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## Molecular dynamics in supercooled di-isobutyl phthalate close to the glass transition

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Received 12 June 1999, in final form 14 July 2000

**Abstract.** The dynamics of the  $\alpha$ -relaxation in a glass-forming low-molecular-weight system, di-isobutyl phthalate (DIBP), has been studied by means of dielectric, nuclear magnetic and mechanical spectroscopies. By using these techniques we have covered a wide timescale ranging from  $10^{-11}$  to  $10^2$  s. Vogel–Fulcher correlation time behaviour and the Davidson–Cole distribution function make possible a simultaneous fitting of  $T_1$ , the nuclear Overhauser enhancement (NOE) factor and dielectric data over the temperature range  $(T_g - 4 \text{ K}) < T < (T_g + 155 \text{ K})$ . These results together with the viscosity data have been analysed in terms of the Debye diffusion.

### 1. Introduction

Dynamic properties of  $\alpha$ -relaxation related to the glass transformation process have attracted considerable attention in recent years [1, 2]. The information is of interest from the theoretical point of view, as it can provide a better understanding of the relation between the microscopic dynamics and macroscopic properties of glass formers. The dynamics of a glass-forming liquid is related to the disorder in the liquid, which is frozen into a variety of metastable states during the transition process. Hence, the relaxation time  $\tau$ , derived from experiments that probe structural and orientation rearrangements in the glass systems, usually exhibits complex behaviour: non-Arrhenius, non-exponential and non-linear.

On approaching the glass transition, the increase of the structural relaxation time with decreasing temperature is well represented by the phenomenological Vogel–Fulcher–Tammann (VFT) law [3]:

$$\tau_{rot} = A \exp(B/(T - T_0)) \quad (1)$$

which was originally interpreted as the reduction of the free volume for diffusion [4] and, more recently, as the enhancement of cooperative motions [5, 6] or as a percolation phase transition between liquid and solid-like clusters [7].

At temperatures higher than  $T_g$ , the rotational diffusion correlation time  $\tau$  can be related to the macroscopic viscosity  $\eta$  and temperature  $T$  by the Stokes–Einstein–Debye (SED) equation [8]

$$\tau_{rot} = \frac{V\eta}{kT} \quad (2)$$

¶ Deceased

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where  $k$  is Boltzmann's constant and  $V$  is the molecular volume. The proportionality between  $\eta$  and  $\tau$  is a consequence of the Maxwell model [4] for viscoelastic liquids. Angell [9] pointed out, however, that such a relationship is by no means guaranteed and suggested the possibility that it could be violated for supercooled liquids if certain relaxation processes decouple from the viscosity. A marked change of both rotational and translational diffusion mechanisms has been observed in organic liquids, corresponding to a breakdown of the SED diffusion law [10–18].

It is of interest to compare the results obtained by different spectroscopic techniques to establish the extent to which the same relaxation process is probed by different observables, i.e., to check for the possible existence of a universal behaviour in the dynamics of supercooled systems. NMR and dielectric techniques are particularly suitable for this purpose, since they can cover a wide range of dynamics of the structural relaxation from the liquid phase down to the glass transition, in addition showing sensitivity to subglass relaxation processes.

The aim of the present paper is to investigate the temperature behaviour of the structural relaxation of a glass-forming system by dielectric and NMR spectroscopy in comparison with results of viscosity measurements performed on the same system. Di-isobutyl phthalate (DIBP) is particularly appropriate for such investigations since it is a fragile glass former, which does not exhibit any appreciable crystallization. It has a permanent dipole moment, which makes possible a detailed dielectric investigation over a wide frequency and temperature range. Dielectric investigations revealed a secondary relaxation whose temperature behaviour was strongly affected by the glass transition. The temperature evolution of the structural relaxation time obtained by these techniques is compared with the viscosity to test the validity of the SED law. Both the relaxation time and the shape parameters are compared with the dielectric ones in order to test how these different techniques account for the same structural relaxation.

We have studied  $\alpha$ -relaxation in a glass-forming low-molecular-weight system, DIBP, over a wide frequency range from  $10^{-2}$  to  $10^{11}$  Hz, by applying dielectric, nuclear magnetic resonance and mechanical spectroscopies.

## 2. Experimental results

### 2.1. Sample

DIBP is a van der Waals liquid, with a simple molecular structure. The sample studied here was kindly provided by Professor W Augustyniak, Department of Chemistry, A Mickiewicz University, Poznan. The purity of the specimen was checked using high-resolution NMR spectra of  $^1\text{H}$  and  $^{13}\text{C}$ . This system has several advantages. First of all it does not crystallize, allowing us to explore a wide temperature range above  $T_g$  without any difficulty. It also has a convenient  $T_g$  of 188 K [20] and a fairly large dielectric moment, which makes dielectric spectroscopy measurements possible.

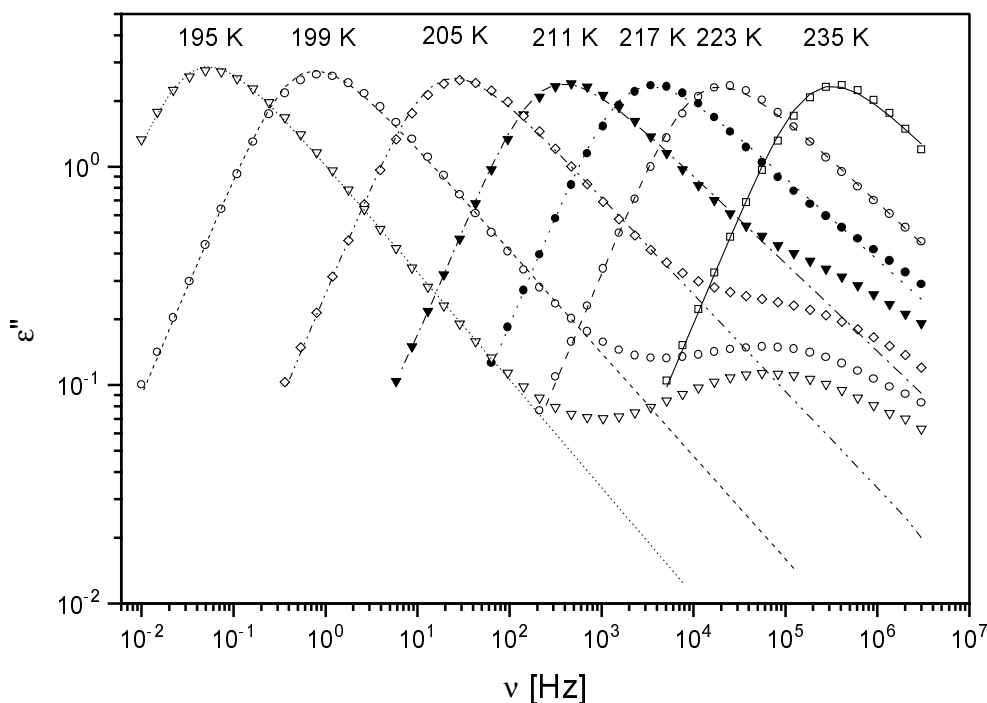
### 2.2. Dielectric relaxation

We will briefly summarize the main observables studied by dielectric spectroscopy and their relationship to the molecular reorientational correlation function. The complex permittivity  $\varepsilon^*(\omega)$  is related to the normalized dielectric response function  $\psi(t)$  via [21–24]

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = 1 - i\omega \int_0^\infty \psi(t) \exp(-i\omega t) dt. \quad (3)$$

Here  $\varepsilon_0$  and  $\varepsilon_\infty$  are the limiting low- and high-frequency permittivity values, and  $\omega = 2\pi\nu$ . In the framework of the linear response theory and under certain assumptions concerning the internal field [21–23], the relaxation function  $\psi(t)$  is identical to the total dipole moment correlation function  $\phi_M(t)$ . This correlation function contains the autocorrelation part and the cross-correlation contribution associated with the molecular dipole moment  $\mu$ . Usually it is assumed that cross-correlation effects are small in simple liquids. This assumption has been made in the investigation of di-*n*-butyl phthalate, a compound with dielectric properties similar to those of the one studied here [25–27]. For instance, in many cases autocorrelation and collective correlation times agree quite well for supercooled liquids [1, 2, 21, 22, 28]. Moreover, one can state that the structural relaxation process in supercooled liquids, i.e. the  $\alpha$ -process, is reflected in a similar way by the various relaxation methods. Thus, we will assume that in the first approximation  $\varepsilon^*(\omega)$  probes the autocorrelation part. In other words, the reorientational correlation function,  $\phi_1(t)$ , associated with the first Legendre polynomial is monitored, i.e.,  $\phi_M(t) \simeq \phi_1(t)$  [28]. This function can be compared with the correlation function studied by means of  $^{13}\text{C}$  NMR where the correlation  $\phi_2(t)$  of the second Legendre polynomial is probed [17, 18, 29].

The dielectric measurements covered the frequency range from  $10^{-2}$  Hz to 3 MHz. In this range we used two systems: a frequency response analyser (Solartron SI-1260) and an impedance analyser (HP-4192A) [30]. The sample temperature was controlled by a temperature controller using a  $\text{N}_2$  gas stream (Unipan 660). In figure 1 we present  $\varepsilon''$  for DIBP close to the glass transition temperature. When we study the  $\varepsilon''$ -data the following features are observed: the peaks are clearly broader than is expected from the Debye function; moreover



**Figure 1.** A plot of the imaginary part,  $\varepsilon''$ , of the dielectric constant versus  $\log \omega$  at the labelled temperatures for the  $\alpha$ -relaxation. The curves are the best fits to the data using the Davidson–Cole function given by equation (6).

they are asymmetrical at high temperatures and the  $\alpha$ -process enters the experimental frequency window from the high-frequency side. The spectral shape of  $\varepsilon^*$  can be well extrapolated using the Davidson–Cole (DC) susceptibility function [28, 31]:

$$\varepsilon_{\text{DC}}^* = \frac{\Delta\varepsilon}{(1 + i\omega\tau_{\text{DC}})} \quad (4)$$

where  $\Delta\varepsilon$  is the relaxation strength and  $\tau_{\text{rot}} = \beta_{\text{DC}}\tau_{\text{DC}}$  the correlation time.  $\beta_{\text{DC}}$  governs the non-Debye behaviour at frequencies above the peak frequency, where power-law behaviour with  $\varepsilon''(\nu) = \nu^\beta$  is found. Equally well, the Kohlrausch–Williams–Watts stretched-exponential decay function (after Fourier transformation) can be applied [1, 2, 22, 23, 32, 33] in order to extrapolate the loss around the  $\alpha$ -relaxation peak.

The solid curves are the best-fitting curves obtained using the Cole–Davidson function. The fit is reasonably good around the peak position, yet it becomes poor in the high-frequency tails, where there is also a contribution from the  $\beta$ -relaxation. As long as the  $\alpha$ - and  $\beta$ -relaxation are well separated,  $\beta_{\text{DC}}$  has a constant value of 0.46 for the temperature range 192–227 K. When these two relaxations coincide, we observe an increase of  $\beta_{\text{DC}}$ , to a value of 0.58 at temperature 253 K. The  $\tau_{\text{rot}}(T)$  behaviour shown in figure 4 (later) is clearly non-Arrhenius and will be discussed below.

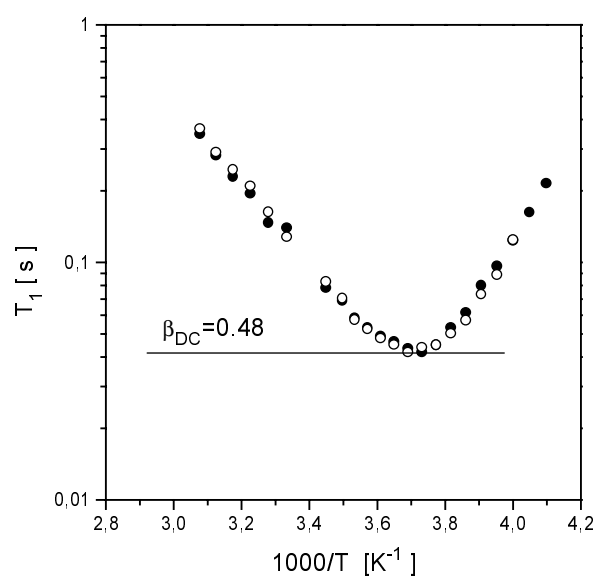
### 2.3. $^{13}\text{C}$ NMR relaxation

The measurements of the relaxation time and the nuclear Overhauser enhancement for  $^{13}\text{C}$  were performed at 20.3 MHz using the inversion–recovery technique on a Tesla BS587A. The experimental procedure used by us has been previously described in [17, 18]. The values of  $T_1$  were estimated from the magnetization–recovery curves using a non-linear two-parameter fitting of line intensity [34]. Curve fitting was carried out by using the Levenburg–Marquardt algorithm [35] to minimize the value of  $\chi^2$ , given by

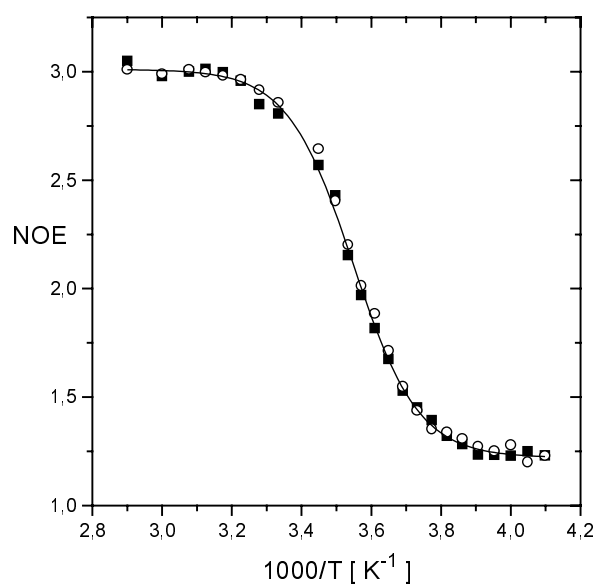
$$\chi^2 = \left( \sum_{i=1}^n [I(t_i) - \bar{I}(t_i)]^2 \right) / \sigma^2 \quad (5)$$

where  $\bar{I}(t_i)$  is the experimental peak intensity,  $\bar{I}(t_i)$  is the intensity predicted at the  $i$ th time point,  $\sigma$  is the uncertainty in the experimental data points and  $n$  is the number of time points recorded. The adequacy of the monoexponential decay function and the accuracy of the value of  $\sigma$  used in equation (3) were evaluated by means of a goodness-of-fit  $\chi^2$ -test [35]. For the  $T_1$ -measurements,  $\nu = 8$  ( $\nu = n - p$  is the number of degrees of freedom, where  $p$  is the number of adjustable parameters) and the  $\alpha = 0.05$  critical value for the exact  $\chi^2$ -statistics is 15.51 [35, 36]. For example, inversion–recovery curves for  $\text{C}_{3,6}$  carbon resonances were analysed and gave an optimized fit with  $\chi^2 = 12.5$  which is less than the critical value given above. Therefore the goodness-of-fit test of the residual  $\chi^2$ -values indicates that inversion–recovery data are adequately described by the monoexponential decay function.

The  $^{13}\text{C}$  high-resolution NMR spectrum of DIBP consists of seven resonance lines corresponding to the respective chemically non-equivalent carbon atoms. In this paper we only consider the line formed by carbons  $\text{C}_{3,6}$  and  $\text{C}_{4,5}$ , which are located in the benzene ring and therefore can be used to probe the overall (global) molecular dynamics. The spin–lattice relaxation time of these carbons, plotted versus inverse temperature in figure 2(a), shows a minimum of about 40 ms at 293 K. The temperature dependence of  $\text{C}_{3,6}$  and  $\text{C}_{4,5}$  relaxation in DIBP are very similar and the  $T_1$ -values of these carbons are almost the same, implying that the overall motion of the molecule may be considered as isotropic. Figure 2(b) depicts the behaviour of the NOE factor of carbons  $\text{C}_{3,6}$  and  $\text{C}_{4,5}$  versus inverse temperature. It can



(a)



(b)

**Figure 2.** (a) Spin–lattice relaxation times of carbons  $C_{3,6}$  (open circles) and  $C_{4,5}$  (solid circles) in DIBP against inverse temperature. The value of the minimum of  $T_1(T)$  obtained using a DC spectral density function is shown. (b) Nuclear Overhauser enhancement of carbons  $C_{3,6}$  and  $C_{4,5}$  in DIBP against inverse temperature. The solid line shows the dependence predicted by a Davidson–Cole distribution of correlation times.

be seen that in the highest-temperature region the NOE is constant and equals  $\approx 3$ . As the temperature of the sample is lowered, this value decreases gradually to about 1.4 at 244 K.

The relaxation rates of nuclei with spin 1/2 (such as  $I = {}^{13}\text{C}$ ) are dominated by dipole–dipole relaxation due to protons ( $S = {}^1\text{H}$ ) directly bonded to the I nuclei. These heteronuclear

relaxation rates are often measured under conditions of complete proton decoupling. If this is the case, relaxation rates describe single-exponential processes [37]. Cross-relaxation between the I spin and the proton leads under decoupling to an increase of the I signal intensity by the NOE factor. For carbons, assuming that the relaxation is caused only by the directly bonded proton, the relaxation rates become [38]

$$\frac{1}{nT_1} = C[J_0(\omega_H - \omega_C) + 3J_1(\omega_C) + 6J_2(\omega_H + \omega_C)] \quad (6)$$

$$\text{NOE} = 1 + \frac{\gamma_H}{\gamma_C} \frac{6J_2(\omega_H + \omega_C) - J_0(\omega_H + \omega_C)}{J_0(\omega_H - \omega_C) + 3J_1(\omega_C) + 6J_2(\omega_H + \omega_C)} \quad (7)$$

where the factor  $C = (\mu_0/4\pi)\gamma_H\gamma_C\hbar r_{\text{CH}}^{-3}$ , the dipolar coupling constant, is related to the dipolar interaction strength of the two nuclei and the internuclear distance  $r_{\text{CH}}$  (taken to be 1.09 Å);  $\gamma_H$  and  $\gamma_C$  are the gyromagnetic ratios for hydrogen and carbon, and  $\omega_H$ ,  $\omega_C$  are their Larmor frequencies.

$T_1$  and the NOE factors are sensitive to the form of the spectral density function  $J(\omega)$ .  $J(\omega)$  is defined as the one-side Fourier transformation of the self-correlation function  $G(t)$  of the carbon–proton relative position. For the Debye process,  $G(t)$  displays an exponential decay and  $J(\omega)$  is given by the Lorentzian  $J(\omega) = \tau/(1 + \omega\tau^2)$ . Under these conditions, equation (6) predicts a value of 0.031 s for the  $T_1$ -minimum corresponding to DIBP at  $\omega_C/2\pi = 22.08$  MHz and  $\omega_H/2\pi = 88$  MHz. However, the experimental value obtained (0.045) is much larger. This is expected for a distribution of reorientation correlation times. Therefore, we will again describe the experimental behaviour of  $T_1$  and the NOE factor by a spectral density function  $J_{\text{DC}}(\omega)$  derived from the Cole–Davidson relaxation function. Thus for  $J(\omega)$  we can write [29]

$$J_{\text{DC}}(\omega) = \frac{\sin[\beta_{\text{DC}} \arctan(\omega\tau_{\text{DC}})]}{\omega[1 + (\omega\tau_{\text{DC}})^2]^{\beta_{\text{DC}}/2}} \quad (8)$$

$$\tau_{\text{rot}} = \beta_{\text{DC}}\tau_{\text{DC}} \quad 1 \geq \beta_{\text{DC}} \geq 0.$$

Equations (6) and (8) predict a  $T_1$ -minimum given by  $T_{1\text{min}} = 1/(C^*F)$ , where  $F$  is a number which depends on the value of  $\beta_{\text{DC}}$ . Smaller values of  $\beta_{\text{DC}}$  correspond to larger values of  $F$  and larger values of  $T_{1\text{min}}$  (see also reference [39]). The value of  $\beta_{\text{DC}} = 0.48$  has proved to be adequate for fitting the  $T_1$ -value at the minimum,  $T_{1\text{min}}$  (see figure 2(a)). Hence, this value was used to derive the temperature dependence of the rotational correlation time  $\tau_{\text{rot}}$  from the relaxation times shown in figure 4, later. The rotational correlation time varies over the measuring range from  $10^{-11}$  to  $10^{-7}$  s, showing a strong non-Arrhenius behaviour.

To check the validity of the model adopted, we have used the calculated correlation times to reproduce the experimental NOE values. The temperature dependence of the calculated NOE factors is shown with a solid line in figure 2(b). It can be seen that the Davidson–Cole distribution represents the NOE factors fairly well.

NMR studies on simple supercooled liquids have shown that both  $T_1$  and NOE are well described by applying equations (6), (7) assuming a spectral density  $J(\omega)$  of the Davidson–Cole (DC) type [31]. In the case of  $^2\text{H}$  and  $^{13}\text{C}$  NMR, this approach has already been proved to provide correct correlation times for several decades of viscosity [17, 18, 40].

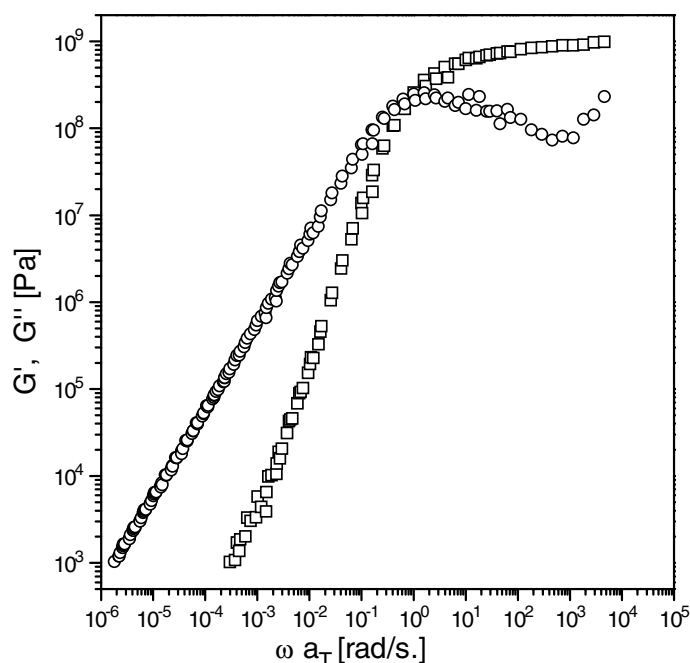
#### 2.4. Mechanical relaxation

Rheological measurements were performed by means of the Rheometrics mechanical spectrometer (RMS 800) with a plate–plate geometry, covering over nine decades in viscosity and four decades in frequency ( $10^{-2} < \nu < 10^2$  Hz) for the shear modulus  $G(\nu)$ . To measure  $G(\nu) \equiv \sigma_\nu(t)/\gamma_\nu(t)$  we applied an oscillatory strain,  $\gamma_\nu(t) = \gamma e^{i2\pi\nu t}$ , where  $\nu$  was kept

small to ensure a linear response. Using the time–temperature superposition (TTS) [4], master curves of the storage and loss modulus,  $G'$  and  $G''$ , were obtained for DIBP with the reference temperature  $T_0$  at 191.8 K as shown in figure 3. For the sake of clarity, all data obtained for  $G'$  and  $G''$  at different temperatures are displayed with the same symbols. The vertical correction of  $T_0/T$  was applied to all data obtained at different temperatures. The shift factor was fitted to the WLF equation [4]

$$\log a_T = \frac{-C_1(T - T_0)}{C_2 + T - T_0} \quad (9)$$

and the constants  $C_1$  and  $C_2$  obtained from the fit are 14.2 and 42.4 respectively. A Maxwell model  $G_M(\nu) = G_\infty[1 - (1 + i2\pi\nu t)^{-1}]$  does not fit the spectrum adequately. However, a satisfactory fit can be obtained with the Fourier transformation of  $-d(\varphi_{\text{KWW}})/dt$ , where the Kohlrausch–Williams–Watts (KWW) stretched-exponential function  $\varphi_{\text{KWW}}$  is equal to  $\varphi_0(\exp[-(t/\tau_{\text{KWW}})^{\beta_{\text{KWW}}})]$ .



**Figure 3.** Master curves obtained from the linear dynamic shear data for DIBP. The reference temperature is 191.8 K. Shown here are the storage ( $G'$ : open squares) and loss ( $G''$ : open circles) moduli.

There is no simple analytical form of this function in the frequency domain. This form is generally successful in describing relaxation processes for  $\omega \leq 1/\tau$ . The constants  $\tau_{\text{KWW}}$  and  $\beta_{\text{KWW}}$  obtained from the fit are 2.5 s and 0.47 respectively, and  $\langle\beta_{\text{KWW}}\rangle = 5.6$  s where

$$\langle\tau_{\text{KWW}}\rangle = \tau_{\text{KWW}}/\beta_{\text{KWW}}\Gamma(1/\beta_{\text{KWW}}).$$

Lindsey and Patterson [41] have already pointed out the close similarity of the KWW stretched-exponential function and the Davidson–Cole correlation function. The corresponding parameters of each function are related to one another [42]. Rössler and Eiermann [29] have obtained an interpolation formula by fitting the DC correlation function with the



KWW function:

$$\begin{aligned}\beta_{\text{KWW}} &= -0.3\beta_{\text{DC}}^2 + 1.23\beta_{\text{DC}} + 0.069 & 0.1 \leq \beta_{\text{DC}} \leq 1 \\ \tau_{\text{KWW}} &= \tau_{\text{DC}}(1.2\beta_{\text{DC}} - 0.22) & 0.3 \leq \beta \leq 1.\end{aligned}\quad (10)$$

Applying equation (8), a conversion can be made from  $\beta_{\text{KWW}}$  and  $\tau_{\text{KWW}}$  to  $\beta_{\text{DC}}$  and  $\tau_{\text{DC}}$ , obtained from mechanical relaxation data. If we look at the shapes of the different response functions, we see a discrepancy between the dielectric ( $\beta_{\text{DC}} \approx 0.46$ ) and mechanical data ( $\beta_{\text{DC}} \approx 0.34$ ). Intuitively it is appealing to say that dielectric measurements only couple the charged modes and it is possible that some of the slow modes, important to the glass transition, do not carry any dipole moments. As a result, the width of the dielectric absorption is narrower than that obtained by mechanical spectroscopy.

We also obtained the viscosity

$$\eta = \lim_{\nu \rightarrow 0} [G(\nu)/2\pi\nu t].$$

Our technique made extrapolation of  $\eta$  to its zero-shear-rate value possible. At higher temperatures, the zero-shear viscosity was determined directly from the plateau observed in frequency sweeps, but at lower temperatures, an extrapolation to the plateau regime, using the time–temperature superposition, was necessary. Viscosity values ranging from  $1.4 \times 10^{11}$  P to 0.028 P obtained within the temperature range 188–377 K are shown in figure 4. These data are consistent with those of Barlow and co-workers [44].

### 3. Discussion

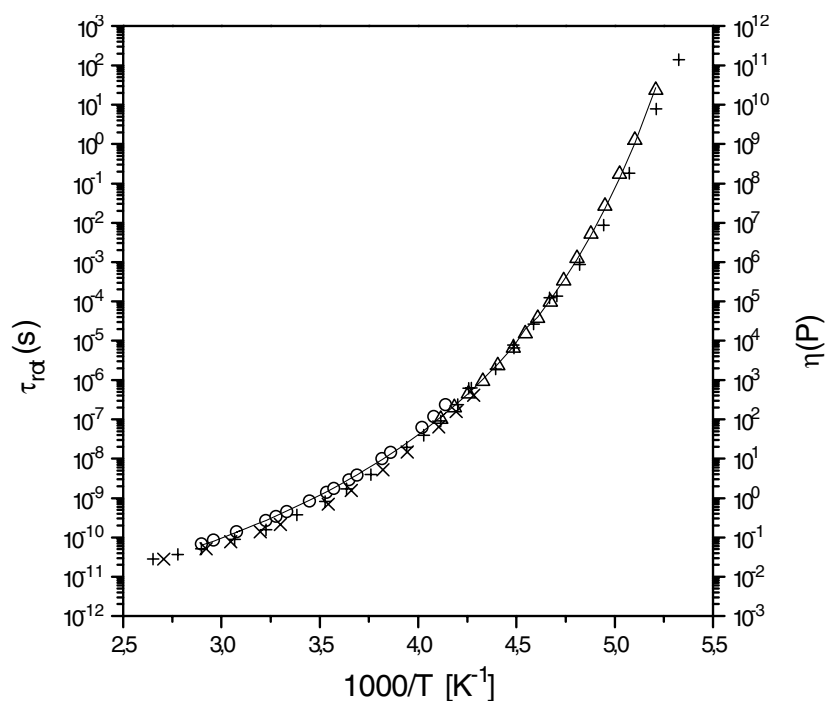
By comparing the temperature behaviour of the correlation times obtained from dielectric and nuclear magnetic resonance spectroscopies (figure 4), it is clear that the values of  $\tau_{rot} = \beta_{\text{DC}}\tau_{\text{DC}}$  obtained by different relaxation experimental techniques have not only the same temperature behaviour but also similar absolute values. Therefore, the temperature behaviour of the correlation times controlling dielectric and NMR behaviour can be parametrized by the Vogel–Fulcher law (see equation (1)). As can be seen from figure 4, the Vogel–Fulcher law portrays well the temperature dependence of the correlation times  $\tau_{rot}$  of the macroscopic  $\alpha$ -relaxation. From the fitting process, the following values of the Vogel–Fulcher parameters were obtained:  $A = 9.72 \times 10^{-14}$  s,  $B = 1229$  K and  $T_0 = 155$  K. Moreover, that the same temperature behaviour of the correlation times was obtained from different experiments indicates that different susceptibilities over a wide frequency range ( $10^{11}$ – $10^{-2}$  s $^{-1}$ ) can be scaled by the shift factor, which follows the same temperature behaviour, i.e., the dynamics of the  $\alpha$ -relaxation exhibits universality.

As a result of the continuing interest in rationalizing the origins of VFT/KWW (or DC) behaviour for relaxation in glass-forming systems, the concept of fragility, introduced by Angell [45, 46], has been developed extensively [47–50]. A measure of the fragility of the  $\alpha$ -relaxation is  $m = d[\log \tau(T)]/d(T_g/T)$  at  $T = T_g$  where  $T_g$  is usually chosen as the temperature at which  $\langle \tau \rangle = 100$  s (see, e.g., references [47] and [49]). Analysis of the  $\alpha$ -relaxation data, obtained using different techniques, for about 70 different supercooled liquids [47, 50] shows that  $m$  ranges from minimum values  $m_{min} = 16$  up to  $m = 200$ . If the VFT equation is rewritten as

$$\langle \tau(T) \rangle = A \exp(DT_0/(T - T_0)) \quad (11)$$

then the Böhmer [50] result is

$$m = m_{min} \frac{T_g}{T_g - T_0} \quad m = 16 + \frac{590}{D}. \quad (12)$$



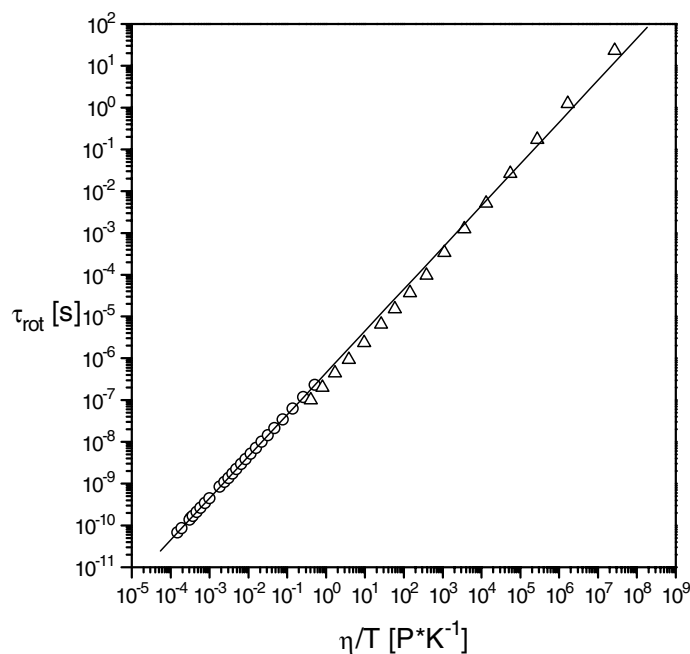
**Figure 4.** A comparison of the temperature dependencies of the overall correlation time  $\tau_{rot} = \beta_{DC} \tau_{DC}$  obtained (i) from dielectric relaxation measurements (open triangles) and (ii) from NMR relaxation measurements (open circles) with that of the viscosity for DIBP. The temperature dependence of the viscosity has been plotted with the data obtained in our experiment (+) and those taken following Barlow and co-workers [44] ( $\times$ ). The solid line is the best Vogel–Fulcher fit to the NMR and dielectric data. The left- and right-hand axes have been shifted with respect to each other so that the data coincide in the lower left-hand corner.

Thus DIBP is a fragile liquid in the Angell sense. Böhmer *et al* [47, 50] have given data, from different techniques, for about 70 glass formers in a plot of  $m$  against  $\beta_{KWW}$ , where  $\beta_{KWW}$  is the spreading parameter at  $T_g$ . The point  $[m, \beta]$  for DIBP is thus [90, 0.5] and is found to lie well within the band of correlation in the Böhmer plot [50].

Independent measurements of the viscosity ( $\eta$ ) and rotation relaxation times ( $\tau_{rot}$ ) allowed us to test the applicability of the Einstein–Debye relation (see equation (2)) [11, 51, 52]. Recent works [9–12] have indicated the deviation of equation (11) from linearity for highly viscous liquids approaching the glass transition. This has been taken to signify a qualitative change in the dynamics of a liquid as it is cooled towards the glass phase. The mechanism responsible for the proposed change has been assumed to be either the onset of cooperative dynamics [12] or a decoupling of certain relaxation processes from the viscosity [9–11].

In figure 5 we have plotted the mean rotational correlation times  $\tau_{rot} = \beta_{DC} \tau_{DC}$  versus  $\eta/T$ . It shows that within experimental accuracy ( $\chi^2 = 0.9994$ ) the  $\tau_{rot}$ -values are well described by a straight line fulfilling the Einstein–Debye relation (equation (11)). The most remarkable fact is that  $\tau_{rot}$  is proportional to  $\eta^{-1}$  at temperatures down to  $T_g$ , indicating that rotational motions remain coupled to structural relaxation on approaching the glass transition, at least in fragile glass-forming liquids composed of non-spherical molecules [11].

To evaluate the deviation from Einstein–Debye behaviour, we have calculated the ratio  $R = \tau_{rot} T / \eta$ . There is a very weak dependence of  $R$  on  $T$ : it increases only by a factor



**Figure 5.** A log–log plot of the overall correlation time  $\tau_{rot}$  versus the shear viscosity divided by temperature  $\eta/T$  for DIBP.

of 3.5 as temperature changes by 180 K and the rotation relaxation time increases by 11 orders of magnitude. The small increase of  $R$  with  $T$  might be due to experimental artefacts in comparing different time constants with very high-temperature dependencies. Careful measurements in the high-viscosity regime of the viscosity and rotation relaxation times are important in ascertaining whether non-Arrhenius behaviour also persists at low temperatures, since claims of the return to Arrhenius behaviour are most often made on the basis of viscosity data obtained in the high-viscosity regime [43]. Our viscosity measurements are inconsistent with the Arrhenius behaviour. These data do not support the suggestion of a correlation length extracted either from  $G_{\infty}/T$  or  $R = \tau_{rot}T/\eta$  which increases for the supercooled liquid [12]. We have also found no evidence for a discontinuous change in the diffusion mechanism [10] or for a critical temperature in the neighbourhood of the glass transition that such a discontinuity might imply. Our study of di-isobutyl phthalate is in good agreement with the previous results for di-*n*-butyl phthalate reported by Menon, Nagel and Venerus [51].

#### 4. Conclusions

Combining  $^{13}\text{C}$  spin–lattice and NOE factor measurements on the one hand and the analysis of the dielectric relaxation on the other, we have been able to extract reorientational correlation times related to the  $\alpha$ -relaxation process which cover the whole supercooled regime. Furthermore, information on the shape of the reorientational correlation function has been obtained. Concerning these points, the following conclusions can be drawn:

- (I) The reorientational correlation times derived from these techniques can be described by using just one Vogel–Fulcher functional form. This implies a self-consistent description of the dynamics obtained by different probes.

- (II) The parameter  $\beta_{DC}$  shows virtually no temperature dependence. In other words, the TTS principle holds for DIBP at least at  $T < 235$  K.
- (III) The separation of the timescales for reorientational motion and viscous flow is very small for DIBP, if it occurs at all.

Similar results have been reported for OTP [11], but there are other examples where a larger decoupling of the two processes has been observed [13, 14].

### Acknowledgments

Two of us (MP and JZ) would like to acknowledge the financial support of KBN (the Committee for Scientific Research), Grant No 2 P03B 030 12.

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