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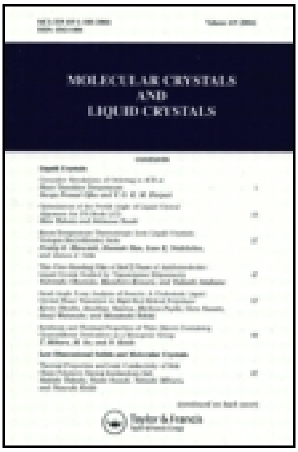

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Structural Characterization of Bitumen System by Prony-Like Method Applied to NMR and Rheological Relaxation Data

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Structural Characterization of Bitumen System by Prony-Like Method Applied to NMR and Rheological Relaxation Data

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In order to characterize colloidal structures, T_2-nuclear magnetic resonance (NMR) and rheological relaxation times are used. NMR Car–Purcell sequence and mechanical stress relaxation experiments have been performed on a bitumen system at different temperatures. The rheological relaxation times spectra are fingerprints of the aggregates that constitute the system. These typical relaxation times have been obtained from an exponential fitting of the experimental data, based on a Prony-like method. The unknown parameters are estimated on the basis of a linear regression equation that uses altered signals obtained directly from the NMR and rheological measurements. This approach uses the derivative method in the frequency domain, yielding exact formula in terms of multiple integrals of the signal, when placed in the time domain. These integrals are explicitly solved by projecting signal on some set of orthogonal basis functions or, more in general, by using a polynomial that fits data in the least-squares sense. The method is able to deal with the case of nonuniform sampled signal.

Keywords Bitumen structure; NMR; rheology; Prony method; relaxation time

1. Introduction

A bitumen is a complex system of different chemical constituents, mainly hydrocarbons and, to a lesser extent, heteroatoms. After bitumen fractionation by specific solvents, four main chemical families are obtained, i.e., saturates, aromatics, resins, asphaltenes [1–4]. Asphaltene sheets are essentially highly polycondensed pseudomonomers with a carbon backbone, chemical functions, and heteroatoms surrounded by aliphatic chains. The aggregation of asphaltenes within the oily medium maltenes leads to formation of macrostructures so that the system is similar to a micellar arrangement.

To obtain structural information about bitumens, microscopy and diffusion techniques have to be implemented. As matter of fact, the presence of an oil phase disturbs normal observation through microscopy and the bitumen has to endure preparation to exclude the

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oil phase. Clearly, this creates artifacts as the original structure is lost. Diffusion techniques always have to be performed in very diluted systems; hence, changes in the concentration of the components can change the structures and structural properties because bitumens behave as colloidal systems.

To preserve the bitumen structure, a freeze-fracturing method can be used. Dickie et al. [5], by means of spraying/evaporation techniques of diluted (0.1%) Boscan asphalt, found associated asphaltene particles with a length of 15–30 nm, and 2–3 nm for individual polyhedral particles. Donnet et al. [6] used scanning electron microscopy (SEM), and observed that pure asphalt consists of a network structure. Loeber et al [7] compared three different microscopy techniques, namely SEM, atomic force microscopy (AFM), and fluorescence microscopy. They found comparable results for the bitumen they studied and concluded that pure gel bitumen forms a network structure made of small spherical particles, the asphaltenes, with a diameter of about 100–200 nm and a network porosity of about 6 μm.

According to the colloidal picture, asphaltenes form micelles that are dispersed in an oily medium and stabilized by resins [8]. The nature of the interactions between asphaltene micelles decides the sol (Newtonian) or gel (non-Newtonian) character of a given bitumen. Structurally, the sol type occurs when the asphaltenes micelles are fully dispersed and noninteracting each other. The non-Newtonian behavior is due to a gel arrangement resulting from the interconnected asphaltene micelles [9]. The sol–gel structure is a coexistence of sol-type micelles and a gel structure. The role of the resins as stabilizers of asphaltenes was confirmed, and it was demonstrated that the asphaltenes would precipitate from the oily bitumen components if resins are not present [10].

New methods for the characterization of bituminous materials are developing [11–16]. Many rheological techniques are demonstrated to be a valuable and more sensitive way to assess bitumen properties than the conventional tests [17]. In addition, a deeper knowledge of the chemical composition as well as the morphology of the bituminous binder is essential to design new additives and the relative obtained materials.

Hence, we performed rheological tests and exploited nuclear magnetic resonance (NMR) to find new analytical approaches and a correlation between molecular organization and mechanical behavior. In the present work, we have investigated pure bitumen, and the morphological characterization was performed by means of stress relaxation rheology and ^{1}H-NMR spin-spin relaxation (T_2) [18].

We assumed that the NMR and rheological relaxation times spectra are fingerprints of the structures present in the system [19,20]. We have obtained these typical relaxation times from a multiexponential fitting of the experimental data, based on a Prony-like method.

Additionally, for the first time, we commented on a possible a correlation between NMR and rheological relaxation spectra. In fact, the interaction nature of the NMR T_2 relaxation times is strongly related to the rigidity of the system, and consequently, to the rheological relaxation times.

2. Experimental Section

2.1. Material and Samples

As fresh standard, a 70/100 penetration-grade bitumen made in Saudi Arabia was used. Samples were simply produced by warming up the material to 120°C and pouring it onto the rheometer plate and into the NMR tube.

2.2. Rheological Measurements

The rheological study in this contribution was performed using a strain-controlled rheometer (Rheometrics RFS III; Rheometrics Inc., Piscataway, NJ) equipped with parallel plates ($\varphi = 25$ mm) in the temperature range 20°C–120°C ± 0.1°C (by a Peltier temperature system). Stress relaxation experiments were performed. For all experiments, a strain value of $\gamma_0 = 10\%$, within the linear viscoelastic region, was applied (chosen by preliminary strain sweep tests).

Stress relaxation experiments were conducted by applying a constant strain throughout the experiment and recording the stress decay $\sigma(t)$ versus time. The transient shear modulus, $G(t)$, was obtained as $G(t) = \sigma(t)/\gamma_0$, where γ_0 is the applied strain. The sample was loaded at 100°C, giving a liquid phase. Then, the temperature was cooled to 20°C and kept for 10 minutes, which were sufficient to reach the micellar equilibrium phase. Successively, the sample was heated to the desired temperature to be investigated. This procedure guarantees to have the same initial structure and to observe reproducible $G(t)$ decays.

2.3. NMR Relaxation Experiments

For the ^{1}H spin-spin relaxation measurements, a home-made NMR instrument has been used. It operates at a proton frequency of 15 MHz. Measurements have been performed at different temperatures ranging from 100°C to 40°C, with an error of ±0.1°C. A classic Carr–Purcell (CP) pulse sequence has been used to record the echo decay [21]. The applied width of $\pi/2$ pulse was 5.9 μsec. The delay time was 0.05 msec. In a basic NMR concept, atom nuclei are excited by absorbing a specific radiofrequency. To relax back to equilibrium, nuclei follow two mechanisms, which correspond to characteristic times of the systems, namely T_1 and T_2. The first accounts for the so-called spin-lattice relaxation process. The second is called the spin-spin relaxation time, because the relaxation is concerned with the exchange of energy between spins via a flip-flop-type mechanism.

In a perfectly homogeneous field, the NMR time constant of the decay would be T_2, but, in fact, the signal decays in a time $T_2{}^*$, which often is determined primarily by field inhomogeneity. A method for overcoming the inhomogeneity problem is to apply the CP technique [21]. If the CP envelope has a mono-exponential decay, the relaxation time T_2 of the sample can be obtained by fitting the data to the following equation:

$$A_n = A_0 e^{-\frac{2n\tau}{T_2}}, \tag{1}$$

where A_n is the amplitude of the nth echo in the echo train and A_0 is a constant depending on the sample magnetization, filling factor, and other experimental parameters. Since the T_2 relaxation time varies all over the sample, a multiexponential attenuation of the CP envelope should be observed.

3. Discussion

In general, decaying experimental data in various scientific fields can be interpreted as combination of decreasing exponential functions, according to an expression of the type

$$y(t) = A \int_0^{\infty} P(\tau) e^{-\frac{t}{\tau}} dt, \tag{2}$$

where $P(\tau)$ is the probability density function of the decaying time τ [15]. This τ assumes different physical-chemical meanings and notations depending on whether it represents the spin-spin relaxation time (T_2) or the rheological stress relaxation time.

If $P(\tau)$ is significantly different from zero only around a finite number N of discrete values, as we expect in our case, it is possible to approximate (2) as weighted discrete sum of exponential functions:

$$y(t) \cong \sum_{i=1}^{N} A_i e^{-\frac{t}{\tau_i}}, \tag{3}$$

with

$$A > 0 \text{ and } \tau > 0, \tag{4}$$

where τ_i represents the local ith maximum of the related $P(\tau)$. This exponential sum model is frequently used in heat diffusion, diffusion of chemical compounds, time series in medicine, physical sciences, and technology [22].

However, the use of (3) to fit experimental data is a notoriously ill-conditioned problem, very sensitive to the presence of noise [23], and already with only two or three exponentials, small changes in experimental data can lead to dramatic fluctuations in fitting parameters. Also, the determination of the correct number of terms to be used in the fit is an open question [24].

Then, it is crucial to find a good method for the evaluation of parameters in exponential sums (5). In this work, a Prony-like method for noisy and nonuniform sampling [25] is used to perform an exponential fitting in the form:

$$y(t) = \sum_{i=1}^{N\text{exp}} R_i \cdot e^{t \cdot p_i}, \tag{5}$$

with

$$R_i, p_i \in \mathbf{C}. \tag{6}$$

Clearly, $A_i = R_i$ and $\tau_i = -\frac{1}{p_i}$.

In general, Prony's method is a noniterative parametric technique for modeling damped signals with a linear combination of decaying exponentials. In its original version, it is based on two separate least-squares solutions, each of order N, with the first least-squares solution resulting in the frequencies of the signal, and the second yielding the weighting terms (or residues) in the summation. Various changes to the original procedure have been introduced to increase the performance of the method, especially in the case of experimental data with noise. In particular, the fitting method in [25], based on the algebraic derivative method in the frequency domain [25,26], uses a new linear regression equation that utilizes filtered signals obtained directly from the experimental measurements. More in detail, multiple integrals of $y(t)$ in the regression equation give a very robust estimation even in the case of large measurement noise superimposed on the signal.

While in the classical Prony's method, the roots of the regression equation are expressed in terms of the elementary symmetric functions [27] on $e^{t_s \times p_i}$ ($i = 1, \ldots, N_{\text{exp}}$), where t_s is the sampling time ($s = 1, \ldots, k$), in the method [25], the roots contain the elementary symmetric functions on p_i, $i = 1, \ldots, N_{\text{exp}}$. Furthermore, this method does not require that the experimental data are sampled at a constant time interval.

In this work, for each series of experimental data $y_{\text{exp}}(t) = \{y_{\text{exp}}(t_1), y_{\text{exp}}(t_2), \ldots, y_{\text{exp}}(t_K)\}$, the fitting function (5) has been calculated for $1 \leq N_{\text{exp}} \leq 4$. For each fitting function $y_{\text{exp}}^{(N)}$ thus obtained, the "distance" from the experimental data has been calculated as

$$d_N = \sqrt{\sum_{j=1}^{K} \left(y_{\text{fit}}^{(N)}(t_j) - y_{\text{exp}}(t_j)\right)^2}. \tag{7}$$

The choice of the optimal number N of terms in the exponential fit (5) was performed according to the minimum value of (7), also taking into account the "behavior" of the Prony-like method used in this work, varying N. The adopted method obeys the conditions (6), which are more general than (4), which, however, guarantee the physical sense of the problem under discussion.

If therefore, increasing N, R_i and p_i do not satisfy (4), this result is rejected, even if the distance (7) between the experimental data and the new fitting function is improved.

Another possible situation occurs if N increases: two pairs of complex conjugated values (R_l, p_l) and (R_m, p_m) appear [25]. In this case, if $R_l = a + ib$, $p_l = \alpha + i\beta$, and $R_m = a - ib$, $p_m = \alpha - i\beta$ are the complex values obtained, the contribution to the (5) of the two terms in l and m is

$$\begin{aligned} R_l \cdot e^{t \cdot p_l} + R_m \cdot e^{t \cdot p_m} &= (a + ib) \cdot e^{t \cdot (\alpha + i\beta)} + (a - ib) \cdot e^{t \cdot (\alpha - i\beta)} = \cdots \\ \cdots &= 2e^{t\alpha} \left(a \cos t\beta - b \sin t\beta\right). \end{aligned} \tag{8}$$

Therefore, in the case of complex conjugate values for R_l and p_l, instead of having two exponentials, a single exponential function multiplied by an oscillating factor is obtained.

In conclusion, to determine the number N in (5), the minimum value of (7) is considered, excluding, however, the cases in which there are fit parameters that do not satisfy (4) or that are in the form (8). This mathematical treatment has been applied to the practical case of the bitumen as it is a colloidal system trying to extrapolate the relaxation times that correspond to the given aggregates within the material.

The relaxation behavior for bitumen in the temperature range 40°C–100°C was examined by mechanical stress relaxation and NMR echo-decay experiments. Figure 1 shows the modulus decay and the NMR echo decay versus time at 50°C and 80°C.

Relaxation times greater than recording time ($\gg$700 seconds), contained in this stress decay, were excluded by removing the offset on $G(t)$ before the Prony-like method application.

At low temperature, the rheological decay reaches the equilibrium time slowly, while the NMR echo decay goes quickly to zero. In fact, the more rigid is the system (gel-like system), the less is the dissipative stress. Furthermore, if the system is rigid, dipole interactions are more efficient.

This can be appreciated in Figs. 2 and 3, where the τ_i relaxation times obtained by the application of the Prony-like method to the rheological and NMR experiments are shown. For each temperature that was investigated, two relaxation times were found. This indicates that the material is made of two macroaggregates, denoted as asphaltenes and maltenes in Fig. 2, that have different characteristic relaxation times. In other words, in order to extrapolate the typical relaxation times in a general decay experiment, a mono-exponential fitting is usually performed. However, this practice results in an averaged relaxation time that

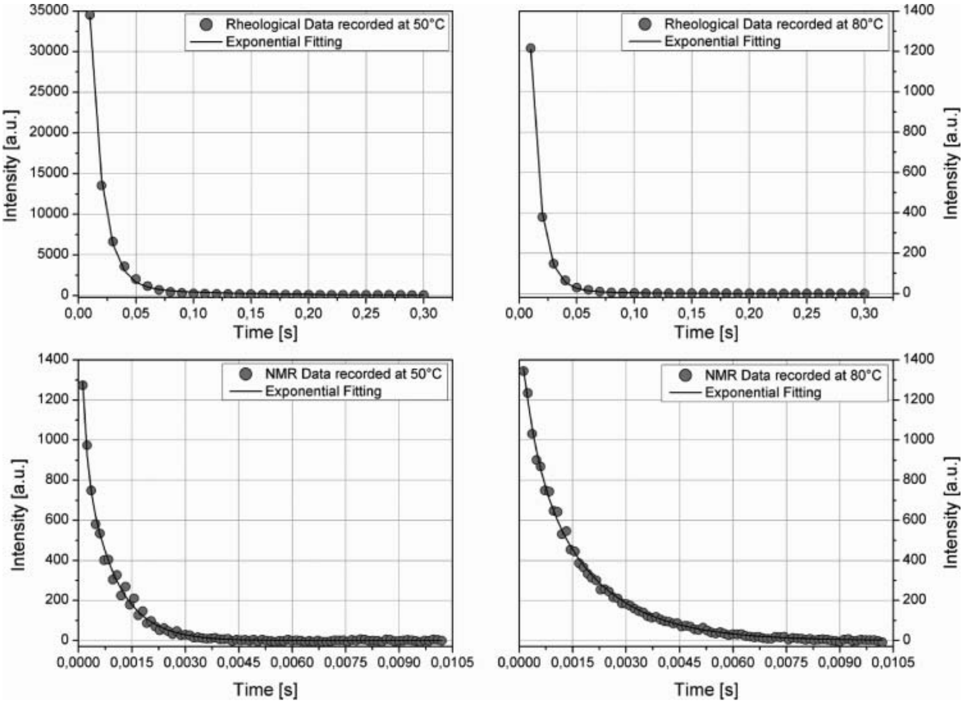

Figure 1. Rheological stress relaxation measurement (upper graphs) and ^{1}H-NMR echo decay for the spin-spin relaxation measurements (lower graphs).

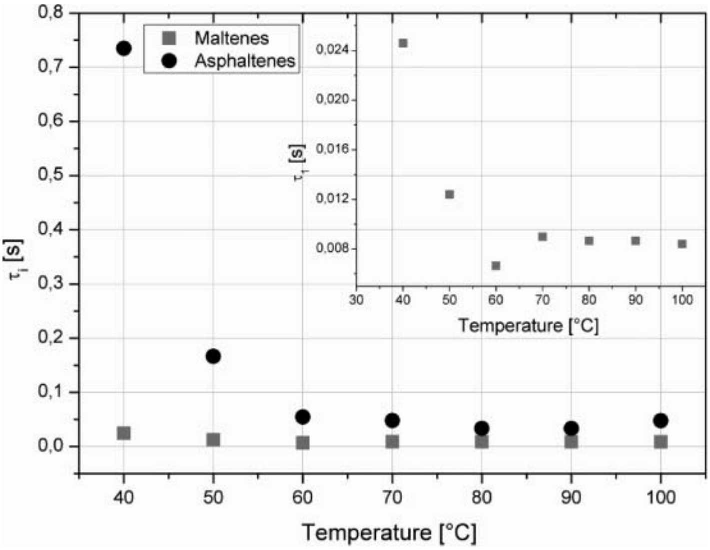

Figure 2. Temperature evolution of the rheological relaxation times obtained by applying the Prony-like method to the stress relaxation decay. The inset shows the enlarged representation of the maltenes τ_1 to remark the exponential decay.

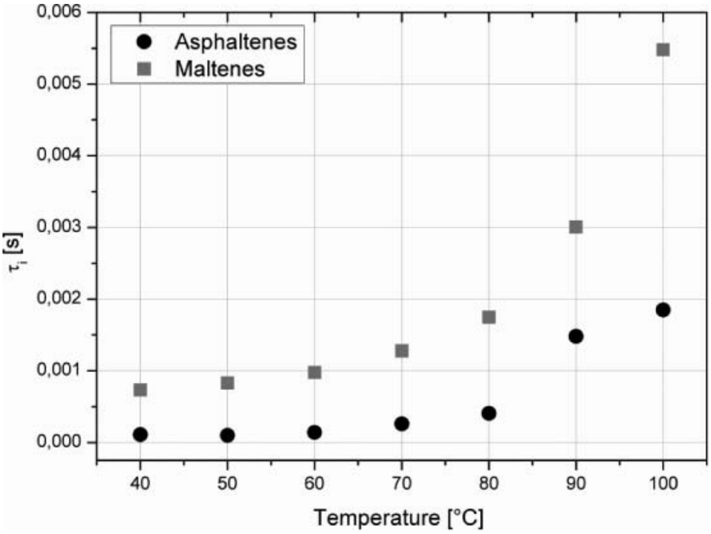

Figure 3. Temperature evolution of the NMR relaxation times obtained by applying the Prony-like method to the exponential echo decay.

does not allow distinguishing the different molecular aggregates that eventually contribute to the decay envelope.

A multiexponential fitting may provide further information on the system, allowing to discriminate between different contributions of the diverse aggregates to the experimental decay. As for the NMR measurement, the shorter relaxation times are due to the asphaltene aggregates, as they are more rigid than the maltenes dispersing oil. Also, rheological

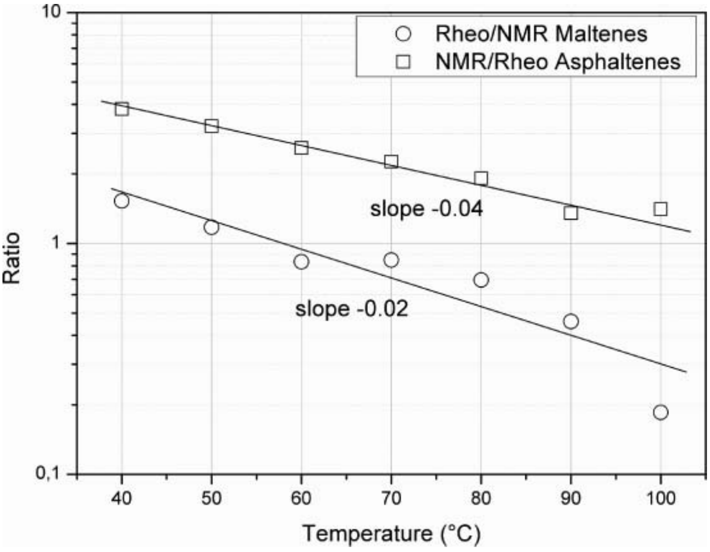

Figure 4. Ratio between rheological stress and NMR relaxations signals in function of the temperature. The line is the linear fitting in semilogarithmic scale.

measurements found two relaxation times, but in this case, the longer times correspond to the asphaltenes fraction. Despite the apparent discrepancy, the results obtained from both techniques are similar if we compare the NMR highest relaxation time to the rheological lowest time at a given temperature.

Data also indicate the occurrence of a complex stress relaxation process characterized by short and long time scales. The relaxation processes relative to the fast times (<1 second) can be attributed to the disruption and formation of aggregates [28,29]. The long relaxation times probably correspond to the progressive orientation loss of the aggregates in order to reach an equilibrium structure within a sample.

Figure 4 shows rheological/NMR relaxation time ratios as a function of the temperature, and it is worth noting that the trend is linear. This may indicate that a correlation between the two relaxation processes exists.

4. Conclusions

This work reports on the application of Prony-like method to the rheological and NMR decay experiments performed on a bitumen binder. This method has been described and implemented here, and it revealed itself as efficient in allowing the identification of two different mean relaxation times, which correspond to the maltenes and asphaltenes fractions of the investigated bitumen. We observed also the relaxation times' temperature dependence and found also the typical sol–gel transition for this system. By comparing data from the two experimental techniques we used here, we also conclude that a correlation between the rheological and the NMR relaxation times could be observed, which although deducible, was never shown before.

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