

**SOLID STATE CARBON-13 NUCLEAR MAGNETIC RESONANCE
STUDY OF AMORPHOUS AND CRYSTALLIZABLE
PARAFFIN WAX FRACTIONS IN ASPHALT.**

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KEY WORDS

Solid State NMR, Wax, DSC

ABSTRACT

An asphalt cement is a viscoelastic material and as such its rheological properties are dependent on temperature. The temperature dependency of the rheological properties in turn can be attributed to the motion of the numerous chemical structures present in asphalt. With time, the molecular associations and the formation of crystalline structures tend to restrict molecular motion. Nuclear magnetic resonance is a powerful technique to record data on molecular motion. Solid state carbon-13 nuclear magnetic resonance measurements have been made at room temperature to characterize crystalline and amorphous methylene carbon atoms in asphalts. Cross-polarization with magic angle spinning experiments were performed on five asphalt samples with varying wax content. The amounts of amorphous and crystallizable methylene carbon atoms were determined using spectral deconvolution methodology and correlated with the wax content determined from differential scanning calorimeter measurements.

INTRODUCTION

Properties of asphalt cements are dependent on temperature and in a recent study, Lessueur *et al.* [1] have demonstrated that asphalt behaves like a Newtonian liquid between 60 to 180 °C, a viscoelastic material between the glass-transition temperature to 60 °C, and a rigid material below the glass-transition temperature. The temperature dependency of the asphalt properties can be attributed to the motion of its numerous chemical structures. At any given temperature, the extent of molecular motion depends on the intramolecular configuration of the various asphalt components and the manner in which they interact by intermolecular association. Among these components, the wax content in asphalt strongly influences asphalt properties.[2,3] In addition these wax components can produce crystalline material with time. The type and extent of molecular motion can be obtained from Solid-State carbon-13 Nuclear Magnetic Resonance (SS-NMR).[4,5] In these experiments variable contact time and dipolar dephasing sequences were conducted to obtain information on the crystalline and the amorphous aliphatic components in asphalt. Using the same type of methodology, it was interesting to see if SS-NMR measurements of the crystalline and amorphous components in asphalt are correlated to wax content determined using the Differential Scanning Calorimeter (DSC) measurements.

EXPERIMENTAL

Cross-Polarization with Magic Angle Spinning (CP/MAS) measurements were made using a Chemagnetics 100 solid-state nuclear magnetic resonance spectrometer operating at a carbon-13 frequency of 25 MHz. Experiments were conducted using a 7.5 mm rotor spinning at a rate of 4.5 kHz. Parameters included a pulse width of 5 μ s, a pulse delay of 1 s, a contact time of 1 ms, a sweep width of 16 kHz, a free induction decay size of 1024 points, and 3600 acquisitions.

Conventional DSC measurements were performed on a TA instrument model 2920 Modulated DSC. After annealing, the sample was cooled at 10 °C/min to below 60 °C, held isothermally for 15 min, and then heated at 10 °C/min to the annealing temperature. The

different regions in thermogram were integrated with baseline correction. The energy associated with the melting endotherm was used to calculate the percentage of wax given in Table 1.

RESULTS AND DISCUSSION

Cross-polarization experiments were performed on five asphalts: A (Venezuelan crude), B (Middle East crude), C (Italian crude), D (African crude), and E (Middle East crude). These asphalts were provided by Elf-Antar France and were selected to have a large range in wax percentage (see Table 1). The NMR measurements were made at room temperature for the initial asphalt and after two months of phase evolution in the rotor. The aliphatic part of the spectrum was deconvoluted into fourteen different carbon types in accordance with the work of Netzel *et al.* [5] Figure 1 shows an example for asphalt D. The two peaks at 32 and 30 ppm correspond respectively to the crystalline methylene and to the amorphous methylene carbon atoms present in the paraffinic component of asphalt. The relative fraction for the two peaks (f_{CH_2-crys} and f_{CH_2-amor}) are given in Table 2. These values permit a calculation of the percentage of rigid (% C-rigid) and flexible (% C-flexible) carbon atoms (see Table 3) using the following expressions:

$$(\% \text{ C-rigid}) = (\% \text{ C})(f_{\text{C-aliph}})(f_{CH_2-crys}) \text{ and } (\% \text{ C-flexible}) = (\% \text{ C})(f_{\text{C-aliph}})(f_{CH_2-amor})$$

In these calculations, the % C is the percentage of total carbon atoms determined by elemental analysis and $f_{\text{C-aliph}}$ is the fraction of aliphatic carbon in the aromatic part of the ^{13}C SS-NMR spectrum.

After two months, an increase in the rigid carbon atoms content and, at the same time, a decrease in the flexible carbon atoms content were observed. This result suggest that, with time, crystalline materials are formed in a asphalt.

Most investigators report that the crystalline part of the asphalt corresponds to the wax fraction. Figure 2 shows the plot of the percentage of wax versus the percentage of rigid and flexible carbon atoms initially and after two months of phase evolution. The correlations obtained are relatively good (R^2 in the range 0.80 to 0.99). The high correlation suggests that the wax content of an asphalt is very well characterized by the two methylene carbon atom peaks at 32 and 30 ppm. The correlation is better with the amorphous part of the methylene carbon atoms because this part represents around 85 % of the total methylene carbon initially and 82 % after the two months of transformation.

CONCLUSIONS

Solid-state nuclear magnetic resonance spectroscopy appears to be a powerfull tool to study the crystalline and amorphous content of an asphalt. In this work, it has been demonstrated that the crystalline and the amorphous methylene carbon atoms present in an asphalt are correlated with the wax content.

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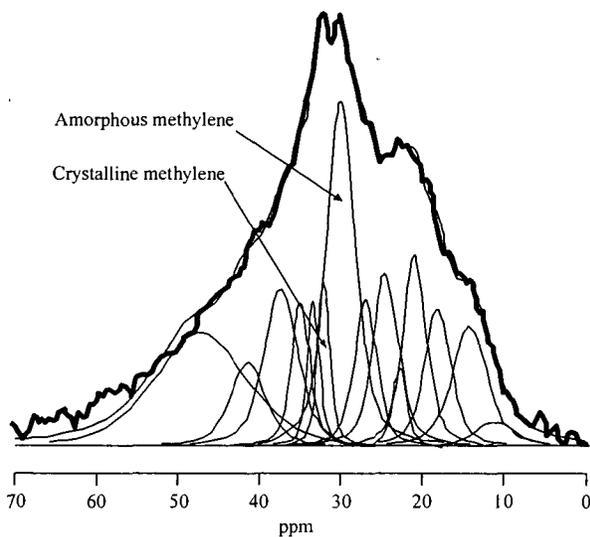


Figure 1: Deconvoluted ¹³C NMR cross-polarization spectrum for asphalt D.

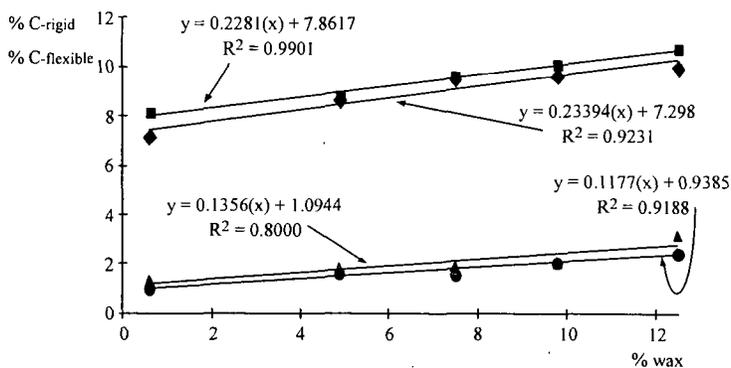


Figure 2: Correlation for the five asphalts between the percentage of wax and the percentage of rigid and flexible carbon atoms. The squares and the diamonds correspond to the flexible carbon atoms respectively initially and after two months of phase evolution. The circles and the triangles correspond to the rigid carbon atoms respectively initially and after two months of phase transformation.

Table 1: Percentage of wax determined by DSC measurements.

Asphalt	A	B	C	D	E
% of wax	0.60	4.90	7.50	9.80	12.50