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## $^{13}\text{C}$ NMR relaxation in supercooled di-methyl phthalate

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**Abstract.** Spin–lattice relaxation times ( $T_1$ ) and nuclear Overhauser enhancement factors (NOE) for the individual ring carbons in di-methyl phthalate (DMF) were measured over a wide range of temperatures. The results show that the reorientational correlation function corresponding to the global dynamics in supercooled liquid can be well described by a Davidson–Cole distribution. The viscosity dependence of the reorientational correlation time  $\tau$  derived is analysed to investigate the adequacy of the modified Debye equation to description of the microscopic behaviour of supercooled systems.

### 1. Introduction

The elucidation of relaxation behaviour of high viscosity systems has been the topic of several studies over the years [1–4]. In particular, a considerable amount of work, both experimental and theoretical, has been devoted to studying the adequacy of the hydrodynamic Stokes–Einstein model to describe the microscopic molecular dynamics in liquid systems and in particular to elucidate the relationship between the microscopic reorientational correlation time  $\tau$  and the macroscopic viscosity  $\eta$  of the medium [5–11]. In many cases the modification of the hydrodynamic model based on the concept of anisotropy of intermolecular potentials, introduced by McClung and Kivelson [12], is used. According to the latter the Debye formula takes the form:

$$\tau = \kappa V_H \frac{\eta}{kT} + \tau_H \quad (1)$$

where  $\eta$  is the viscosity,  $V_H$  is the hydrodynamic volume and  $\tau_H$  is the zero viscosity correlation time, often associated with the free rotor correlation time. The McClung–Kivelson constant  $\kappa$  represents the ratio of the mean square intermolecular torque on the solute molecules to the mean square intermolecular forces on the solvent molecules. The total intermolecular potential energy determines both the torques and the forces, but only the anisotropic part of this potential gives rise to the torques. Therefore, the McClung–Kivelson constant reflects the extent of coupling between the rotational and translational motions. In addition it provides information about the degree of anisotropy characterizing the motions. Jonas and co-workers examined the validity of the Debye equation over a wide range of fluidity changes, conducting an extensive study on low viscosity fluids [6, 7] and on a series of highly viscosity liquid monosubstituted benzenes [8, 9].

Artaki and Jonas [8] have shown that for anisotropically reorienting molecules the rotational–translational coupling parameter increases with increasing density, in contrast to molecules that possess a symmetry axis, which allows for relatively unhindered reorientation, where the coupling parameter decreases with increasing density.

The main objective of the present paper was to study the temperature dependence of the coupling parameter in viscosity liquid systems consisting of isotropically reorienting molecules, which possess no symmetry for unhindered reorientations. To gain this information we have performed a complete and careful NMR study of the dynamics in supercooled di-methyl phthalate (DMF), a simple glass-forming liquid of structural formula  $C_6H_4[COO(CH_3)]_2$ . The schematic diagram of the molecule is shown in figure 1.

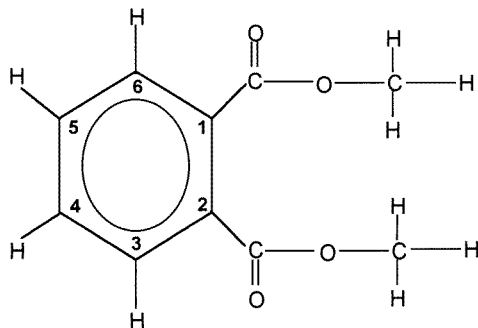


Figure 1. Schematic structure of di-methyl phthalate molecule.

## 2. Theory

The dipole–dipole relaxation rate and the nuclear Overhauser enhancement factor (NOE) for  $^{13}C$  directly bonded to the proton, under conditions of complete proton decoupling, may be written in terms of the spectral density function  $J(\omega)$  as [13]:

$$T_1^{-1} = C[J_0(\omega_H - \omega_C) + 3J_1(\omega_C) + 6J_2(\omega_H + \omega_C)] \quad (2)$$

$$\text{NOE} = 1 + \frac{\gamma_H}{\gamma_C} \frac{[6J_2(\omega_H + \omega_C) - J_0(\omega_H - \omega_C)]}{[J_0(\omega_H - \omega_C) + 3J_1(\omega_C) + 6J_2(\omega_H + \omega_C)]} \quad (3)$$

where the relaxation constant  $C = 0.1(\gamma_H\gamma_C/r_{CH}^3)^2$ ,  $r_{CH}$  is the carbon–hydrogen internuclear distance (taken to be 1.09 Å),  $\gamma_H$  and  $\gamma_C$  are the magnetogyric ratios for hydrogen and carbon and  $\omega_H$  and  $\omega_C$  their Larmor frequencies.

The particular form which the spectral density  $J(\omega)$  takes depends on the model for molecular reorientation. We shall consider two different models herein:

(i) The simplest  $J(\omega)$ , describing the isotropic reorientation and assuming an exponentially decaying correlation function. It is expressed in terms of the correlation time  $\tau$  of the motion by the relation [14]

$$J(\omega) = \frac{\tau}{1 + (\omega\tau)^2}. \quad (4)$$

(ii) The isotropic reorientation assuming a distribution of correlation times  $g(\tau)$  of the motion [15]:

$$J(\omega) = \int_0^\infty \frac{\tau g(\tau) d\tau}{1 + (\omega\tau)^2}. \quad (5)$$

A single random motion described by (4) is often not successful in explaining relaxation in viscous liquids, glass formers and disordered solids. To account for experimental observations in these systems various motional models invoking nonexponential correlation

functions or a distribution of correlation times  $g(\tau)$  have been tested with varying degree of success [16]. Spectral density functions relevant for NMR experiments and their properties are extensively discussed in the literature [15]. Therefore, here we give only the equations predicted by the Davidson–Cole asymmetrical distribution [17], that has been found to fit our experimental results.

$$g(\tau) = \frac{\sin(\beta\pi)}{\pi} \left( \frac{\tau}{\tau_0 - \tau} \right)^\beta \quad \text{for } 0 \leq \tau \leq \tau_0$$
$$= 0 \quad \text{for } \tau \geq \tau_0 \quad (6)$$

where  $\tau_0$  is the limiting correlation time and  $\beta$  the distribution width, that may take on values between 0 and 1. The average correlation time  $\bar{\tau} = \beta\tau_0$  and  $J(\omega)$  is given by:

$$J(\omega) = \frac{\sin[\beta \tan^{-1}(\omega\tau_0)]}{\omega[1 + (\omega\tau_0)^2]^{\beta/2}} \quad (7)$$

For  $\beta = 1$  this reduces to equation (4) predicted by model (i).

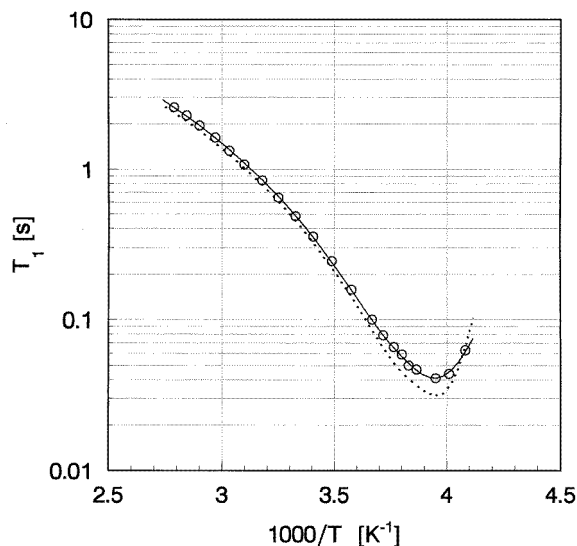
### 3. Experiment

The sample studied was received from Aldrich. The purity of the specimen was checked using high resolution NMR spectra of <sup>1</sup>H and <sup>13</sup>C. The sample investigated was degassed by the usual freeze–pump–thaw technique and then sealed under vacuum in carefully cleaned Pyrex tubes. To minimize the problem associated with liquid to vapour exchange [18] the tube used for <sup>13</sup>C high resolution NMR study had two bulbs separated by a long capillary, with the liquid in the capillary section extending well above the top of the r.f. coil. Such a construction is of particular importance for NOE measurements at high temperatures. The tube with bulbs fitted precisely in a Wilmar 10 mm o.d. tube. A deuterium source for the internal lock system was placed in the space between the tubes. The relaxation time measurements of <sup>13</sup>C were performed at 20.3 MHz using the inversion-recovery technique on a Tesla BS587A spectrometer equipped with an IBM computer. The values of  $T_1$  were evaluated from the magnetization recovery curves using a nonlinear two parameter fitting of line intensities [19]. Relative intensities were taken as peak heights after application of an exponential line broadening about three times bigger than the natural linewidth. The nuclear Overhauser enhancement was measured using the gated decoupling technique and a waiting time at least 10  $T_1$  between transients [20]. The temperature of the sample was controlled by a gas-flow cryostat and monitored with an accuracy of 1 K. To maintain stable conditions of the experiment the sample was kept at a given temperature for half an hour before collecting the data.

### 4. Results

The <sup>13</sup>C high resolution NMR spectrum of DMF consists of five resonance lines corresponding to the respective chemically nonequivalent carbon atoms (figure 1). In this paper we consider only the line due to protonated carbons C<sub>3,6</sub> and C<sub>4,5</sub>, which are located in the benzene ring and therefore can be used to probe the overall molecular dynamics. The spin–lattice relaxation time of these carbons, plotted versus inverse temperature in figure 2, shows a minimum of about 40 ms at 253 K.

In contrast to the monosubstituted benzenes [8], where the axial molecular symmetry leads to an anisotropy of motion causing different behaviour of the nonequivalent ring



**Figure 2.** Spin–lattice relaxation times of  $C_{3,6}$  and  $C_{4,5}$  carbons in di-methyl phthalate against inverse temperature. The broken line shows the dependence predicted by the Debye model; the solid line by an asymmetric Davidson–Cole distribution of correlation times.

carbons, the relaxation dependences of  $C_{3,6}$  and  $C_{4,5}$  carbons in DMF are identical and the  $T_1$  values of these carbons are almost the same, implying that the overall motion of the latter molecule may be considered as isotropic.

Figure 3 depicts the behaviour of the NOE factor of carbons  $C_{3,6}$  and  $C_{4,5}$  versus inverse temperature. It is seen that in the highest temperature region the NOE is constant at about 3. As the temperature of the sample is lowered this value decreases gradually to about 1.4 at 244 K, where the sample solidifies.

## 5. Discussion

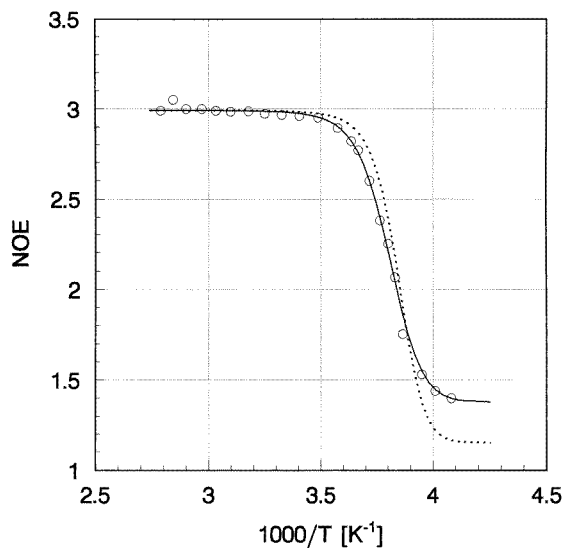
When analysing the above data first we attempted to fit it using model (i), i.e. assuming the isotropic molecular rotation described by an exponentially decaying correlation function (4). The best fit predicted by this model is shown using broken lines in figures 2 and 3. The agreement between measured and calculated  $T_1$  and NOE values may be considered as fairly good only in the high temperature interval, but the exponential correlation function fails to describe the data in the supercooled liquid.

We found that the data can be successfully explained by the Davidson–Cole distribution correlation time approach. Taking the advantage of the  $T_1$  minimum we obtained the value of the  $\beta$  parameter, equal to 0.49, which was then used to derive from the measured  $T_1$  values the temperature dependence of  $\tau$  shown in figure 4.

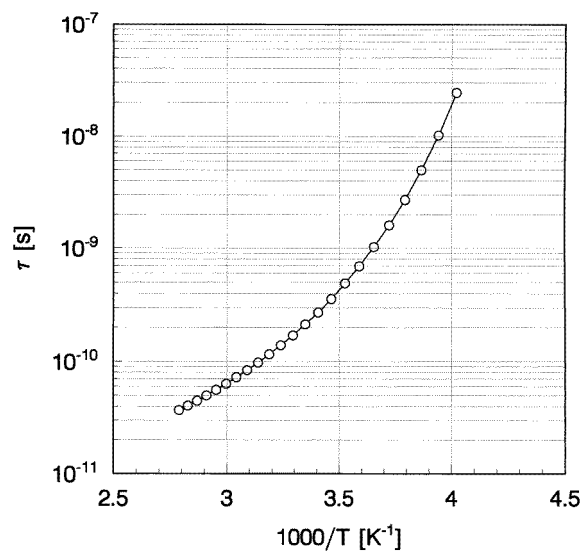
This dependence does not follow the Arrhenius behaviour. Instead we were able to fit it to the Vogel–Fulcher equation:

$$\bar{\tau} = A e^{B/(T-T_0)}. \quad (8)$$

The analysis involved substitution of (8) into (7) and use of the resulting form of the spectral density function in (2). The latter equation, written in terms of four adjustable parameters



**Figure 3.** Nuclear Overhauser enhancement factors of C<sub>3,6</sub> and C<sub>4,5</sub> carbons in di-methyl phthalate against inverse temperature. The broken line shows the dependence predicted by the Debye model; the solid line by an asymmetric Davidson–Cole distribution of correlation times.



**Figure 4.** The temperature dependence of the overall rotational correlation time in di-methyl phthalate.

$\beta$ ,  $A$ ,  $B$  and  $T_0$ , was used to fit the experimental  $T_1$ –temperature plot. The fitting computer program searched the parameter space for a minimum value of  $\chi^2$  given by:

$$\chi^2 = \sum_{i=1}^n \left[ \frac{T_1(\text{expt}) - T_1(\text{calc})}{T_1(\text{expt})} \right]^2 \tag{9}$$

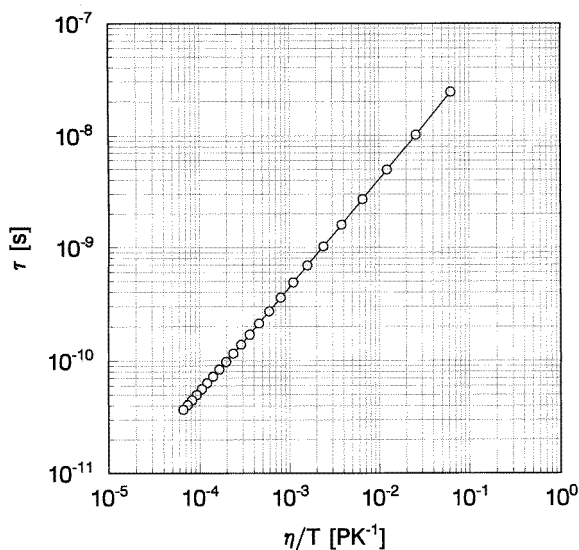
where  $n$  is the number of experimental  $T_1$  values.

The best fit of the  $T_1$  is represented by the solid line in figure 2. The distribution parameter  $\beta$  derived from the fit is equal to 0.49 and the value of parameters  $A$ ,  $B$  and  $T_0$  are  $2.038 \times 10^{-12}$  s, 460.8 K and 199.6 K, respectively. It is seen that the model used describes well the relaxation data in the whole temperature range studied. We realize that one may question the used procedure arguing that, with four adjustable parameters, it is possible to fit the data, but not truly represent the physical condition of the system. Therefore, as a check of its correctness we attempted to reproduce the experimental NOE values. This was done by substituting the optimized parameters yielded by the fit of  $T_1$  into (3). The calculated results are shown by the solid line in figure 3. It is seen that the Davidson–Cole model describes the NOE data in the whole temperature range studied as satisfactorily as it does the  $T_1$  results. The rotational correlation time varies in this range from  $10^{-11}$  to  $10^{-7}$  s showing a strong non-Arrhenius behaviour.

Figure 5 presents the dependence of the derived rotational correlation time  $\tau$  on viscosity. It can be seen that  $\tau$  is a linear function of  $\eta/T$  but having a non-zero intercept. For low viscosity fluids an empirical modification of the Debye equation was suggested to account for this observation [5, 6]:

$$\tau = C \frac{\eta}{T} + \tau_H \quad (10)$$

where  $C$  is constant ( $C = \kappa V/k$ ; see (1)). Our  $\tau$  data can be well described by (10) yielding the slope  $C = 2.5 \times 10^{-7}$  [K s P $^{-1}$ ] and the intercept  $\tau_H = 3.5$  ps. The intercept value has been often associated with the reorientation time  $\tau_{FR}$  of the classical free rotor ( $\tau_{FR} = (2\pi)/(I/kT)^{1/2}$  [7, 21], where  $I$  is the moment of inertia). For DMF we calculated the value of  $\tau_{FR}$  to be 1.8 ps.



**Figure 5.** Correlation time of the overall rotational motion in di-methyl phthalate against  $\eta/T$ .

Based on the obtained constant  $C$  we calculated the rotational–translational coupling parameter  $\kappa = Ck/V$ . It should be noted that the result of calculation depends strongly on an unambiguous and accurate determination of molecular volume. Edward has argued in favour of the van der Waals volume ( $V_w$ ) concept [22]. Following this concept we evaluated, using atomic increments of Edward [22], the van der Waals volume  $V_w$  to be  $190 \text{ \AA}^3$ ,

and the coupling parameter  $\kappa = 0.2$ . The derived value compares with those observed in low viscosity organic fluids [7]. This is contrary to the expectation that rotational–translational coupling in the supercooled state should invoke a  $\kappa$  parameter of significantly higher magnitude.

## 6. Summary

From the above discussion it is seen that the temperature behaviour of molecular relaxation times in DMF is, within the limit of rotational diffusion, very well described by (1). The global dynamics features characteristics typical for an asymmetric Davidson–Cole distribution of correlation times. The functional form of the temperature dependence of the correlation time describing global dynamics in DMF shows the Vogel–Fulcher behaviour.

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