



Full Length Article

Integrative mass spectrometry strategy for fingerprinting and tentative structural characterization of asphaltenes

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ABSTRACT

Heavy oils are characterized by high proportions of asphaltenes, a class of polyaromatic hydrocarbons whose structures remain unknown. Previous work based on asphaltene physical-chemical properties and extensive spectroscopic and computational methods has generated controversy about two possible general conformations: island and archipelago. To address this controversy, this study employed a systematic integrative approach involving ion mobility (IMS), theoretical calculations, ultra-high resolution mass spectrometry (UHR MS), and pyrolysis gas chromatography coupled to high-resolution mass spectrometry (Py-GC-HR MS) to evaluate the composition and structure of asphaltenes. Two Brazilian oils with different API grades (heavy and light) were analyzed and compared. The comparison of IMS data demonstrated that isobaric asphaltenes from light and heavy oils shared similar collisional cross sections (CCS) with different homologous series in the experiments. Two-dimensional (2D) difference mobility plots showed that minor compounds in these fractions possess different CCS. The combination of CCS data with UHR MS and Py-GC-HR MS still was not enough to indicate if there is a single asphaltene architecture in the studied samples. However, the obtained data were structurally slightly more consistent with the island architecture. Furthermore, the systematic combination of mass spectrometry techniques and calculations provided a reliable method for fingerprinting complex geological samples and providing structural information.

1. Introduction

Heavy oils are crude petroleum sources with higher viscosity and lower API gravity than that of lighter oil sources. Some of the highest volume remaining reserves in North and South America are classified as heavy oils (Alaska Heavy, 8 to 14° API) or extra heavy oils (Athabasca oil sands, 6 to 10° API, and Venezuelan, 10° API) due to their high amount of asphaltenes [1–3]. These large polyaromatic compounds constitute the most polar and heaviest compounds in crude petroleum and their structural elucidation has been a challenge that has been and subject of several studies [4]. In solution, asphaltenes tend to form complex colloidal structures [5]. This behavior can cause serious problems during petroleum transport and processing, such as rapid deactivation of catalysts, coking within the reactor or fractionator, and formation of sludge in distillation products [6]. An understanding of

asphaltene chemistry is vital, as heavy oils comprise a growing proportion of the world's remaining deposits of crude oil.

Asphaltene science has advanced significantly in recent years, however, the real structure of asphaltenes still is unknown, and none of the proposed models is completely accepted. In this debate, island [4] structures with a single central polyaromatic core and archipelago [7] structures with multiple polyaromatic cores connected by alkyl chains are among the possible architectures, the former being the most widely accepted based on the Yen-Mullins model [4,8]. Determining the structure of asphaltenes is of interest to the petroleum industry as new structural features of asphaltenes may better explain their physical-chemical properties, affording new insights to heavy oil extraction and refining [9–14].

Several methods for the structural characterization of asphaltenes have been applied, such as nuclear magnetic resonance (NMR) spectroscopy,

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centrifugation, direct-current conductivity, small-angle X-ray scattering (SAXS), and molecular orbital calculations (MOC) [15–22]. Mass spectrometry (MS), in particular, has been one of the principal techniques used for asphaltene characterization [23,24]. Due to its intrinsic characteristics (speed, sensitivity, selectivity, and low analysis cost), MS has become a routine technique in asphaltene science [25]. The combination of chromatographic methods and MS (especially at ultra-high mass spectral resolutions, $m/\Delta m_{50\%} > 100,000$) have been extensively applied to oils and their derivatives in the field known as petroleomics [26]. This blend of techniques allows an expansion of the analytical window [27], comprising a reliable strategy for fingerprinting and characterizing complex carbon materials, such as asphaltenes. The combination of these techniques with others that have recently become commercially available (e.g. ion mobility) may be able to address the remaining questions about asphaltene structure and chemistry.

Ion mobility spectrometry (IMS) is a gas-phase ion separation technique that was introduced in the 1960s, but only became commercially available in the 2000s [28]. In IMS, species are separated based on their charge states and sizes/shapes, which is more rigorously described as their collision cross sections (CCS). Traditionally, ions are injected into a drift cell (DC) filled with an inert gas (typically helium), in the presence of a weak electric field applied at the end of the cell, and are detected separately with respect to the time they take to traverse the cell. Smaller ions collide less frequently with the buffer gas compared with larger ions, thus crossing the DC faster. The subsequent combination of IMS with MS (IMS-MS) extended the application of ion mobility for analyses of carbon clusters [29], peptides and proteins [30], synthetic polymers [31], petroleum samples [32], and more recently asphaltenes [25]. Traveling wave ion mobility (TWIM) has been introduced more recently as a new mode of ion propulsion for IMS experiments [33]. Briefly, in TWIM, ions are accumulated and periodically released into a stacked-ring ion guide (T-wave cell), where they drift under the action of a continuous train of transient voltage pulses (traveling waves) applied to pairs of stacked ring electrodes, encompassing a very compact drift cell (18.5 cm long), but with advantages in ion transmission and separation resolution [33].

The aim of this work was to evaluate the application of an integrative approach to fingerprint/characterize asphaltene samples by comparing analytical data from experimental TWIM MS derived CCS and theoretical CCS calculations in combination with UHR MS data as a new strategy in petroleomics for geological fingerprinting approaches. Additionally, a systematic study of the chemical composition of Brazilian asphaltene samples was conducted to evaluate the strategy and its significance to the ongoing asphaltene structure debate.

2. Experimental section

2.1. Materials and sample preparation

The standard compounds used as model compounds 1-naftol, 8-quinolinol, coronene (CRN), 2,7-diheptylbenzo[*lmn*][3,8]-phenanthroline-1,3,6,8(2*H*,7*H*)-tetrone (DHBPT), (*E*)-1-(2-(naphthalene-1-ene) vinyl pyrene (TNVP), and fullerene C₆₀ (FUL) were purchased from Sigma-Aldrich (St. Louis, MO, USA). HPLC grade solvents: toluene, dichloromethane, and methanol were from Tedia (Fairfield, OH, USA). Crude oil samples were ceded by PETROBRAS (Rio de Janeiro, RJ, Brazil). As recommended by PETROBRAS, the oil samples were named petroleum 1 (P1, 12.8° API, heavy type) and petroleum 3 (P3, 31° API, light type). Standard compounds were dissolved in dichloromethane to a final concentration of 50 µM. The oil samples were dissolved in toluene at 0.5 mg/mL prior to analysis. The respective asphaltene fractions from the two oil samples (AP1 and AP3) were obtained by precipitation with *n*-heptane (*n*-C₇) according to a previously described methodology [34]. Co-precipitated resins were thoroughly removed with boiling *n*-C₇ using a Soxhlet apparatus until the *n*-C₇ became clear (3 days) [34].

2.2. Ion mobility experiments

TWIM MS experiments were performed on a Waters Synapt G1 HDMS (Manchester, UK). Gas-phase ions were generated by a laser desorption/ionization (LDI) probe operating in positive mode. LDI acquisitions were carried out using a 200 Hz solid state laser (Nd:YAG) (Waters). LDI-specific instrumental parameters were as follows: MALDI laser firing rate 200, MALDI plate speed 20 V, MALDI laser energy 400 au, focal length 60 mm, MALDI extraction 10 V. The oa-TOF mass analyzer was operated in V mode (7500 $m/\Delta m_{50\%}$) with a range of m/z 50–3000. Separations were carried out in the T-wave cell of the same mass spectrometer. This cell was filled with nitrogen gas (N₂, 0.545 mbar). Optimized separation conditions were: trap collision energy 4 V, transfer 2 V, nitrogen IMS gas flow 44 mL/min, wave height start 2 V, wave height end 30 V, wave velocity start 500 m/s, wave velocity end 500 m/s. Prior to all analyses, the instrument was calibrated using sodiated polyethylene glycol ions between m/z 50 and 3000. Data acquired were processed with the software packages MassLynx v.4.1, Driftscope Mobility Environment v.2.0 and HDMS Compare v.1.0.

2.3. Ultra-high resolution time-of-flight mass spectrometry

UHRTOF MS analyses were performed in a prototype mass spectrometer equipped with a folded flight path time-of-flight mass analyzer (FFP-TOF), which is based on the reflectron arrangement (200,000 $m/\Delta m_{50\%}$) of the Citius mass spectrometer (LECO, St. Joseph, MI, USA) [35]. Crude oil analyses were performed using an electrospray ionization source (ESI) operating in positive and negative modes. For the asphaltene fractions, a prototype atmospheric pressure photoionization (APPI) source was constructed based on an atmospheric pressure chemical ionization (APCI) [35] source (LECO) with a kryptonium lamp (Syagen Technology, Tustin, CA, USA). ESI-specific instrumental parameters were as follows: spray voltage 2.8 kV, extractor cone 80 V, desolvation temperature 600 °C, mass range 190–725 (m/z). For APPI instrumental parameters were as follows: desolvation temperature 500 °C, extractor cone 110 V, mass range m/z 90–1000. Prior to all analyses, the instrument was calibrated with phosphoric acid cluster ions covering the same m/z ranges. The data, obtained using ChromaTOF software, were processed in the software PetroOrg [36] for internal recalibration, classification and double bond equivalent (DBE) versus carbon number plot generation.

2.4. Pyrolysis-GC-HRTOF MS analysis

Asphaltene samples (1 mg) were placed into a quartz tube of a Pyroprobe Model 5200 (CDS Analytical Inc., Oxford, Pa, USA) interfaced to an Agilent 7890A GC (Palo Alto, CA, USA). Flash pyrolysis was performed at 800 °C for 20 s. Pyroprobe interface, valve oven and transfer line were set at 300 °C. Helium was used as the carrier gas from the pyroprobe to the GC at 1 mL/min flow rate. GC inlet, transfer line and ion source were respectively maintained at 300, 320, and 250 °C. Separation by GC was achieved with a Restek (Bellefonte, PA, USA) Rxi-5MS column (30 m length, 250 µm I.D., 0.25 µm film thickness) using a constant 1 mL/min flow of helium. The GC oven had an initial temperature of 50 °C held for 2 min, increased to 320 °C at 6 °C/min, and held at the final temperature for 10 min. For MS analysis a Pegasus GC-HRT (LECO) was used in high resolution mode (25,000 $m/\Delta m_{50\%}$, mass accuracy less than 1 ppm) with an electron ionization source. Data were recorded in full MS mode from 45 to 650 m/z at an acquisition rate of 6 spectra/s, and 1.5 kHz extraction frequency. Data was acquired and processed using ChromaTOF software.

2.5. CCS measurement calibration

For the CCS calculations in the T-wave cell, the modified Mason-

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