes and also about their average molecular structure, with a special focus on the aromatic ring system.

Acknowledgements

References

1. O. León, E. Rogel, J. Spidel, G. Torres, *Energy Fuels* **14** (2000) 6.

2. V. Calemma, *Energy & Fuels* **9** (1995) 225.

3. J. T. Miller, R. B. Fisher, P. Thiyagarajan, R. E. Winans, J. E. Hunt, *Energy and Fuels* **12** (1998) 1290.

4. M. A. Bestougeff, R. J. Byramjee, "Chemical Constitution of Asphaltenes", in Yen, T. F & Chilingarian, G. V. (Editors), *Asphaltenes and Asphalts, 1. Developments in Petroleum Science* **40** (1994) 67.

5. J. G. Speight, *Journal of Petroleum Science and Engineering* **22** (1999) 3.

6. M. H. Hassan, *Fuel* **62** (1983) 000.

7. Standards for Petroleum and Its Products, Standard nº IP143/96, Institute of Petroleum, London.