**1H DOSY NMR: An effective technique to investigate asphaltenes behavior.**

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**Introduction**

New energy sources need to be developed to face the growing worldwide energy demand. Heavy and extra-heavy crude oils have attracted attention because they represent an additional source of energy. The main problem to deal with during hydrotreatment processes of heavy oils is the presence of asphaltenes which are the heaviest and least reactive molecules in crude oils. These macromolecules are responsible for many problems during production and transport. Getting a better understanding of these products is required to develop new catalysts and novel conversion processes.

Asphaltenes characterization is still a challenge because they are composed of thousands of heavy compounds. Many analytical techniques are commonly used to analyze asphaltenes. However, it is difficult to establish their physico-chemical properties by conventional techniques because they tend to form aggregates depending upon their concentration and upon the solvent. 1H Diffusion Ordered SpectroscopY NMR (DOSY), based on pulsed field gradient (PFG) sequences is a powerful tool to analyze polydisperse petroleum samples. It aims at measuring self-diffusion coefficients, which can provide structural and dynamic information (molecular size and also aggregation states), in complex mixtures.

In the present study, 1H-DOSY NMR experiments were carried out on three unconverted asphaltenes samples (Buzurgan, Athabasca and Maya asphaltenes) diluted in deuterated toluene.

**Materials and Methods**

Asphaltenes were prepared by precipitation in an excess of n-heptane. A wide range of concentration (from 0.01 to 20 wt%) in toluene-d8 (D, 99.8 %) was analyzed at 20°C. DOSY NMR experiments were performed on a Varian INOVA 600 narrow bore spectrometer equipped with a Performa II gradient pulse amplifier and fitted with a triple resonance (HCN) probe capable of producing up to 60 G cm⁻¹. The pulse sequence used was the Doneshot sequence. NMR data were processed with the NMRNotebook software with a DOSY module (using Maximum Entropy Laplace inversion) incorporated from NMRrec.

**Results and Discussion**

The influence of Maya and Buzurgan asphaltenes concentration on their diffusion coefficient is presented in Figure 1. The Buzurgan asphaltenes show a complete different behavior from the Maya. For the Buzurgan sample, lighter species were detected above 3 wt%. This illustrates that intermolecular interactions (solvent – solute interactions and solute – solute interactions) are highly dependent upon solute concentration and also upon the origin of the sample. In the dilute regime (<0.5 wt%), average molecular weight can be determined for each mono-entity of asphaltenes detected by NMR (Table 1) according to a polystyrene calibration curve performed. Radii were calculated taking into account the size of the solvent as explained elsewhere. These results show that 1H DOSY NMR is an effective tool to analyze asphaltenes.

![Figure 1. Diffusion coefficient of asphaltenes (Asph.) in toluene vs asphaltenes concentration.](image)

<table>
<thead>
<tr>
<th>Table 1. Physical data determined by 1H DOSY NMR</th>
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<tbody>
<tr>
<td><strong>Asphaltenes Origin</strong></td>
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<td>-------------------------</td>
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<tr>
<td>Average Molecular weight (eq. PS)</td>
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<td>Average Radius (Å)</td>
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**Significance**

Asphaltenes represent the most enigmatic components of the crude oil. Basic scientific notions like molecular weight, size, shape and molecular structure represent big issues and are not yet clearly established. This work is expected to enable a deeper insight into the physico-chemical characterization of asphaltenes to develop new catalysts and conversion processes.

**References**