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Characterization of Algerian Hassi-Messaoud asphaltene structure using Raman spectrometry and X-ray diffraction

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Abstract

Asphaltenes derived from Algerian oil wells were characterized by Raman spectrometry to investigate their molecular structures in solid-state. The aromatic sheet diameter (L_a) was estimated using the integrated intensities of the G and the D1 mode, along with the Tuinstra equation [Tuinstra F, Koenig JL. J Chem Phys 1970;53:1126]. The values obtained for three Algerian Hassi-Messaoud asphaltene samples are on the same order as the literature values and also consistent with the X-ray diffraction results. The Raman spectra corresponding to the G and the D bands can be fitted with Gaussian, Lorentzian, and Gaussian/Lorentzian hybrid functions in a self-consistent manner. A three peak fitting procedure found that the Gaussian/Lorentzian hybrid function with G being Gaussian and D Lorentzian is the best combination. Incorporation of the X-ray data on the height of the crystallite, L_c, gives rise to an estimate of eight asphaltene molecules in each asphaltene aggregate.

Keywords: Asphaltene; Raman spectrometry; X-ray diffraction; Aromatic sheet diameter; Fitting functions

1. Introduction

Asphaltenes are a fraction of petroleum liquids insoluble in *n*-heptane but soluble in some aromatic solvents such as toluene, pyridine, or benzene [1]. Since the definition is based on solubility, asphaltenes represent a class of compounds (a mixture of compounds of different structures) with similar solubility property rather than a pure substance with a well-defined molecular structure. This complicates the selection of characterization techniques and choice of processes for handling asphaltene containing materials. Despite of this microscopic complexity, asphaltene molecules have been shown to generally comprise a poly-condensed aromatic (PCA) core with hydrocarbon side chains attached to it. In addition, the aromatic core may include heteroatoms, such as nitrogen, oxygen, sulfur and metals [2]. These heteroatoms are likely relevant to their high propensity of self-aggregation, flocculation and precipitation [3].

These micro phase separations often aggravate into macro phase separations and hinder the production flow, storage stability, transportation liability, and refining. To avoid such potential operational disaster, it is vital to interactively optimize operational parameters during production, to control asphaltene flocculation, precipitation, or their corresponding kinetics. Controlling these parameters requires thorough understanding of the molecular interplays among different species in asphaltenic materials. It is thus important to study the relevance between the asphaltene molecular structures and their impact on the bulk physical properties.

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The aromatic moiety in asphaltenic molecules, through π–π and dipole interactions, was thought to be one of the dominant contributors to asphaltene self-association. The aromaticity changes during both upstream production or down stream refining processing [4]. Due to this, a simple and reliable method for characterization of the asphaltene PCA contents and the molecular structure can serve as a gateway toward controlling asphaltene self-association led flocculation and precipitation during field operations [5]. On the research end, it can possibly lead to elucidation of the structure-driven thermodynamic and transport properties under natural geological conditions, which are difficult to simulate in a laboratory [6].

The number of aromatic hexagons in a graphene or a carbonaceous material (equivalent to the aromatic sheet diameter) has been a subject of interests and much work has been explored using various techniques – NMR [7], XANES [8], and AFM [9]. On the asphaltene structure, experimental evidence had shown that an average aromatic sheet comprises of 4–10 benzene-condensed rings [5]. This was a breakthrough but with tremendous amount of work and cumbersome data interpretation processes. In looking for a field friendly technique or any potential techniques with different probes that can either confirm or invalidate this important result, Raman spectroscopy stands out, from both experimental convenience and data interpretation point of view. This technique has been applied for characterization of various carbonaceous materials and fundamental data analysis schemes are readily available [10].

Incorporation of X-ray diffraction (XRD) with Raman spectroscopy has been the most frequently used “twin-technique” for characterizing aromatic containing carbonaceous materials [10–12]. They characterize the aromatic portion of the molecules via different mechanisms. XRD evaluates the interplays between the aromatic sheets of carbonaceous materials (or asphaltene molecules) [13]. Through Bragg diffraction law, it provides dimension of the molecules stacking. The (10) band, which normally appears around 43° for carbonaceous materials, is related to the diameter of the basal area of the molecule (L_a). Raman spectrometry on the other hand provides evidence of the molecular bond vibrations that are regulated by the intra and inter molecular interactions. When applied to aromatic compounds, Raman scattering carries information about the crystallinity (or the crystalline domain dimension) of the system and is sensitive to the edge of an irregular structure [14,15]. Because of its sensitivity to the edge structure in 2-D, the local PCA structure can be extracted [16]. In this work we adopted the Tuinstra and Koenig equation [17] to estimate the extent of the aromatic structure using the integrated intensities of the so-called G band (near 1580 cm^{-1}) and the D1 band (near 1350 cm^{-1}) [17]. The diameter so obtained is an estimate of the diameter of the fused benzene condensed rings, from which the number of rings can be roughly calculated.

Raman spectrometry is popular for studying commercial graphite-like or diamond-like polycyclic aromatic hydrocarbon (PAH) compounds, as well as carbon blacks that are commonly used for high-tech industry and environmental products [11–15]. This technique, however, was rarely used for characterizing asphaltenes, even though it should be a potential candidate for such applications. To the best of our knowledge, there was only one attempt in using Raman scattering for asphaltene characterization. Bergmann et al. [18] applied X-ray Raman to study asphaltene, which allowed them to evaluate the molecular inside of this complex system. However, a synchrotron based X-ray source is needed to perform such an experiment, which is not practical for field applications. Lacking Raman works for asphaltene characterization might be attributed to the fact that in graphite systems, the existence of D bands was only unambiguously identified and proved lately [19].

In an attempt to apply this potential technique to asphaltene characterization, we set a rather focused goal here. We employed Raman spectrometry as an alternative to characterize the average molecular dimension of asphaltene and used it in conjunction with X-ray diffraction measurements to confirm its applicability. Algerian asphaltenes samples obtained from the Hassi-Messaoud field were used for testing this technique. The goal was to estimate the PCA diameter with accuracy to the first order of approximation. The analyses used here are (1) fitting the spectra using Gaussian, Lorentzian, or Gaussian/Lorentzian hybrid functions to represent G and/or D bands and extract the integrated intensities for each band (2) calculate the integrated intensity ratio of the G and the D1 bands, and subsequently use of the Tuinstra and Koenig equation to estimate the molecule dimensions.

2. Experiments

2.1. Asphaltene sample preparation

Four asphaltene samples were investigated by Raman spectroscopy. The asphaltene sample, DP45, was from a deposit of the Hassi-Messaoud oil field in Algeria. A solution containing 1 g of deposit and 40 ml of heptane was prepared. The solution was stirred at 60 °C for 2 h, followed by standing at ambient temperature overnight. The insoluble part was filtered using a 0.45 μm diameter pore membrane. Following the filtration, the insoluble fraction was dissolved in enough amount of hot toluene (50 °C) and re-filtered with a 0.45 μm diameter pore membrane. The filtered solution was then dried using a Rotavapor. The retrieved asphaltene powder was further air-dried in an autoclave at 140 °C for one week to evaporate the trace amount of toluene. The other three samples were prepared in a similar way. HH1 asphaltene was directly derived from the oil in one of the Hassi-Messaoud wells, RSV asphaltene was from a refinery residue, and HM-3077 was from a deposit of the Hassi-Messaoud oil field at a 3077-m depth