

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY FOR THE CHARACTERIZATION OF ASPHALT

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INTRODUCTION

Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful tool used in a broad array of disciplines to describe the character of atoms, molecules and assemblies of molecules. This information may be gathered from samples solubilized in solvents or in the solid state. While carbon (^{13}C) and proton (^1H) characterizations are typically used, there is a variety of NMR active nuclei which include oxygen, phosphorus, nitrogen, silicon and many metals. With regard to applications, this tool has been used to characterize simple organic and inorganic compounds, proteins, carbohydrates, enzymes, coal and polymeric materials. Thus, it has broad use in a variety of disciplines. With regard to asphalt, NMR spectroscopy has been applied but not to the extent that it has in the areas previously mentioned.¹⁻⁶

Before describing some of the results from our laboratory, it is appropriate to briefly describe the character of asphalt and some of the goals for which answers are sought. Asphalt is a hydrocarbon mixture containing minor elements, in bonded form, of O, N, S, V, Fe and Ni. None of these minor elements is present in more than a few percent. The hydrocarbon portion is approximately 25% aromatic and 75% aliphatic with average molecular weights in the range of 700-1000 amu. Thus, average structures for asphalt contain 4 or 5 aromatic rings joined in a planar polynuclear fashion and a couple of aliphatic chains (5-10 carbons in length). In every 2-3 molecules there is a heteroatom (O, N, S) as either an aromatic or aliphatic moiety. A variety of functional groups is present and includes carboxylic acids (COOH), phenols (ArOH), ketones (C=O), ethers (-O-), esters (-COOC-), amines (pyroles and pyridines) and sulfur derivatives (\approx 60-70% thiophenic and 30-40% sulfides).

The goals to be achieved in the characterization of asphalt include answers to the following questions.

1. What are the functional groups and how many of each are present?
2. How are the aromatic rings arranged and how many substituents are present?
3. How long are the aliphatic chains, how many are there and how many branches are present?
4. How are the heteronuclear aromatic nuclei arranged?
5. What is the sulfide content?

Finally, the big questions are derived from the interactions of these components in a macrosystem.

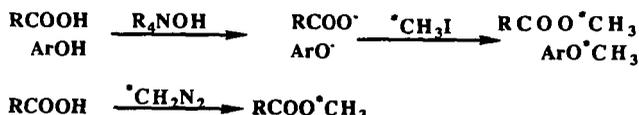
6. How do these components assemble for form the substance called asphalt?
7. How do these assemblies differ among the asphalts?
8. How do these features relate to performance?
9. How do these features change with modifiers, treatments and additives?

With this introduction, perhaps the results described below will be in context and more readily understood.

RESULTS AND DISCUSSION

Functional Group Analysis

In this portion of the work, carboxylic acid and phenol content of a variety of asphalts were measured. Two reactions were run to prepare derivatives which provided a NMR active probe for the analysis. They are:



The first reaction involves a phase transfer type base followed by methylation with enriched ^{13}C .^{7,8} For the carboxylic acid analysis a sharp resonance should result and does in a few cases. However, there often is a broader resonance band on the downfield side of the carboxylate which interferes with the correct analysis. Therefore, the diazomethane reaction was used to analyze carboxylic acids. In this case a sharp resonance was obtained. The phenolic content was analyzed using the phase transfer methodology. Due to the variation in aromatic residue these resonances are broad. Numerical results of these analyses are tabulated in Table I for selected asphalts and asphalt fractions.

The conclusions drawn here are that there is some variation among asphalts but there is not very much carboxylic acid or phenolic content since the numbers displayed are $\times 10^{-5}$ moles/gm. POV stands for pressure oxygen vessel and refers to an aging process used in the SHRP studies. Given the error associated with these analyses, it is concluded that POV aging does not reflect any increase in the carboxylic acid content of an asphalt.

Size exclusion chromatography on a preparative scale by WRI⁹ provided these fractions. SEC-1 represents the larger molecular sized materials while SEC-2 fractions have smaller molecular sized units. The former are thought to have molecular assemblies of components while SEC-2 has fewer assemblies and are necessarily smaller. This separation was conducted using toluene which destroys pi-pi aromatic assemblies and facilitates polar interactions. Thus, it is interesting to note that there is little disparity for carboxylic acids between these two fractions, save asphalts F, G and K in which SEC-2 shows enhanced values. These authors are not

willing to speculate at this time on the application of these results to performance testing.

Hydrocarbon Characteristics

Both proton and carbon spectroscopy were used to characterize aromatic and aliphatic content. The numerical results for carbon are displayed in Table II. The conclusions here are that there is very little variation among the whole asphalt samples. Among the fractions it is noted that the aromaticity is less for SEC-2 vs SEC-1 and that the neutral fraction derived from ion exchange chromatography (IEC) has the least aromaticity among that group.

Two-Dimensional NMR Spectroscopy

From the one-dimensional data results cited above, we turned to the use of two-dimensional NMR spectroscopy in an effort to provide additional data on the aromatic and aliphatic resonances. Figures 1 and 2 are for the whole asphalt and represent the typical ^{13}C spectrum for comparison with a DEPT 135 spectrum, respectively. Using these data, one can better determine which resonances are due to CH_3 , CH_2 , CH and C . The DEPT 135 data nulls quaternary carbons which is particularly noticeable in the region of 130-150 ppm. Figure 3 reinforces this feature as it is run under conditions which facilitate quaternary carbons and suppress all others. The peak at 97 ppm is an impurity and the one at 78 ppm is CHCl_3 . Those in the aliphatic region represent incomplete suppression of CH_2 resonances. The broad aromatic CH resonances occur from 115 to 129 ppm, with a rather sharp demarcation on the downfield side, Figure 3a. At this juncture, the quaternary carbons arise in earnest and range from 120 to 145 ppm, Figure 3b. In looking at the entire spectrum, Figure 1, one can readily see the break between these two moieties at 130 ppm. Given the relative amounts of these two moieties, one must conclude that a number of polynuclear aromatic sheets must be present.

Due to the long-standing conception that benzylic carbons bearing protons are sites for oxidation, it was desired to find a way to analyze for these units. After trying some direct methods such as HETCOR without success, we turned to looking for long-range coupling between the benzylic protons and the aromatic ipso carbons. Success was readily achieved with model compounds and asphalt was subsequently attempted. The results are shown in Figures 4, 5 and 6. In Figure 4, the correlation of interest occurs at intersection 2.3 ppm on the proton axis and 120 to 140 ppm on the carbon axis. These are protons on benzylic carbons attached to two different types of aromatic moieties. The first at 120-130 ppm is likely a substituent on a typical carbon based aromatic ring. The correlation at 130-145 ppm is likely to be of a heterocyclic ring system. From model compounds, it is believed that these are benzylic methyl groups. Figure 5 shows a similar correlation but now the CH_2 units are also present. This is achieved by altering the spectrometer parameters. Finally in Figure 6, the graph shows a projection of these peaks when the parameters have been adjusted so as to project benzylic CH (2.7 ppm), CH_2 (2.5 ppm) and CH_3 (2.3 ppm) on the proton axis. Efforts to investigate the effects of oxidation are underway.

CONCLUSION

A few techniques within the scope of solution NMR spectroscopy have been applied to the complicated mixture called asphalt. Through these uses, one can gain considerable insight into the details of asphalt compounds. These, in turn, should provide future scientists with data for correlations with performance and physical testing.

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- (9) WRI - Western Research Institute in Laramie, Wyoming provided SEC and IEC samples. We are deeply grateful for their generosity.

Table I. Carboxylic Acid and Phenol Content Asphalts and Asphalt Fractions.

| Asphalt | [COOH] x 10 ⁻⁵ moles/g | [ϕOH]** x 10 ⁻⁵ moles/g | [ϕOH]*** x 10 ⁻⁵ moles/g |
|----------------------|--------------------------------------|---------------------------------------|--|
| AAA-1* | 1.1 | 3.5 | 2.5 |
| POV ⁽¹⁾ | 1.9 | | |
| SEC-1 ⁽²⁾ | 1.6 | 13.0 | 6.8 |
| SEC-2 | 1.9 | | |
| AAB-1 | 0.5 | 4.2 | 3.1 |
| POV | 0.3 | | |
| SEC-1 | 0.5 | 10.0 | 5.5 |
| SEC-2 | small | | |
| AAC-1 | 0.5 | 1.8 | 1.7 |
| POV | 0.4 | | |
| SEC-1 | 0.9 | 9.3 | 4.5 |
| SEC-2 | 0.6 | | |
| AAD-1 | 1.1 | 2.2 | 2.2 |
| POV | 1.7 | | |
| SEC-1 | 3.2 | 14.0 | 7.8 |
| SEC-2 | 3.2 | | |
| AAF-1 | 0.1 | 6.3 | 3.2 |
| POV | 0.1 | | |
| SEC-1 | 0.1 | 17.0 | 7.6 |
| SEC-2 | 0.4 | | |
| AAG-1 | 4.5 | 4.2 | 5.5 |
| POV | 3.5 | | |
| SEC-1 | 0.3 | 11.0 | 7.0 |
| SEC-2 | 1.7 | | |
| AAK-1 | 1.6 | 2.5 | 1.5 |
| POV | 1.5 | | |
| SEC-1 | 0.75 | 7.4 | 2.0 |
| SEC-2 | 5.1 | | |
| AAM-1 | 1.0 | 3.5 | 2.4 |
| POV | 0.6 | | |
| SEC-1 | 0.8 | 3.2 | 3.2 |
| SEC-2 | 0.9 | | |

*Asphalts from SHRP-Whole Asphalt

**Hindered phenols

***Unhindered phenols

⁽¹⁾Aged by pressure of oxygen

⁽²⁾Sized Exclusion Chromatography with toluene solvent from WRI

Table II. % Aromaticity from ^{13}C Analyses of Asphalt and Fractions.

| Asphalt | Whole | SEC I | SEC II | Strong Acids | Strong Bases | Neutrals |
|---------|-------|-------|--------|-----------------|-----------------|----------|
| AAA-1 | 27.9 | 36.7 | 26.2 | 38.1 | 32.2 | 19.8 |
| AAB-1 | 31.2 | 47.1 | 27.6 | 46.7 | 38.3 | 16.8 |
| AAC-1 | 27.8 | 40.1 | 25.4 | 44.7 | 34.6 | 18.3 |
| AAD-1 | 23.4 | 30.9 | 24.0 | 32.2 | 34.1 | 19.7 |
| AAF-1 | 32.8 | 45.6 | 29.9 | 37.4 | 39.9 | 24.5 |
| AAG-1 | 29.0 | 30.3 | 28.3 | 37.0 | 29.0 | 16.6 |
| AAK-1 | 26.2 | 37.9 | 26.9 | 33.5 | 34.8 | 18.4 |
| AAM-1 | 25.6 | 23.0 | 27.1 | 35.1 | 32.3 | 14.7 |

*Fractions from an ion exchange chromatograph (IEC) separated at Western Research Institute, Laramie, Wyoming⁹

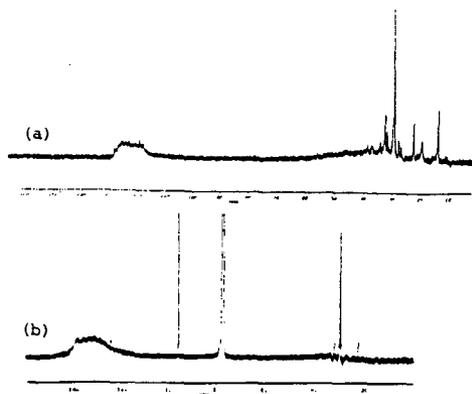


Figure 3. Selected DEPT Spectra of Asphalt: (a) DEPT 45 Where Quaternary Carbons Are Suppressed, (b) QUAT Spectrum Where Quaternary Carbons Are Emphasized and Other Resonances Are Suppressed.

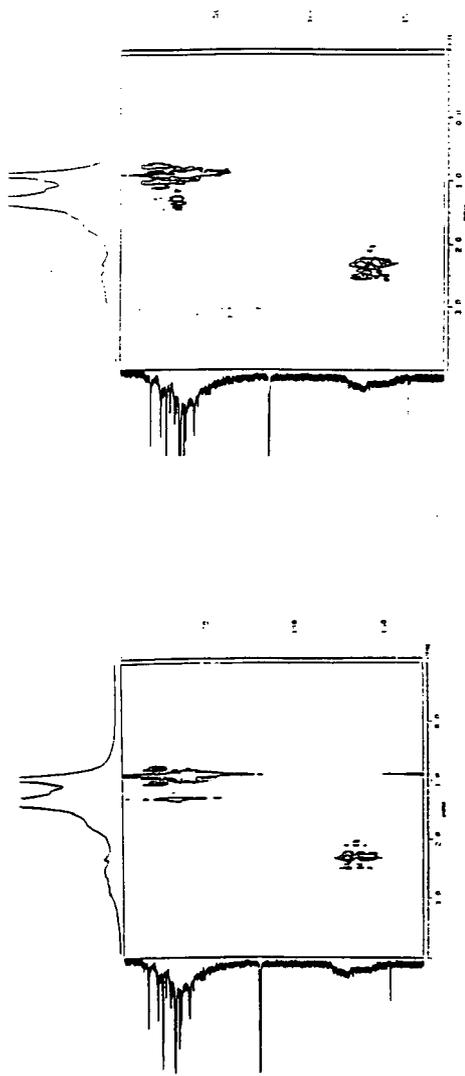


Figure 4. 2-Dimensional Correlation Between Benzyl Methyl Protons (Horizontal Axis) and Quaternary Aromatic Carbons (Vertical Axis).

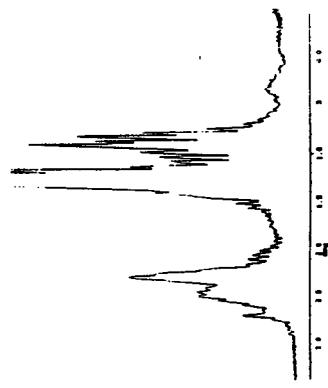


Figure 6. A Projection on the Proton Axis of a 2-Dimensional Correlation Between Benzyllic Protons (CH, CH₂, CH₃) and Aromatic Carbons.

Figure 5. 2-Dimensional Correlation Showing Benzyllic Methyl and Methylene Groups.