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An evaluation of the aromaticity of asphaltenes using atmospheric pressure photoionization Fourier transform ion cyclotron resonance mass spectrometry – APPI(±)FT-ICR MS

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HIGHLIGHTS

- We evaluate the aromaticity of asphaltenes using APPI(±)FT-ICR MS.
- APPI(±)FT-ICR MS data were compared and discussed with aromaticity parameters obtained from elemental analyses and ^{1}H NMR.
- An inverse correlation was observed between aromaticity degree and the N and O concentrations.
- The slopes of DBE *versus* carbon number plots are direct indicative of variation of aromaticity.

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ABSTRACT

Asphaltenes can be considered like the 'bad guys' when heavy petroleum are transported or upgraded. These compounds are not classified by the their chemical structures but by the solubility class, that is defined as solubles in aromatic solvents, such as toluene, and insolubles in *n*-alkanes, such as *n*-heptane. Here, we analyze three crude oil samples (classified as extra-heavy, heavy and asphaltic having API degree of 17.3, 22.0 and 13.5, respectively) and their asphaltenes by atmospheric pressure photoionization (APPI) coupled to Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) in positive and negative ionization modes, APPI(±)-FT-ICR MS. We apply the DBE (double bond equivalent) *versus* carbon number (CN) plots as the aim of to predict the aromaticity of crude oil and their asphaltenes. Additionally, average molecular weight, M_w, heteroatomic-containing compounds profile and van Krevelen diagrams were constructed to visualize and interpret the MS data. MS data were compared and discussed with aromaticity parameters obtained from elemental analyses and ^{1}H NMR measurements. For three crude oils analyzed with different magnitude of the viscosities (III > II > I), the amount of the asphaltene extracted follower the behavior analogous (7.63 ± 0.65 wt%; 2.23 ± 0.25 wt%; and 0.41 ± 0.01 wt%, respectively). The aromatic hydrogen content (H_{ar}, in molar%) was determined from ^{1}H NMR, where the heavier crude oil and its asphaltene ($H_{ar} = 4.90$ and 27.3 M%, respectively) were slightly more aromatic than other. An inverse correlation was observed between H_{ar} values and the N and O concentrations determined from elemental analyses. For APPI(±)FT-ICR MS data, the values of M_w observed for asphaltenes (m/z 200–650) were significantly distinct, being correlated with the physico-chemical characteristics of their parent crude oil. Using the concept of planar limited, the line generated by connecting maximum DBE values at given CN in the DBE *versus* carbon number plots, it was possible to extract the aromaticity degree from APPI FT-ICR MS data. The slopes of these lines determined by DBE/carbon number ratio were calculated by linear regression for protonated hydrocarbons (HC[H]) and basic nitrogen (N[H]) compounds classes. We observed an increase in slopes in function of an increasing of the H_{ar} values.

1. Introduction

Asphaltenes can be considered like the 'bad guys' when heavy petroleum is transported or upgraded [1]. Their precipitation represents a serious concern to the petroleum industry, requiring a

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large capital investments for removal, prevention of deposit formation and researches funding designed to better clarify its chemical composition [2–5]. The process of deposit formation can be induced by variations from pressure, temperature, reservoir fluid composition, flow shear rate, surface characteristics, particle size to chemical interactions [2,6].

It is well-known that asphaltenes are the heaviest and most complex molecules of the crude oil [7]. These compounds are not classified by their chemical structure but by the solubility class, that is defined as compounds soluble in aromatic solvents, such as toluene, and insoluble in *n*-alkanes, such as *n*-heptane [2,8]. Several physicochemical properties of crude oil are affected by presence of high content of asphaltenes such as viscosity, emulsion stability, flow assurance problem, rheological properties and refraction index [4].

The asphaltenes can structurally be classified based on "island"-type structures (models of one aromatic core) or "archipelago"-type structures (models of multiple aromatic centers bridged by alkyl chains) [5,9] and have a high tendency to associate into larger aggregates [10,11]. Their stability in petroleum fluids can be disrupted by pressure drop or compositional changes, which lead to asphaltene precipitation and deposition in subsurface formations, wellbores, or transportation pipelines [4,5].

Successful prediction of asphaltene precipitation requires the understanding of mechanisms of asphaltene aggregation in terms of its composition. It is known that intermolecular forces play an important role on asphaltene aggregation [12]. Recently, a modified Yen model (also called Yen–Mullins model) stipulated that asphaltene nanoaggregates consist of less than 10 molecules stacked on top of each other. The aggregation stops beyond nanoaggregation; however, nanoaggregates can coagulate due to their high molar weight forming clusters of aggregates, which can eventually lead to flocculation. The driving force of aggregation is the π–π stacking or aromatic interactions from the aromatic core of asphaltenes, and the force limiting their aggregation is the steric hindrance caused by aliphatic side chains. Aromatic interactions occur due to electrostatic attraction between the negative π electron cloud and positive σ frame of aromatic rings [11,12]. Thus, a clear picture of the aromaticity degree or aromatic content of asphaltenes is a prerequisite to predict aggregation.

Usually, advanced NMR techniques can provide the degree of aromaticity, the average aromatic core number and the size distribution in asphaltene fraction. However, the NMR results provide the average molecular structures, being routinely found that more one structure might be compatible with a set of NMR data. For a successful prediction model, it is important to know the chemical composition of various compound classes, the carbon number distribution in each compound classes and the carbon center distribution for each carbon number. Among numerous analytical techniques for asphaltene characterization, atmospheric pressure photoionization (APPI) coupled to Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry provides the most extensive molecular characterization of nonpolar petroleum compounds. FT-ICR MS provides an unsurpassed mass resolution and mass accuracy, thus enabling, a molecular level analysis of complex petroleum mixtures and asphaltenes [13,14]. Accurate mass measurements [15,16] define a unique elemental composition ($C_cH_hN_nO_oS_s$) and DBE (double bond equivalent), facilitating material classification by heteroatom content and the degree of aromaticity [17–23]. APPI is well-suitable to characterize purely cycloalkane hydrocarbon and aromatic species, thiophenes, and furans that are inaccessible to electrospray ionization because the molecules are insufficiently basic or acidic to accept or lose a proton. APPI can positively charge these species to produce both radical cations $[M]^{+\cdot}$ and protonated molecules $[M+H]^+$ [24,25]. Specifically, APPI ionizes species that can either undergo direct ionization from 10 eV photons (aromatics, such as asphaltenes) to gas-phase proton transfer or charge exchange reactions.

In 2006, Purcell et al. [24] have analyzed naphtho[2,3-a]pyrene and crude oil by APPI(±)-FT-ICR MS, where the results reveals that APPI(±) can produce protonated molecules, $[M+H]^+$, deprotonated molecules, $[M-H]^-$, and radical molecular ions, $M^{\cdot+}$ or $M^{\cdot-}$, consequently, producing mass spectra of ca. >12 000 peaks, being that 63 species are identified for each nominal mass unit. In 2008, Qian et al. [26,27] demonstrated that APPI(+) provides soft ionization of Vanadyl porphyrins, sulfur-containing Vanadyl porphyrins [25] and Nickel porphyrins [26]. All were present in petroleum asphaltene, generating primarily molecular ions $M^{\cdot+}$. The changes in hydrocarbon and sulfur classes during deep hydrotreatment processes were also observed, being successfully applied to identify and catalog diverse structures of Vanadyl porphyrins. In 2009, McKenna et al. [25] have analyzed Vanadyl porphyrins by APPI(+)FT-ICR MS. Despite the rich literature related to asphaltenes characterization using APPI FT-ICR MS, there is few studies that correlate between the APPI FT-ICR MS data and other analytical techniques with of aim of predicting any physico-chemical properties. Here, we analyze three crude oil samples (classified as heavy, extra-heavy, and asphaltic oils) and their asphaltenes by APPI(±)-FT-ICR MS. We apply the concept of planar limits, defined as lines generated by connecting maximum DBE values at given carbon numbers in a plot of DBE *versus* carbon number as the aim of to predict the aromaticity of crude oil and their asphaltenes. We use the slopes of the lines determined by the DBE/carbon number ratios as indicative of degree of aromaticity. These data were compared and discussed with aromaticity parameters obtained from elemental analyses and ^1H NMR spectrometry measurements.

2. Experimental

2.1. Reagents

Heptane and toluene (analytical grades with purity higher than 99.5%), were used for extraction procedure of asphaltenes and characterization by APPI(±)FT-ICR MS, respectively. Both were supplied by Vetec Química Fina Ltda, Brazil. Ethylenediamine tetraacetic acid (EDTA), acetanilide, chromium(III) acetylacetonate ($Cr(acac)_3$), deuterated chloroform ($CDCl_3$) and tetramethylsilane (TMS) were purchased from Sigma–Aldrich Chemicals USA (purity of 99.8%) and used for elemental analysis (CHNSO) and ^1H NMR measurements. All reagents were used as received.

2.2. Petroleum characterization and asphaltene fraction extraction

Three samples of crude oil (termed in crude oil I, II and III) were characterized according to the standards of the ASTM by Laboratory of Petroleum Characterization of Federal University of Espírito Santo (LabPetro/UFES-Brazil). A primary characterization was conducted to determine density (ASTM D5002-99), [28] API degree (ASTM D1298-99) [29], and kinematic viscosity (ASTM D7042-04) [30]. The characterization data obtained for three crude oils are describe in Table 1, thus classifying the crude oils I, II and III as heavy, extra-heavy and asphaltic oils, respectively [31].

Three different asphaltene samples were obtained from crude oils (I, II and III) by precipitation with *n*-heptane ($30\ mL\ g^{-1}$ of crude oil) and washed in a soxhlet system using the same solvent. The precipitated asphaltenes were filtered and solubilized with toluene. After, the solutions were evaporated to obtain asphaltene fraction samples (termed in asphaltene I, II and III) according to the ASTM 6560-00 [26]. The asphaltene extraction from different crude oils was done in triplicate and their total weight recovery