

Structural comparison of Gilsonite and Trinidad Lake Asphalt using ^{13}C -NMR technique

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Abstract. The recent increased importance of natural asphalt as an alternative binder for sustainable road pavement has dictated that more knowledge should be acquired about its structure and properties. Earlier, Carbon-13 NMR spectroscopy has been applied to very few natural bituminous materials. In this work, two types of raw binders namely Gilsonite and Trinidad Lake asphalt (TLA) have been subjected to an extensive investigation by using ^{13}C -NMR technique. Results have shown that valuable chemical data can be readily withdrawn on aromatic ring structures and ring substituents in natural asphalts derived from different sources. The chemical significance of these findings will be discussed.

1. Introduction

Asphalt chemistry is a complex field and poses a considerable challenge to the chemist. Asphalts are known to be comprised of an exceedingly large number of organic molecules, ranging in size, mainly composed of carbon and hydrogen atoms. A better understanding of their compositions and properties is of utmost importance in the asphalt industries in order to apply adequate processing facilities.

The petroleum asphalt (PA) has been primarily used in road construction where it is employed as a glue or binder mixed with aggregate particles to create asphalt concrete. Its other main uses are for bituminous waterproofing products, including production of roofing felt and for sealing flat roofs [1]. It has been readily available, easy to handle, offers excellent performance, and has been the most economical. Today's environment however, has the asphalt industry searching for alternative asphalt sources. Concerns of energy independence, the exorbitant increase in oil prices and growing environmental concerns have invigorated the interest for alternative energy sources. The asphalt industries and the highway agencies have escalated research in the area of alternative PAs in order to meet the challenges presented today.

The use of alternative PA is not a new concept. Early in the 19th century, researchers investigated various forms of natural asphalts throughout the development of new building products. Gilsonite and Trinidad Lake asphalt (TLA) are among the fossil oils being evaluated as promising natural materials for the construction of flexible pavements. They are the black or dark brown bitumens found in seeps, veins, or permeating limestones or dolomites as a part of them. The Gilsonite of Utah is free from impurities, while the asphalt in the Trinidad Pitch Lake contains sand, clay, and shells up to 30 wt. % of the mass [2].

Gilsonite, originally known as "Uintaite", is found in commercial quantities in the Uinta Basin of northeastern Utah, in Uintah and Duchesne counties. It is a hard, brittle, native bitumen of variable but high softening point. Uintaite is uniform in purity, extremely low in sulfur, has a low specific gravity,



a high content of volatile matter, a lustrous fracture varying from brilliant conchoidal to dull hackly or pencillated form, a typical brown streak and characteristic odor [3, 4]. It is composed mainly of aromatic asphaltite [5]. The low melting point, high solubility in oils, and near-perfect insulator qualities of Gilsonite historically has lent it to a wide variety of uses. Gilsonite has been used in manufacturing storage batteries, foundry forms, paints, varnishes, inks, and lacquers, and as a binder for road pavement [6].

TLA was first reported for paving in the United States about 1874. Trinidad asphalt exists in a number of deposits on the island of Trinidad, near the northeast coast of Venezuela. This asphalt has been used for pavement constructions and other applications throughout the world. TLA has a relatively uniform composition of 29 wt. % water and gas, 39 wt. % bitumen soluble in carbon disulfide, 27 wt. % mineral matter on ignition, and 5 wt. % bitumen that remains adsorbed on the mineral matter. The refined product averages 36 wt. % mineral ash with a penetration at 25 °C of about 2 (0.2 mm), a softening point of 99 °C, a flash point of 254 °C, and a sulfur content of 3.3 wt. %. The mineral matter typically contains particle sizes from 40 wt. % finer than 10 µm to 10 wt. % from the 30-75 µm range. Because of the influence of the fine mineral particles, many of them colloidal in size, the viscosity of TLA is higher than that of normal bitumens [7-9].

The use of Gilsonite and TLA as raw materials for diverse fields of application requires an immediate knowledge of their compositions and the existing molecular interactions. The molecular composition affects directly the physical properties of asphalt, such as softening point and viscosity, and in turn the performance of the final product. Therefore, in order to develop a rational approach to the conceptual understanding and practical resolution of the structural ambiguity, one must start with the study of natural asphalt itself. The molecular structure of this material has not yet been completely understood and is still the subject of some conjecture. Apart from its pertinence to road pavement technology, knowledge of the molecular structure of natural asphalt is the key to its possible future commercial utilization, to the elucidation of its origin and diagenetic history, and may conceivably shed some light on the history of the natural asphalt formations.

In our recent work on the "chemical characterization of Gilsonite bitumen" [10] published in the Journal of Petroleum & Environmental Biotechnology, substantial efforts have been devoted to elucidate the composition, structure, and properties of Gilsonite and TLA by using elemental analysis (EA), thin layer chromatography-flame ionization detection (TLC-FID), Fourier transform-infrared (FT-IR) and proton-nuclear magnetic resonance (¹H-NMR) spectroscopies. The chemical study led successfully to the unravelling of the mystery of the source and origin of the asphalt formations in Utah and Trinidad Island, the relation between the natural asphalt deposits and their interrelation with conventional oil accumulations of the region. To provide further insights into the poorly defined structures of Gilsonite and TLA, the ¹³C-NMR spectroscopy was carried out accordingly.

2. Materials and methods

2.1. Natural asphalts

Gilsonite was collected from Uintah Basin in northeastern portion of the state of Utah, the United States. It is made up of predominantly of pure asphalt, mineral matter, and other minor constituents. Gilsonite is a shiny, black substance similar in appearance to the mineral obsidian. It is brittle and can be easily crushed into a dark brown powder (Figure 1 A). In order to enable a more comprehensive discussion of the results, reference was made to other natural asphalt from the Pitch Lake at La Brea in the Island of Trinidad known as Trinidad Lake asphalt (TLA). TLA is a dark-brown colored cementitious substance. It is brittle and broke into small cellular glossy fragments (Figure 1 B). This asphalt is approximately 63 wt. % bitumen and the remainder being mineral and organic material. All asphaltic specimens were analyzed by the same ¹³C-NMR technique to provide directly comparable chemical information.

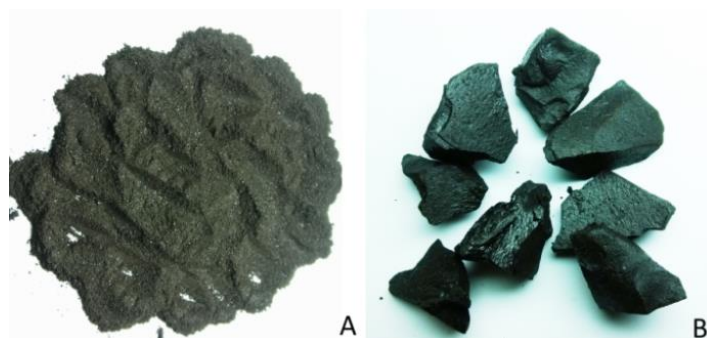


Figure 1. Gilsonite (A) and Trinidad Lake asphalt (B) specimens.

2.2. ^{13}C -NMR spectroscopy

^{13}C -NMR spectra of natural asphalts were recorded on a VNMRS-400 spectrometer (Agilent Technologies Korea Ltd., Seoul, South Korea). NMR experiments were performed using 20~50 mg of bitumen dissolved in 0.6 mL of deuterated chloroform containing Tetramethylsilane as a chemical shift reference. The NMR spectra were collected with relaxation delay of 10.0 s, acquisition time of 1.3 s, and 5,000 repetitions.

3. Results and discussion

3.1. ^{13}C -NMR analysis

The ^{13}C solution NMR spectra of Gilsonite and TLA are displayed in Figure 2. The strong absorption between 76.5 and 78 ppm is due to solvent CDCl_3 . The low field absorptions between 10 and 45 ppm are due to aliphatic sp^3 carbons, while the weak absorptions between 100 and 160 ppm are due to aromatics sp^2 carbons.

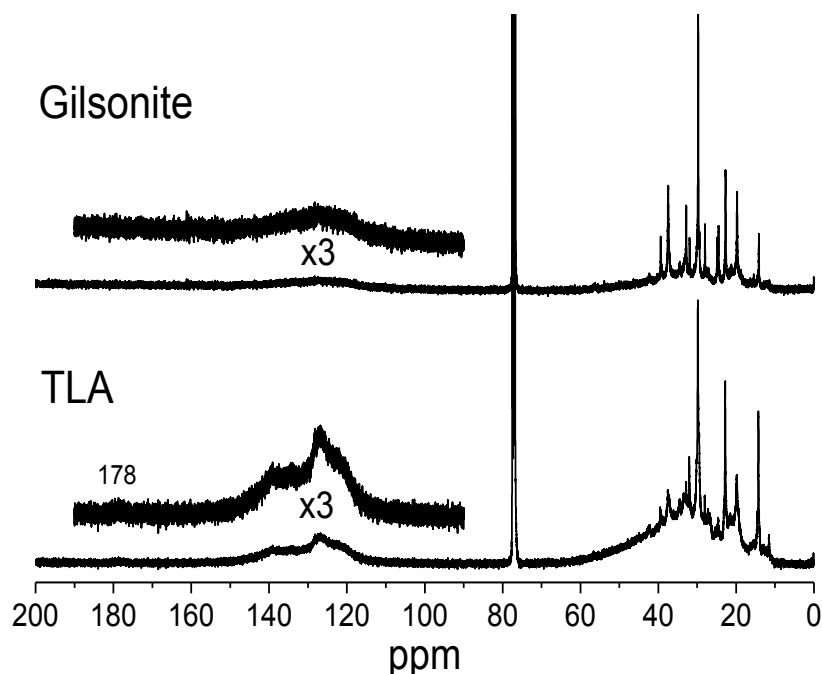


Figure 2. ^{13}C solution NMR spectra of Gilsonite and TLA.

In the ^{13}C -NMR spectrum of Gilsonite, the aromatic carbon band is very weak compared to that of TLA. This suggests that Gilsonite contains the major part of aromatic moieties of pyrrolic ring with limited mobility, while TLA has mainly the six-membered aromatic carbon rings with higher mobility.

This fact corroborates FT-IR spectra and TLC-FID analysis [10]. TLC-FID analysis showed that Gilsonite contains negligible amount of aromatics (~ 0 wt. %) and moderate quantity of resins (18.7 wt. %), while TLA contains 22.9 wt. % of aromatics and 37.4 wt. % of resins. The very small peak in ^{13}C spectrum of TLA appeared around 178 ppm is probably attributed to the C=O group of ester, carboxylic acid, or amide groups.

Figure 3 presents the expanded alkyl portion of the ^{13}C solution NMR spectra of Gilsonite and TLA, respectively. Interestingly, Gilsonite spectrum of the current study shows the major 10 peaks reported by Helms and his colleagues [5]. In this alkyl region, notable differences were detected between TLA and Gilsonite spectra, especially at peaks number 2, 4, 5, 8, 9, and 10, which were much weaker in intensity with TLA than Gilsonite. These differences could be used, of course, as marker bands to differentiate Gilsonite from TLA. Referring to the assignments of Helms et al. [5], it can be admitted that most of these peaks are ascribed to the carbons related to the side-chains, which illustrates that Gilsonite has more side-chains than TLA. This feature is fully supported by the $\text{H}_\gamma/\text{H}_\beta$ ratio in ^1H -NMR spectra and by the higher saturates (4.1 wt. %) and resins (37.4 wt. %) contents in TLA [10]. Even though that Gilsonite appears poor in saturates (1.66 wt. %) and resins (18.7 wt. %) components [10], it comprises a relatively large amount of alkyl portion. This alkyl portion is essentially involved in the connection of pyrrole rings; basic constituents of asphaltene compound. This observation correlates favorably with the proposed model structure of Gilsonite asphaltene by Helms et al. [5].

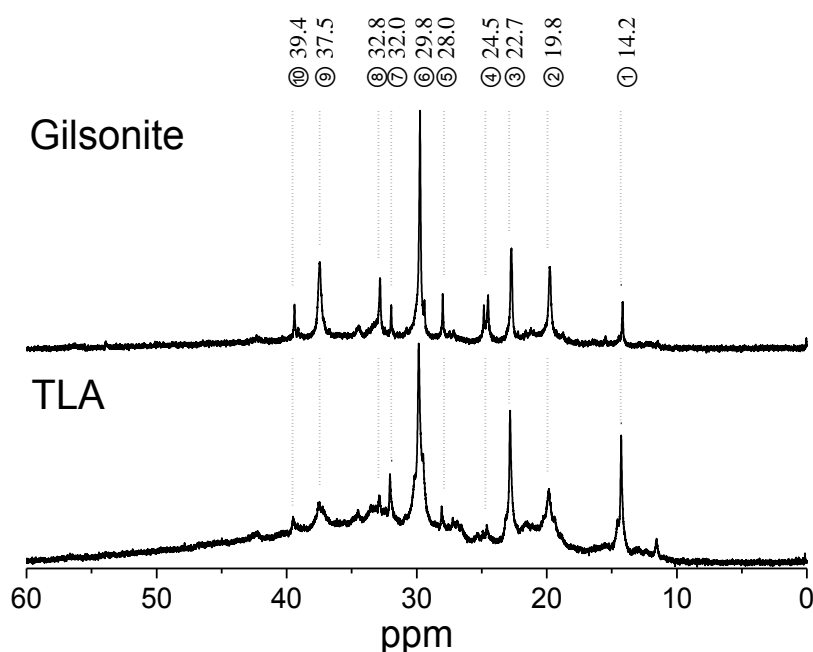


Figure 3. Alkyl portion of ^{13}C solution NMR spectra.

4. Conclusion

The present study enabled us to understand and compare in detail the chemical characteristics of Gilsonite and TLA. The relatively easy and convenient method of ^{13}C -NMR provided useful informations to identify the chemical structure of natural asphalts with the help of elemental analysis, FT-IR, TLC-FID, and ^1H -NMR data. Gilsonite has a significant amount of aromatic moieties with nonprotonated aromatic carbons as compared to TLA. The high content of asphaltenes (79.7 wt. %) found in Gilsonite contains pyrrole N-H groups and aromatic carbons connected with an important fraction of alkyl chains. TLA includes high concentration of oxygenated compounds and aromatic moieties with protonated carbons. The alkyl chains in TLA are more oxidized and sulfurized than Gilsonite; containing carbonyl, sulfide, and ether groups. Future work may involve the inclusion of

additional techniques to characterize the natural asphalts such as X-ray diffraction (XRD), Raman spectroscopy (RS), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), etc.

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