Dynamics of Two Glass Forming Monohydroxy Alcohols by Field Cycling ^{1}H NMR Relaxometry

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ABSTRACT

The dynamics of 2,2-dimethylbutan-1-ol (2,2-DM-1-B) and 3,3-dimethylbutan-1-ol (3,3-DM-1-B), two glass forming monohydroxy alcohols, was investigated by Field Cycling ^{1}H NMR relaxometry in their liquid phase, including the supercooled regime. Nuclear Magnetic Relaxation Dispersion (NMRD) curves (i.e. longitudinal relaxation rate R_1 *vs* ^{1}H Larmor frequency), acquired for the two alcohols at different temperatures in the 0.01 to 35 MHz frequency range, were analyzed in terms of suitable models for internal motions, overall molecular reorientations, and molecular self-diffusion, and the corresponding correlation times were quantitatively determined. In addition, trends of ^{1}H R_1 as a function of the frequency square root at low frequencies, where the contribution of translational motions dominates, were exploited to achieve an independent determination of the self-diffusion coefficients (D), which does not require the separation of different motional contributions to relaxation. Good agreement was found between D values determined by the two methods, thus corroborating the model used for the description of the NMRD curves. Self-diffusion was found to be slower and more strongly dependent on temperature for 2,2-DM-1-B with respect to 3,3-DM-1-B, whereas molecular reorientations were quite similar for the two isomeric alcohols. Correlation times for molecular reorientations were found to be at least one order of magnitude shorter than those reported in the literature for the Debye-like relaxation observed by dielectric spectroscopy in the liquid phase.

KEYWORDS: dimethylbutanol, nuclear relaxation, rotational motions, translational motions, supercooled liquid.

1. Introduction

Monohydroxy alcohols represent a very interesting class of compounds that have been the object of many investigations since the beginning of the 20th century [1]. Research on monohydroxy alcohols has especially concerned the relationship between the molecular architecture (i.e. position of the OH group, steric hindrance of the OH group, and ramification of the alkyl chain), the formation of H-bonded supra-molecular structures, the peculiar dielectric relaxation response in the liquid state, including the so-called Debye relaxation and the structural relaxation (also referred to as α relaxation), and the phase behavior of these materials. Indeed, many monohydroxy alcohols show an outstanding affinity for supercooling and, in some cases, exhibit solid state polymorphism.

The strength of the Debye relaxation, observed by Dielectric Spectroscopy (DS) in the liquid phase, has been found to markedly depend on the position of the OH group within the molecule: an OH group in a terminal site promotes the formation of H-bonded molecule chains, where molecular dipoles orient parallel to each other, and a large relaxation strength is detected. On the other hand, shifting the OH group to the central part of the molecule or attaching lateral groups close to the OH position disfavors the formation of chains and, sometimes, promotes the formation of oligomeric clusters where molecular dipoles orient antiparallel to each other [2,3]. The relative contributions, associated relaxation times, and temperature dependence of the Debye and structural relaxation were also discussed in relation to the alcohol molecular architecture and capacity to form H-bonded supra-molecular chains [1,4,5,6,7,8,9,10].

Nuclear Magnetic Resonance (NMR) relaxometry, including the measurement of spin-spin (T_2), spin lattice in the laboratory frame (T_1) and spin lattice in the rotating frame ($T_{1\rho}$) relaxation times of ^{1}H and, in some cases, ^{13}C and ^{2}H nuclei, at selected Larmor frequencies, has been successfully applied to study reorientational dynamics of monohydroxy alcohols. The possibility to measure relaxation times of different nuclei, also combined with selective isotope labeling, was exploited in order to separate contributions to relaxation from different molecular fragments [5,11,12,13]. In particular, the structural relaxation observed in DS spectra was associated to reorientations of the alcohol alkyl chain [12]. Moreover, the analysis of ^{1}H and ^{2}H T_1 values of n-butanol isotopomers, selectively deuterated either on the OH group or on the whole alkyl chain, revealed to be of aid in formulating the currently accepted model for the microscopic mechanism behind the Debye relaxation, that is the "transient chain model" proposed by Gainaru *et al*. [5].

In recent years, ^{1}H NMR relaxometry with the Fast Field-Cycling (FFC) technique has been increasingly employed to investigate dynamics in condensed matter, with particular attention to viscous liquids, melted polymers, and mesophases [14,15,16,17]. With this technique, ^{1}H T_1 values can be measured over a wide frequency range (from 0.01 to 40 MHz using commercial FFC relaxometers, while frequencies even below 100 Hz can be reached with homemade relaxometers where magnetic earth field is compensated [18,19,20,21]) with a single instrument. Differently from DS, which investigates the reorientational dynamics of molecular electric dipoles, ^{1}H NMR relaxometry probes the fluctuations of the dipole-dipole interaction between pairs of nuclei, either on the same or on different molecules, due to molecular reorientations and translational motion. Thus, the longitudinal ^{1}H relaxation rate (R_1=1/T_1) results from the sum of intra- and inter-molecular contributions: the first contribution is determined by reorientational motions, while the second one is generally assigned to translational motions, although an additional effect may be produced by the relative reorientations of neighboring molecules.

The comparison between DS and FFC ^{1}H NMR relaxometry data allowed the intermolecular contribution to NMR relaxometry to be identified in several viscous liquids [22]. Although the analysis of Nuclear Magnetic Relaxation Dispersion (NMRD) curves (i.e. R_1 *vs* ^{1}H Larmor frequency curves) is not straightforward because of the different contributions to relaxation (i.e. intra- and intermolecular, arising from internal, overall reorientation and self-diffusion motions) and the variety of models devised for their description, FFC NMR relaxometry was successfully applied to determine the self-diffusion coefficient (D) and the rotational correlation times for several materials, including monohydroxy alcohols, in the liquid phase [18,23,24,25]. Moreover, it has been recently demonstrated [18,23,24,25] that an independent determination of D, which does not require an explicit separation of intra- and intermolecular relaxation, can be performed from the characteristic dependence of R_1 on the square root of the Larmor frequency (ν) at low frequencies, theoretically predicted for translational motions in three dimensions [26,27,28,29]. Application of FFC ^{1}H NMR relaxometry for the determination of self-diffusion coefficients in the 10^{-14} to 10^{-9} m^2/s range was reported for several systems, mainly in the liquid phase [18,23,24,25]; D values were found to be in agreement with those determined by field gradient NMR, the leading technique used to access translational diffusion [30].

In the present work, ^{1}H NMR relaxometry was applied to investigate the dynamics of two isomeric monohydroxy alcohols with nearly globular molecular shape, namely 2,2-

dimethylbutan-1-ol (2,2-DM-1-B) and 3,3-dimethylbutan-1-ol (3,3-DM-1-B) (Figure 1). Previous studies performed by differential scanning calorimetry, adiabatic calorimetry, and inelastic incoherent neutron scattering reported that 2,2-DM-1-B shows a plastic crystalline phase that forms a glassy crystal at lower temperatures, while 3,3-DM-1-B forms a structural glass on cooling and shows spontaneous crystallization on heating [31,32,33,34,35,36,37]. Moreover, both alcohols can be supercooled below the melting temperature (found between 224 K and 251 K for 2,2-DM-1-B [32,33,38,39,40,41] and between 230 and 234 K for 3,3-DM-1-B [31,32]), as shown in calorimetric studies [32]. Here, the two alcohols were thermally treated to avoid crystallization and investigated by ^{1}H NMR relaxometry in the liquid phase, also in the supecooled regime. ^{1}H R_1 values were measured as a function of the Larmor frequency in the 0.01 to 35 MHz range using a FFC NMR relaxometer and at 400 MHz with a stationary field NMR spectrometer. The NMRD curves were interpreted in terms of suitable models for internal and molecular motions in order to relate molecular structure and microscopic dynamic processes of the two alcohols in the liquid phase. Correlation times were quantitatively determined at different temperatures between 223 and 303 K. Values of the self-diffusion coefficient D were also independently determined from the slope of R_1 *vs* $\sqrt{\nu}$ at low frequency.

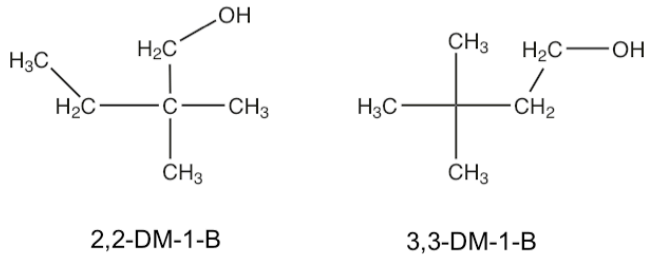

Figure 1. Molecular structure of 2,2-DM-1-B and 3,3-DM-1-B.

2. Experimental

2.1 Materials

2,2-DM-1-B was synthesized at the Institute of Pharmacology of the Polish Academy of Sciences (Kraków). 3,3-DM-1-B was purchased from Aldrich and used as received.

2.2 ^{1}H NMR relaxometry measurements

^{1}H R_1 values were measured in the range between 0.01 and 35 MHz using a SpinMaster FFC-2000 (Stelar srl) relaxometer. The non-prepolarized and prepolarized sequences [14,42] were

used for measurements at high (≥12 MHz) and low (≤12 MHz) frequencies, respectively. The sample was contained in a standard 10 mm NMR tube. The polarizing and detection fields were 0.70 and 0.50 T, corresponding to ^{1}H Larmor frequencies of 30.0 and 21.5 MHz, respectively. The 90° pulse duration was 10 μs, the switching time 3 ms, and a single scan was acquired. All the other experimental parameters were optimized for each experiment. Each longitudinal relaxation trend was acquired with at least 16 values and in all cases a monoexponential function well reproduced the experimental trend with an error on R_1 lower than 2 %. The temperature was controlled within ± 0.1 K with a Stelar VTC90 variable temperature controller and was stabilized for at least 10 min before each measurement.

^{1}H R_1 values were measured at a Larmor frequency of 400.03 MHz on an Infinity Plus 400 spectrometer (Varian) equipped with a 5 mm probe using the Saturation Recovery pulse sequence. The 90° pulse duration was 4 μs. At least 24 spectra at different recovery times were acquired to determine the recovery curve and 4 scans were acquired for each spectrum. In all cases, a monoexponential function well reproduced the experimental magnetization trend, with errors on R_1 values lower than 1 %. The temperature was controlled within ± 0.5 K and was stabilized for at least 10 min before measurement.

All measurements were performed on heating after cooling to 213 K, this treatment ensuring supercooling of the liquid phase.

2.3 Data analysis

The analysis of the experimental ^{1}H NMRD profiles, obtained from the R_1 values measured with the FFC relaxometer between 0.01 and 35 MHz and with the stationary field spectrometer at 400 MHz, was performed using the least-squares minimization procedure implemented in the Fitteia environment [43,44].

3. Results and Discussion

3.1 Trends of ^{1}H R_1 with frequency and temperature

NMRD curves acquired on heating on 2,2-DM-1-B and 3,3-DM-1-B samples (Figure 2) showed a continuous evolution with temperature, typical of supercooled liquids. With increasing the temperature, the R_1 dispersion decreased and the region of stronger change in R_1 shifted to higher

frequencies. At the lower investigated frequencies, the NMRD curves were clearly not flat, suggesting the contribution of self-diffusion to relaxation (vide infra) [18,23,24,25].

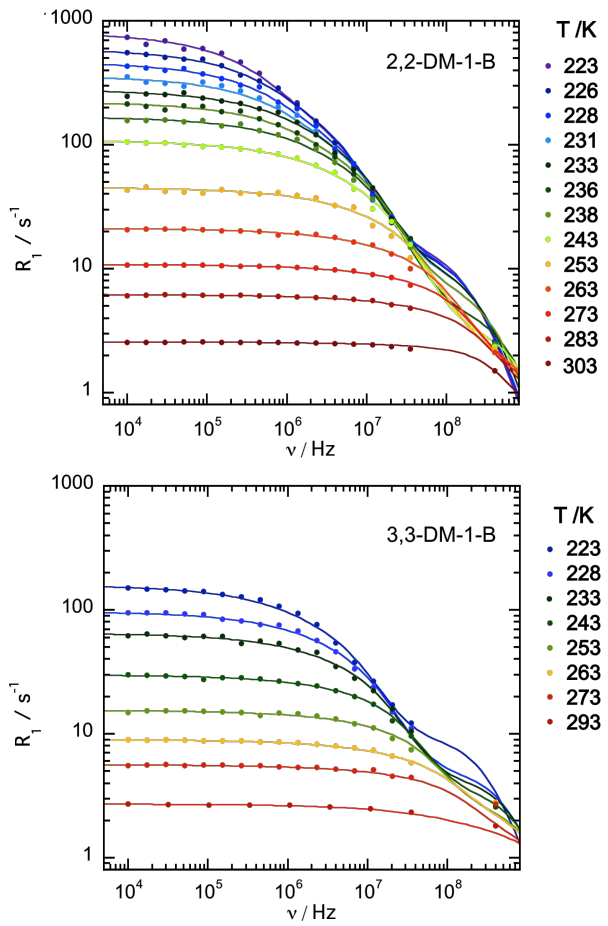

Figure 2. Symbols: experimental NMRD curves of 2,2-DM-1-B and 3,3-DM-1-B at the indicated temperatures. Lines: NMR curves calculated according to the model described in the text (Eq.s 3-4 and 6-7).

In order to better highlight the presence of motions dominating relaxation in different frequency regions the susceptibility representation of the relaxation data was also used (Figure 3), since in this representation such motions may give rise to distinct peaks. On the basis of the fluctuation-dissipation theorem, the NMR susceptibility is defined as $\chi''_{NMR} = 2\pi\nu R_1$ [22]. For both alcohols, at the lower temperatures, a χ''_{NMR} peak with maximum close to 10^7 Hz, shifting to higher frequencies by increasing the temperature, was visible as a shoulder of a much more intense peak with maximum at frequencies similar or higher than the highest one here observed.

The NMR susceptibility curves thus indicated the contribution of at least two motional processes in the temperature range investigated: a slower one with correlation time on the order of 10^{-7}-10^{-9} s and a faster one with correlation time shorter than 10^{-9} s. Considering the molecular structure, the latter motion can be probably ascribed to internal rotations of the methyl group and, for 3,3-DM-1-B, also of the tert-butyl group about their respective threefold symmetry axes. At the higher temperatures, the χ''_{NMR} curves did not show any peak, indicating that all motions are in the fast regime in the whole frequency range investigated.

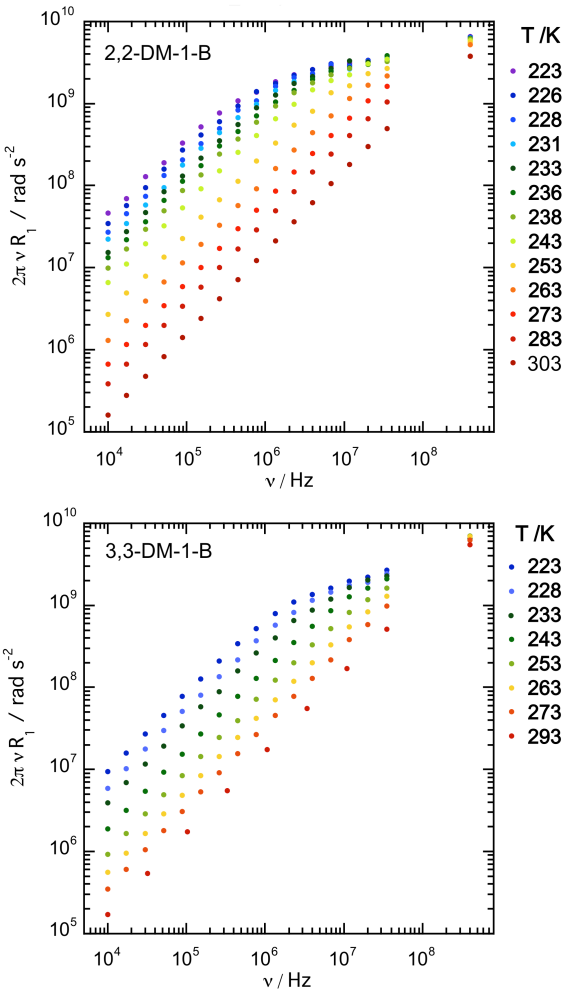

Figure 3. NMR susceptibility representation of the relaxation data at the indicated temperatures for 2,2-DM-1-B and 3,3-DM-1-B.

Similar conclusions can be drawn by looking at the data from a different point of view. In Figure 4 the T_1 values measured for the two alcohols are reported as a function of the inverse

temperature and their trends seem indeed to result from the contribution of more than one dynamic process. In the case of 2,2-DM-1-B, at frequencies between 1 and 35 MHz, the T_1 trends indicated the presence of a minimum at low temperature associated to a motion with a comparable characteristic frequency. However, the broadness of the minimum, as highlighted for frequencies ≥ 21 MHz, suggests the contribution of a faster motion with minimum at lower temperatures. This motion becomes particularly relevant in determining the T_1 trend at 400 MHz. On the basis of previous studies, the slower motion can be identified as overall molecular reorientations, whereas the faster motion corresponds to internal rotations. At frequencies below 1 MHz, no minimum was observed, indicating that for these frequencies also the molecular motions are in the fast regime.

For 3,3-DM-1-B the observed T_1 *vs* 1/T trends and their evolution with Larmor frequency were indeed quite similar to those observed for 2,2-DM-1-B, although motions contributing to 3,3-DM-1-B T_1's were faster.

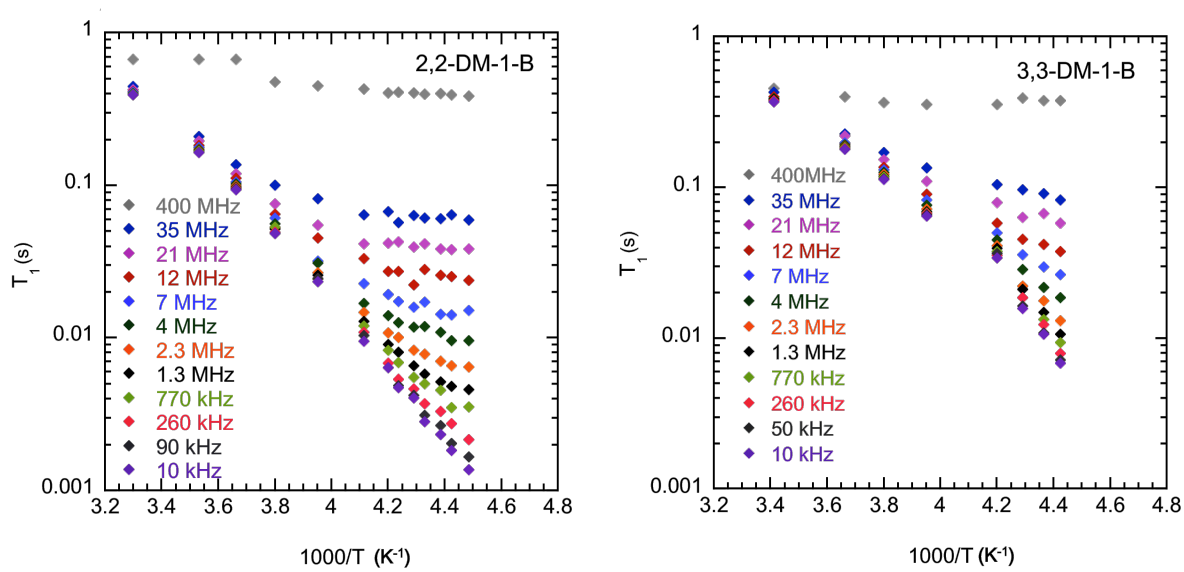

Figure 4. Trends of ^{1}H T_1 *vs* inverse temperature for 2,2-DM-1-B and 3,3-DM-1-B.

3.2 Determination of self-diffusion coefficients

As shown in Figure 5, at low frequencies a clear linear dependence of R_1 on $\sqrt{\nu}$ was found for both samples at all the investigated temperatures, indicating that translational diffusion dominates relaxation [26,27,28,29]. With increasing the temperature, the linear range

progressively extended to higher frequencies and the slope progressively decreased, the motion becoming faster.

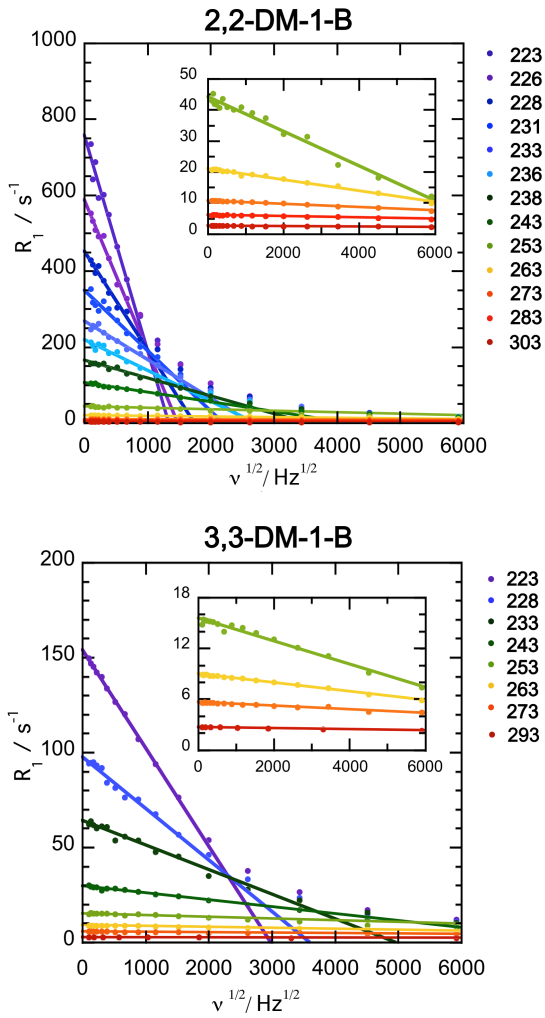

Figure 5. R_1 *vs* $\sqrt{\nu}$ at the indicated temperatures for 2,2-DM-1-B and 3,3-DM-1-B. Insets show expansions of the high temperature data.

The self-diffusion coefficient values for the two samples were determined from the slope of the lines in Figure 5 using Eq. 1:

$$R_1(\omega) \cong R_1(0) - \frac{B}{D^{3/2}}\sqrt{\omega} \qquad (1)$$

with

$$B = \frac{\pi}{30}(1 + 4\sqrt{2})N_H \left(\frac{\mu_0}{4\pi}\gamma_H^2\hbar\right)^2 \quad (2)$$

where N_H is the spin density, γ_H is proton gyromagnetic ratio, and $R_1(0)$ is the value of $R_1(\omega)$ extrapolated to zero frequency. In the calculation, N_H = 6.83 10^{28} spins/m^3 and N_H = 6.96 10^{28} spins/m^3 were considered for 2,2-DM-1-B and 3,3-DM-1-B, respectively, at all the temperatures, these values being determined from the expression $N_H = n\rho N_A/M_{mol}$, where n (= 14) is the number of hydrogen atoms per molecule, ρ is the alcohol density (0.828 g/cm^3 and 0.844 g/cm^3 for 2,2-DM-1-B and 3,3-DM-1-B, respectively, assumed independent of temperature), N_A is Avogadro's number, and M_{mol} the molecular weight. With this assumption, D values on the order of 10^{-13}-10^{-10} m^2/s were found, with $D \leq 10^{-11}$ m^2/s in the supercooled regime (Figure 6), in agreement with previous studies on alcohols [1,11,12,18,45,46]. Smaller values and a steeper temperature dependence were found in the case of 2,2-DM-1-B with respect to 3,3-DM-1-B.

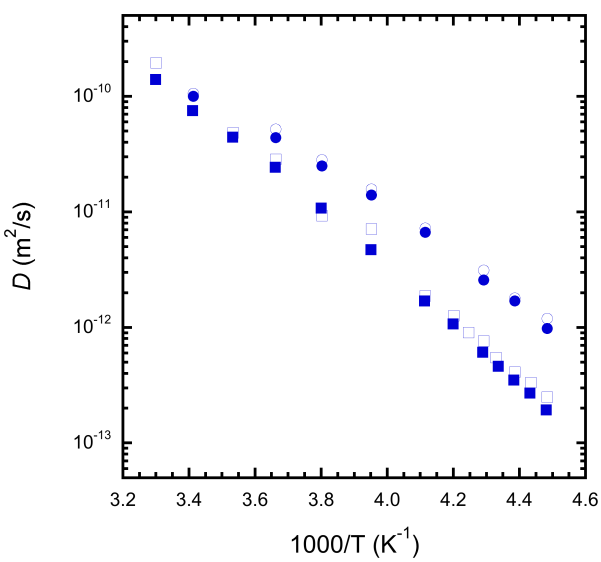

Figure 6. Self-diffusion coefficients (D) determined for 2,2-DM-1-B (squares) and 3,3-DM-1-B (circles) from the slope of R_1 *vs* $\sqrt{\omega}$ using Eq. 1 (empty symbols) and from the fittings of the NMRD curves (full symbols).

3.3 Analysis of ^{1}H NMRD curves

Considering the molecular structure of the investigated alcohols (Figure 1), contributions to R_1 arising from internal motions (R_1^{IM}), overall molecular reorientations (R_1^{MR}), and translational

self-diffusion (R_1^{SD}) are expected in the liquid phase. The contribution of self-diffusion was indeed confirmed by the low frequency slope of the NMRD curves shown in paragraph 3.2 (Figure 5), while the contribution of more than one motion at higher frequencies was highlighted by features of the frequency and temperature dependences of R_1, as described in paragraph 3.1 (Figures 2-4). The criterion of using the minimum number of contributions to R_1 that could well reproduce the experimental trends with physically reasonable parameter values was adopted in the description of the NMRD curves in order to avoid over-interpretation of data. Fitting procedures that minimize the least-squares of residuals between experimental data and R_1 values, calculated considering the models described below, were applied to all the acquired NMRD curves. As usually done, R_1^i contributions were assumed to be statistically independent and/or have distinct characteristic time scales, so that R_1 was written as the sum of the different contributions. R_1^{IM} and R_1^{MR} contributions were expressed as [47,48]

$$R_1^i = C_i[J_i(\omega) + 4J_i(2\omega)] \tag{3}$$

where C_i is a relaxation amplitude factor that depends on the effective homonuclear dipolar interaction, with spectral densities expressed in terms of the correlation time of the motion (τ_i) according to the Bloembergen-Purcell-Pound (BPP) model, where the spectral density, $J_i(\omega)$, is a Lorentzian function [49]:

$$J_i(\omega) = \frac{\tau_i}{1+(\omega\tau_i)^2} \tag{4}$$

It must be pointed out that the phenomenological spectral density function proposed by Davidson and Cole (DC) [50,51] would be more appropriate than the Lorentzian one for describing the contribution of overall molecular dynamics to relaxation (R_1^{MR}) in viscous liquids. The DC function

$$J_{CD}(\omega) = \frac{\sin\left[\beta \arctan\left(\omega\tau_{DC}\right)\right]}{\omega\left[1+(\omega\tau_{DC})^2\right]^{\frac{\beta}{2}}} \tag{5}$$

accounts for non-exponential correlation loss of reorientational motions through the parameter β (0< β ≤1) and reduces to the Lorentzian function for β =1. The parameter τ_{DC} is the upper cutoff correlation time [52]. In our case, since the experimental data did not show features that would allow a reliable determination of β, and in particular no distinct peaks were observed in the NMR susceptibility curves (Figure 3), we preferred to use the simpler Lorentzian function which requires less parameters.

The self-diffusion contribution, R_1^{SD}, was calculated using the force-free hard-sphere model proposed by Hwang and Freed [53] and by Ayant *et al*. [54]. In this model, molecules uniformly distributed outside the distance of closest approach (*d*) are described as hard spheres undergoing Fickian diffusion, with the nuclei of interest assumed to be located in the sphere centers. Following this model, the spectral density was written as [55,56]

$$J_{SD}(\omega) = 72\frac{3}{4\pi}\int_0^\infty \frac{u^2}{81+9u^2-2u^4+u^6}\frac{u^2\tau_{SD}}{u^4+(\omega\tau_{SD})^2}du \qquad (6)$$

where u is an integration variable and τ_{SD} is the translational correlation time defined as $\tau_{SD} = d^2/2D$.

$$R_1^{SD} = \frac{3}{10}N_H\frac{4\pi}{3}\frac{1}{d^3}\left(\frac{\mu_0}{4\pi}\right)^2\gamma_H^4\hbar^2[J_{SD}(\omega) + 4J_{SD}(2\omega)] \qquad (7)$$

For identical molecules the relationship $d = 2a$, where a is the molecular radius, should hold. Since eccentricity effects, related to the fact that also molecular reorientations could cause fluctuations of the intermolecular inter-spin vectors if spins are not located in the centers of the molecules, are not considered in the model, the distance of closest approach in Eq. 7 should be seen as an effective quantity on the order of the molecular size [23,24].

For both alcohols, the chosen model gave a very good reproduction of the NMRD curves at all the temperatures (examples are shown in Figures 7 and 8) considering C_{IM}, C_{MR}, τ_{IM}, τ_{MR}, d, and D as adjustable parameters, while N_H was kept fixed at the above reported values.

After a first screening, C_{IM} and C_{MR} were fixed at the same values at all the investigated temperatures: C_{IM} at 5.1 10^9 s^{-2} and 5.7 10^9 s^{-2} and C_{MR} at 1.4 10^9 s^{-2} and 7.0 10^8 s^{-2} for 2,2-DM-1-B and 3,3-DM-1-B, respectively. The best fitting values of d were of 4.0 ± 0.2 and 5.0 ± 0.2 Å

at all temperatures for 2,2-DM-1-B and 3,3-DM-1-B, respectively, in agreement with their estimated molecular dimensions. The best fitting values of the self diffusion coefficients D are compared to those obtained from the analysis of R_1 *vs* $\sqrt{\omega}$ (Eq. 1) in Figure 6; a good agreement was found between the two series of independently determined values (the only common parameter being the proton density N_H).

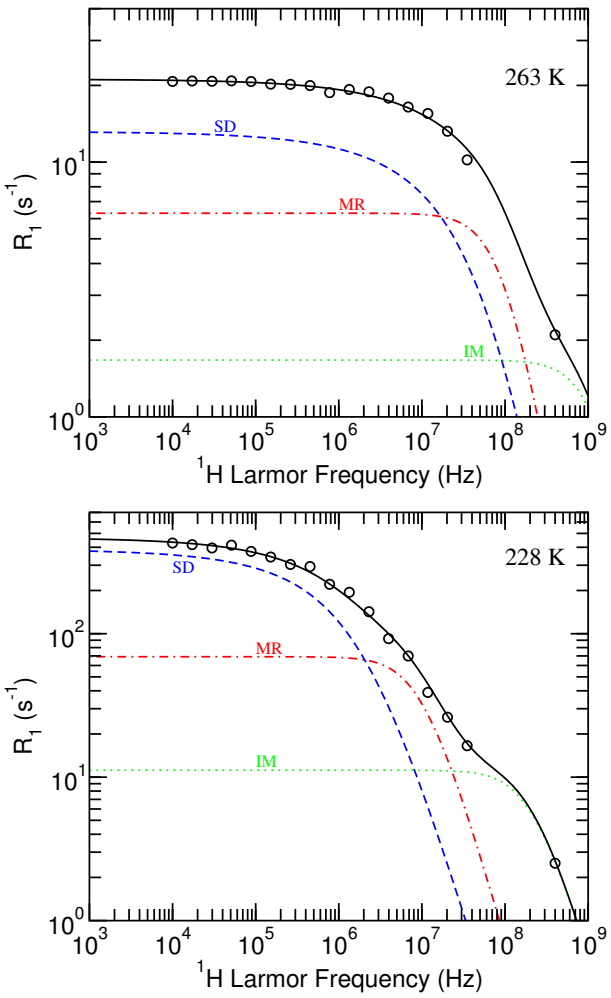

Figure 7. Experimental (circles) and calculated (black lines) ^{1}H relaxation rates of 2,2-DM-1-B at the indicated temperatures. Blue dashed, red dot-dashed, and green dotted lines indicate contributions to relaxation arising from self-diffusion (SD), molecular reorientation (MR) and internal motions (IM), respectively.

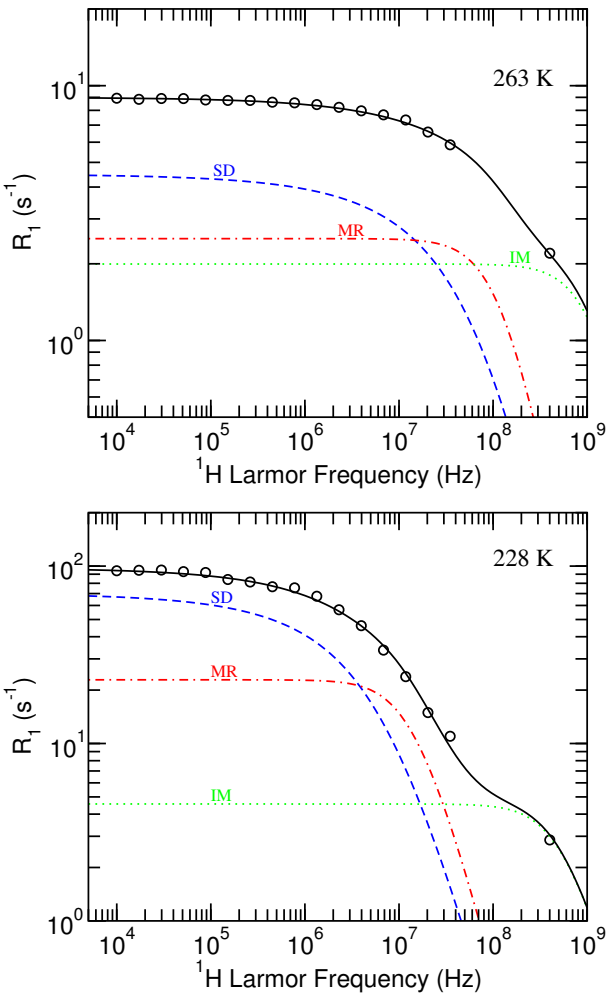

Figure 8. Experimental (circles) and calculated (black lines) ^{1}H relaxation rates of 3,3-DM-1-B at the indicated temperatures. Blue dashed, red dot-dashed, and green dotted lines indicate contributions to relaxation arising from self-diffusion (SD), molecular reorientation (MR) and internal motions (IM), respectively.

The best fitting correlation times for internal (τ_{IM}) and overall (τ_{MR}) motions are shown in Figure 9, together with self-diffusion correlation times (τ_{SD}) calculated from best fitting *d* and *D* values; all correlation times regularly decreased by increasing the temperature. For internal motions, the experimental trends could be well reproduced with the Arrhenius law with activation energy values of 24 ± 1 kJ/mol and 16 ± 1 kJ/mol, for 2,2-DM-1-B and 3,3-DM-1-B, respectively. These values are compatible with those reported in the literature for rotations of methyl and tert-butyl groups about their ternary symmetry axes [57,58,59]. For molecular reorientations, the

temperature trends of correlation times were quite similar for the two alcohols, whereas, as already observed for the diffusion coefficients, translational correlation times had a steeper temperature dependence for 2,2-DM-1-B. This could be probably due to a complex interplay between the degree of association between molecules through hydrogen bonding, the molecular architecture, and the steric hindrance [60].

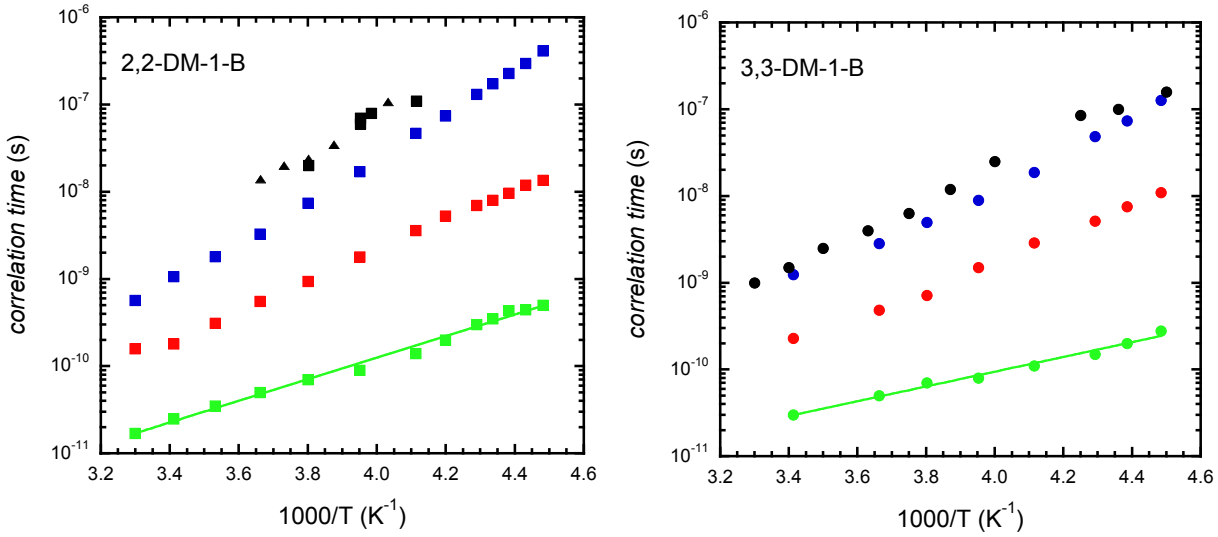

Figure 9. Correlation times for internal motions (τ_{IM}, green symbols), molecular reorientational motions (τ_{MR}, red symbols) and self-diffusion (τ_{SD}, blue symbols) determined from the analysis of the NMRD curves of 2,2-DM-1-B (squares) and 3,3-DM-1-B (circles). Lines represent fittings of τ_{IM} *vs* inverse temperature trends with the Arrhenius equation. Black symbols represent data for the Debye-like process reported in Ref.s 33 (squares) and 61 (triangles) for 2,2-DM-1-B and in Ref. 31 (circles) for 3,3-DM-1-B.

The correlation times here found for the overall reorientational motions of 2,2-DM-1-B and 3,3-DM-1-B are shorter by about one order of magnitude at the higher temperatures and by up to two orders of magnitude at the lower ones than those associated to the main Debye-like relaxation process observed by dielectric spectroscopy at the same temperatures [31,33,38,39,40,61], also reported in Figure 9 for comparison. This behavior is in agreement with data reported for other monohydroxy alcohols [1,8,12]. It must be pointed out that the molecular reorientation process (α relaxation) was not explicitly reported in DS studies performed on 2,2-DM-1-B and 3,3-DM-1-B. Only in the case of 2,2-DM-1-B, a small deviation at the high frequency end of the Debye-

like process was described at low temperatures and ascribed to the presence of an additional relaxation process, faster and with much smaller amplitude than the main one [39]. By considering the much smaller amplitude of the α relaxation process with respect to the Debye one expected for the investigated alcohols and the higher frequencies of the α relaxation process here pointed out, peaks due to molecular reorientations could not be observed in DS measurements because of the limited frequency range investigated.

4. Conclusions

Internal motions, overall molecular reorientations, and self-diffusion were quantitatively characterized for two monohydroxy alcohols (i.e. 2,2-DM-1-B and 3,3-DM-1-B) at several temperatures in their liquid phase by the analysis of ^{1}H spin-lattice relaxation times measured between 0.01 and 35 MHz by means of FFC NMR relaxometry and at 400 MHz with a stationary field spectrometer. To this aim, NMRD curves were described in terms of suitable models for translational and reorientational motions. Though some assumptions were made in the applied description, the self-diffusion coefficients were in good agreement with those independently determined from the dependence of the relaxation rate on the square root of Larmor frequency in the low frequency limit of the NMRD curves, as well as with those reported in the literature for primary alcohols. Correlation times for the molecular reorientational motion were here determined for the first time for these alcohols, the previously reported dielectric spectra being dominated by the Debye relaxation peak and limited in frequency in the high frequency side. In fact, molecular reorientations were found to be faster by at least one order of magnitude than the Debye process to which NMR relaxometry is insensitive.

The two alcohols showed quite similar reorientational motions at the same temperature, whereas self-diffusion motions were slower and with a steeper temperature dependence for 2,2-DM-1-B with respect to 3,3-DM-1-B, most probably because of the different degree of association between molecules through hydrogen bonding, molecular architecture, and steric hindrance of the two alcohols.

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