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Non-Exponential Nuclear Spin-Lattice Relaxation in the Solid Phases of EMC†

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Measurements of the proton spin-lattice relaxation time in the solid phases of ethyl-[*p*-(*p*-methoxybenzilidene)-amino]-cinnamate (EMC) are reported. A model for the non-exponential relaxation observed is discussed as well as a mathematical technique for treating the experimental data. This model, based on the assumption of the coexistence of two non-interacting groups of identical spins, was tested using a model liquid-solid system. Results of the measurements on EMC indicate that the two possible solid phases coexist at low temperatures and that a slow annealing takes place near room temperature. The dominant spin-lattice relaxation mechanism at low temperatures is determined to be a rotational motion with an activation energy of ~ 2.3 kcal/mole.

INTRODUCTION

In the past several years there has been considerable interest in the nuclear spin-lattice relaxation processes in liquid crystals, especially in those liquid crystals exhibiting a nematic structure.[1-12] In particular, anisotropies in the relaxation times and line shapes have been observed and have been discussed at some length elsewhere.[9-12]

The present work details a portion of a study of ethyl-[*p*-(*p*-methoxybenzilidene)-amino]-cinnamate, abbreviated EMC, whose structure is shown in Figure 1. This material exhibits two smectic modifications, a nematic mesophase, and two distinct solid phases, as shown in Figure 2, where the transition tem-

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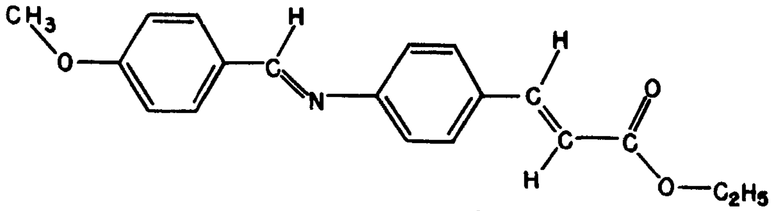

FIGURE 1 Structure of EMC.

peratures shown are taken from the data of Ref. 13. This material is of considerable interest because of the variety of liquid crystal phases and phase transitions present. In the course of our study of this material it was noted that the proton spin-lattice relaxation was non-exponential at and below room temperature. We shall discuss below an interpretation of this non-exponential relaxation due to the coexistance of the two solid phases, making use of a simple mathematical model for treating such mixed systems; a model system to test the limitations of these mathematical techniques; and, finally, present the results of measurements of the correlation times and activation energy associated with the dominant relaxation process in EMC at low temperatures.

EXPERIMENTAL DETAILS

All samples of EMC were obtained commercially[14] and were further purified by repeated recrystallization from ethanol. The samples were prepared as finely divided powder and encapsulated in pyrex tubes under vacuum. The sample temperature was maintained by an electronically regulated nitrogen gas refrigerator, giving long term temperature stability of better than ±0.5 °K and temperature gradients over the sample volume of less than 0.5°k.

The pulsed NMR spectrometer used for all the measurements was constructed in our laboratory following the general design described in Refs. 15–17. All relaxation measurements reported are of the laboratoryframe spin-lattice relaxation time T_1 for the protons and were made using a saturation burst of 90° pulses followed by a single 90° pulse. All second moments were extracted from the free induction decay signals and were averaged on a Nicolet Instruments, Inc. model 1070 signal averaging computer, as discussed below. All measurements were made at a resonance frequency of 30 MHz.

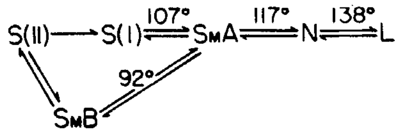

FIGURE 2 Phase transitions in EMC, after Ref. 13.

ANALYSIS OF NON-EXPONENTIAL RELAXATION

It was noted that the proton spin-lattice relaxation was non-exponential at low temperatures and that the relaxation time appeared te depend to some degree on the position along the free induction decay chosen to record signal amplitudes. From this it may be postulated that there are several groups of spins contributing to the magnetization, and, further, that each group of spins has a different line shape and that the spin groups interact weakly with one another. These conditions are satisfied if one assumes that the sample consists of a mixture of the two solid phases with only weak interactions between the hydrogen nuclei belonging to molecules associated with regions of different solid structure.

If one assumes no interaction between such groups of spins, then the amplitude, $G(t, \tau)$ of the free induction decay may be written as:

$$G(t,\tau) = AG_A(\tau)[1 - e^{-t/T_1^A}] + BG_B(\tau)[1 - e^{-t/T_1^B}], \qquad (1)$$

where T_1^A and T_1^B are the spin-lattice relaxation times of the two spin groups, A and B their relative abundances, and where $G_A(\tau)$ and $G_B(\tau)$ are the amplitudes of the free induction decays of the magnetization associated with each group. Here τ is the time along the free induction decay as measured from the middle of a 90° pulse, t is the pulse separation in a 90°–90° T_1 measurement, and the functions $G_A(0)$ and $G_B(0)$ are set equal to unity.

Now, if we restrict our attention to small $\tau(\tau \simeq 0)$, which is the case for an ordinary T_1 measurement, then Eq. (1) becomes:

$$G(t,0) = A[1 - e^{-t/T_1^A}] + B[1 - e^{-t/T_1^B}]. \qquad (2)$$

Since the amplitude of the free induction decay for $\tau \simeq 0$ is the signal amplitude, S, used in the measurement of T_1, that is:

$$S(t) \propto G(t,0) \text{ and } S(\infty) = A + B,$$

we may write Eq. (2) as:

$$S(t) = S(\infty) - Ae^{-t/T_1^A} - Be^{-t/T_1^B} \qquad (3)$$

Now, if T_1^A is sufficently larger than T_1^B then for pulse separations such that $t/T_1^B >> t/T_1^A$, Eq. (3) simplifies to yield:

$$S(t) \simeq S(\infty)\,[1 - \frac{A}{S(\infty)}\, e^{-t/T_1^A}],$$

or:

$$1 - \frac{S(t)}{S(\infty)} \simeq \frac{A}{S(\infty)}\, e^{-t/T_1^A} \simeq \frac{A}{A+B}\, e^{-t/T_1^A} \qquad (4)$$

In this limit, extrapolation to $t = 0$ yields the relative abundance of species A. This limit is the starting point for a technique used to extract the relaxation times and abundances for the two solid species in EMC, and may be used for analyzing data for any system containing two groups of identical non-interacting spins or multiple relaxation due to two different relaxation processes.

The last several points at large t are least squares fit to a single exponential to provide a trial value of T_1^A and the relative abundance of the spin species associated with the longer relaxation time. The trial function obtained is subtracted from all of the original data points, and the residues are least squares fit to yield trial values for the shorter T_1 process. Subtraction of this second function from the original data provides a new set of values for the longer T_1 process. Iteration of this process yields a convergent fit for the parameters for both relaxation processes provided that the relaxation times are sufficiently different and that neither abundance is too small. Convergence, as determined from the r.m.s. errors of the fits usually occurs after a few dozen iterations, but, to be conservative, the computer program used for these analyses was permitted to make 500 iterations for each fit. Figure 3 shows the results of this technique applied to the data from a typical low temperature measurement on EMC. In Figure 4 the separate fits to the long and short relaxation parameters are shown for the data of Figure 3. It is important to note here that this iterative technique utilizes all of the data points in extracting the parameters for each relaxation process.

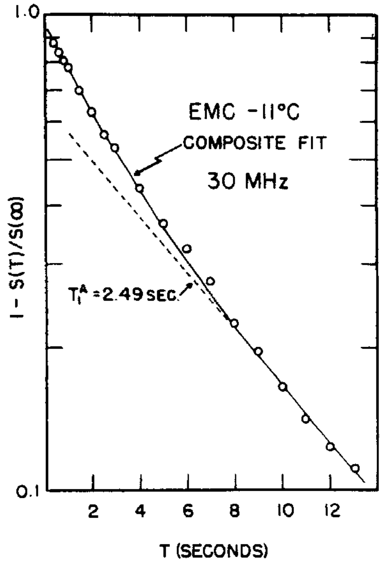

FIGURE 3 Reduced signal vs. pulse separation time for a typical 90°–90° T_1 measurement. Composite fit using iterative technique discussed in text.

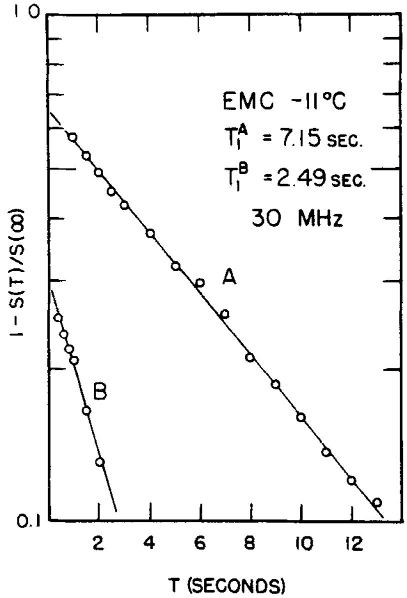

FIGURE 4 Separated reduced signals vs. time for data of Figure 3 using iterative technique discussed in text.

The solid line in Figure 3 is a composite fit using the parameters shown in Figure 4.

EXPERIMENTAL RESULTS

Model non-exponential system

In order to test the effectiveness of the technique derived above for separating the multiple spin-lattice relaxation times, a sample was prepared that approximated the conditions that appeared to hold for EMC below room temperature. In order to simulate these conditions, and those which would obtain for a mixture of liquid crystals phases, a sample exhibiting a typical liquid crystalline free induction decay and two rather different relaxation times and line shapes was constructed. A sample was prepared from *p*-methoxybenzilidene-*p*-*n*-butylaniline (MBBA) and paraffin, each of which exhibit single exponential spin-lattice relaxation. The paraffin was cast in a cylinder whose cross sectional area was approximately half that of the sample tube, and the remaining volume was filled with MBBA, so that the contributions to the signal from each material were approximately equal at short times τ .

The spin-lattice relaxation time of paraffin is shorter than that of MBBA by approximately a factor of two. The free induction decays also differ considerably while that of the composite sample still clearly resembles that of a typical nematic liquid crystal as seen in Figure 5.

On the basis of Eq. (1), one would expect to obtain a measure of T_1 that depends upon the point along the free induction decay chosen to record the signal amplitudes. In particular, one should observe non-exponential relaxation that is dominated by paraffin for short τ, and which becomes more nearly that of MBBA at large τ.

Measurements were made by applying a saturation burst of 90° pulses and then recording the free induction decay following a single 90° pulse at a time t after the burst. The data were accumulated by a signal averaging computer for 1024 repetitions for each of 15 different values of t. The channel width of the signal averaging computer was 1 μsec, so that the data yield a collection of T_1 measurements at 1 μsec intervals along the free induction decay.

For the large number of averages taken, coherent noise and any small amounts of material, such as insulation near the sample coil, could contribute a false base line that could be statistically significant. To minimize these effects, a

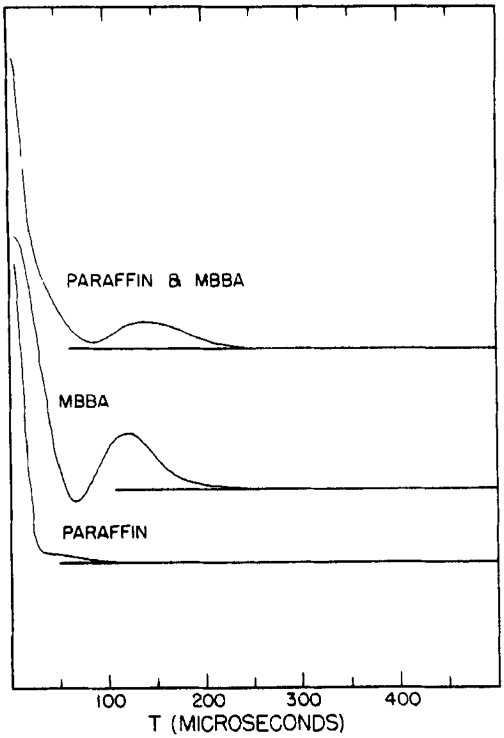

FIGURE 5 Free induction decays of paraffin, MBBA and mixed sample.

final signal was accumulated by averaging the noise produced with the sample removed from the apparatus. This background signal was then subtracted from each of the other measurements. To further reduce coherent noise from the signal averager, which has its largest contributions at high frequencies, a mild 7 point polynomial smoothing was performed separately on the data for each value of t.

The data for each microsecond interval were then treated as a separate T_1 measurement. The results of this experiment are shown in Figure 6. The upper portion of this figure shows the region of the free induction decays of paraffin and of MBBA corresponding to the T_1 measurements shown. The error bars

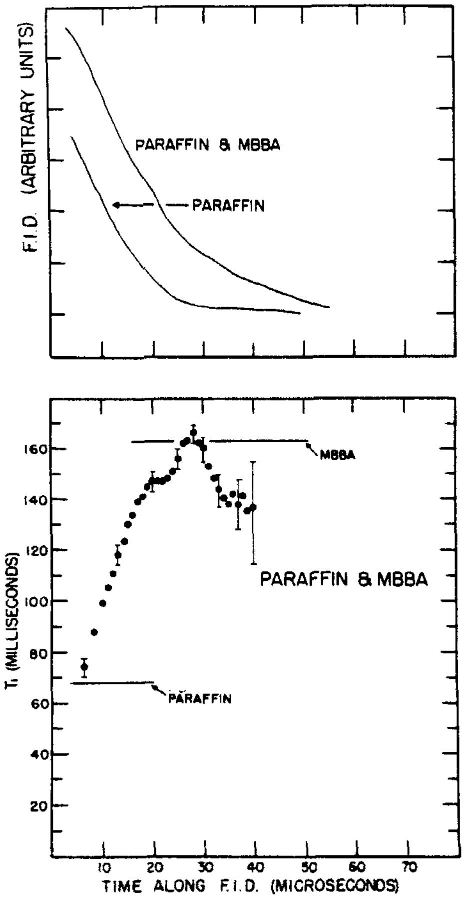

FIGURE 6 T_1 (see text) vs. time along free induction decay at which signal was recorded for mixed sample of paraffin and MBBA. Shown above are corresponding portions of free induction decays of mixed sample and paraffin.

shown are calculated from the r.m.s. error of the least squares fits, and one sees that the uncertainty in the measured value of T_1 increases rapidly as the signal amplitude decreases. For most of the interval shown, the data do not differ perceptibly from a single exponential, and the data analysis described above fails in most cases to resolve the separate relaxation times. In most cases, this algorithm estimates either two relaxation times close to the single exponential fit indicated by the visual appearance of the data, or, in the region where the effective abundances of the two materials differ significantly, yields correct values for the two relaxation times. Note that near approximately 30 μsec, where the MBBA free induction decay is still decreasing, and where the paraffin contribution shows a broadened tail, the total relaxation time decreases as the paraffin contribution to the free induction decay becomes relatively more important. Further, if one measures at larger distances along the free induction decay where a hump appears from the MBBA contribution and where paraffin no longer contributes, then the relaxation time of MBBA is obtained. This region is off the time scale of this figure.

A second result is predicted by the general form of the free induction decay for a sample containing two non-interacting groups of identical spins; that is, that the free induction decay should be a function of the repetition rate of the measurement. This is an important consideration, as the second moment of the resonance line shape can yield valuable information about the order of liquid crystals, and some care must be used in interpreting these data.

Since the free induction decay and the absorption line shape are related by a Fourier transform, it can be shown that the moments of the resonance line shape are related to the coefficients of an even power series expansion of the free induction decay:[18]

$$G(\tau) = \sum_{\substack{n \\ \text{even}}} \frac{M_n \tau^n}{n!}, \text{ where}$$

the M_n are the n^{th} moments of the absorption line shape. Free induction decay data for the mixed MBBA/paraffin sample were acquired on the signal averaging computer from which the second moment was extracted using this power series. The power series fit was carried to high order (through τ^{20}) after the data had been slightly smoothed by a low order polynomial fit to minimize the effects of high frequency noise and the discrete nature of the digitized data.

Figure 7 shows the results of the measurement of the second moment of the mixture of paraffin and MBBA. The experiment consisted of applying a saturation burst of 90° pulses and recording the free induction decay following a single 90° pulse at time τ after the burst. As expected, the second moment has a value near that of paraffin for τ small in comparison to the relaxation time of MBBA, and approaches a value somewhat larger than that of MBBA at large τ.

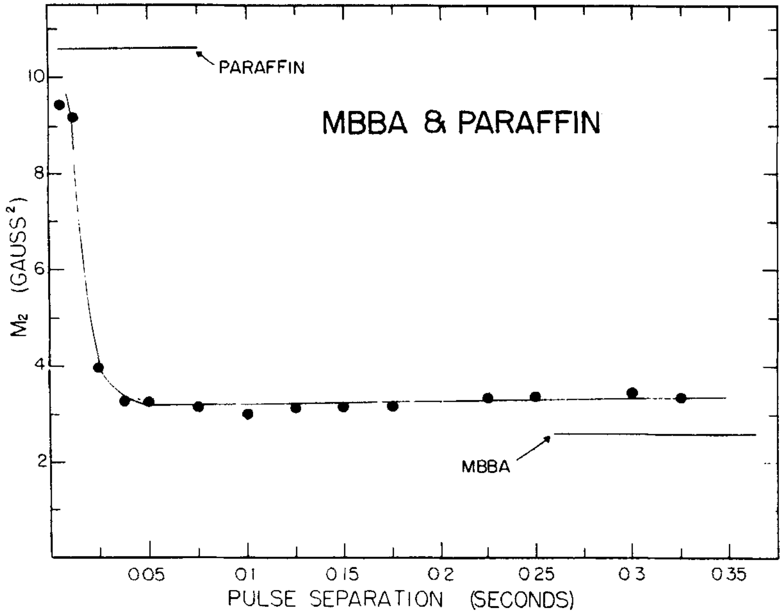

FIGURE 7 Second moment of mixed sample vs. repetition rate.

Low temperature relaxation in EMC

The proton spin-lattice relaxation time of EMC was measured as a function of temperature from liquid nitrogen temperature to 50°C. Several samples were used in the course of this investigation. Figure 8 shows the results of the measurement of the spin-lattice relaxation in two samples prepared from recrystallized material sealed in vacuum at room temperature. These samples were heated to the clearing point and allowed to cool rapidly in air at room temperature. The relaxation time shown is the longer of the two relaxation times. The temperature dependence of the relaxation time has a minimum near 120°K and is characteristic of a motional relaxation process.

Over a period of several weeks the relaxation time became more nearly exponential, indicating that a slow annealing process was taking place. To test this hypothesis, we prepared a sample of very pure material obtained from further recrystallization of the original sample preparation. A finely powdered sample of this material was sealed in vacuum at room temperature. This sample was not heated to the clearing point before measurements were made. Results of measurements of the relaxation time of this sample are shown in Figure 9. The relaxation in this case was more nearly exponential than in the previous samples,

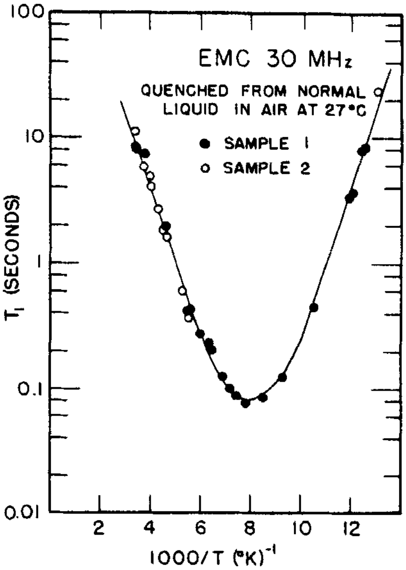

FIGURE 8 T_1 vs. inverse temperature for two solid samples of EMC quenched from the normal liquid.

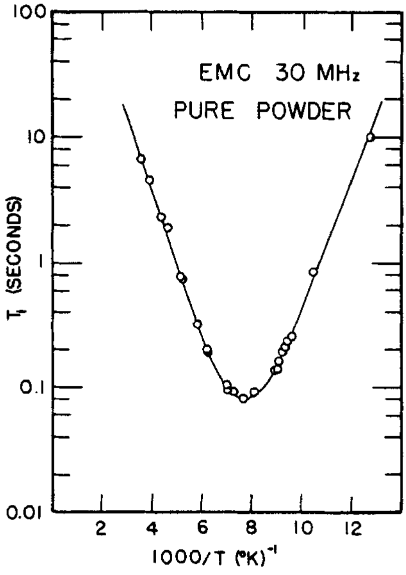

FIGURE 9 T_1 vs. inverse temperature for freshly recrystallized sample of EMC.

but has the same temperature dependence as the data in Figure 8. Again, the longer relaxation time is plotted.

Assuming that the longer relaxation process can be described by a single correlation time τ_c, then T_1 is given by:[19]

$$1/T_1 = C\left[\frac{\omega_0\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\omega_0\tau_c}{1+4\omega_0^2\tau_c^2}\right] \tag{5}$$

where ω_0 is the Larmor frequency.

Further, assuming that the temperature dependence of τ_c is governed by an activation energy, E, the τ_c as a function of temperature is given by:

$$\tau_c = \tau_0\, e^{E/RT}\,. \tag{6}$$

Figure 10 is a semilogarithmic plot of τ_c vs. reciprocal temperature, where τ_c is extracted using Eq. (5) in the regions where $\omega_0\tau_c << 1$ and where $\omega_0\tau_c >> 1$, and C is determined from the minimum in T_1 for which $\omega_0\tau_c \simeq 0.616$. From the slope of the data in Figure 10, an activation energy of ~ 2.3 kC/m is obtain-

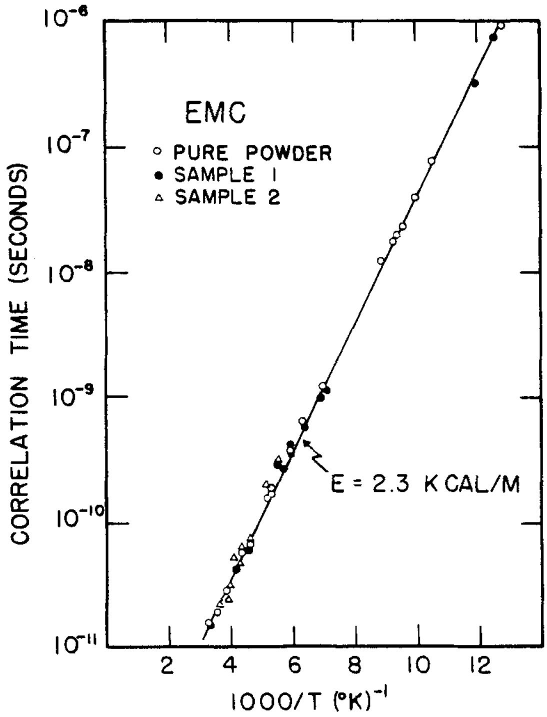

FIGURE 10 Correlation time vs. inverse temperature for data of Figures 8 and 9.

ed. Since this plot appears to be linear, we conclude that the longer relaxation is governed by a single motional process described by a single activation energy.

We also conclude, that rapid cooling from the normal liquid phase results in a solid mixture of the two solid phases, and that this mixture slowly anneals to the solid (1) phase. This conclusion is supported by the fact that the unheated powder sample exhibited nearly exponential relaxation. Further, no anisotropies were noted in the relaxation in any of the samples. The relaxation mechanism in all cases appears to be a rotation, probably of the ethyl group.

As a final test of these conclusions, a sample was heated to the clearing point and cooled to room temperature. The relaxation time measured for this sample was the same as that for the two samples discussed previously that were treated in this manner. This sample was then heated to 50°C, well below the melting point of the material, and maintaind at this temperature for several hours. Upon cooling to room temperature, the relaxation time was again measured and found to be nearly exponential, as was the case in the powder sample.

CONCLUSION

In summary, the non-exponential relaxation and annealing observed in EMC at low temperatures seems to be adequately explained by the coexistence of the two solid phases. The activation energy measured for EMC indicates that the dominant relaxation process is due to rotational motion, probably of the ethyl group.

The results of the measurements on EMC and on the mixture of MBBA and paraffin indicate that the simple iterative technique for extracting multiple relaxation times requires a minimum ratio of T_1 's of between 2 and 4 to yield clear results. Also, the general behavior for the mixed sample agrees quite well with the predictions of the simple expression for the free induction decay as a function of position on the free induction decay and pulse separation.

Finally, it is in interesting to note that over a wide range of positions along the free induction decay, the spin-lattice relaxation in the mixed sample of paraffin and MBBA was not easily distinguished from a single exponential process.

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