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Pressure and Temperature Studies of NMR Translational Relaxation in Hydrogen Bonded Liquids*

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Spin-lattice and spin-spin relaxation time have been measured using the spin echo method in three hydrogen bonded liquids: glycerol, 1,3-butanediol, and 2-methyl-2,4-pentanediol as a function of temperature through the region of the T_1 minimum and at seven pressures in the range 0-3000 kg/cm². The results of this study lead to the conclusion that the translational model for NMR relaxational presented by Torrey is satisfactory for representing the diffusive motion of molecules in these viscoelastic liquids. Agreement between the experimentally measured values of the self-diffusion constant and those theoretically predicted by the translational theory provides verification of this assumption. Recent measurements of quadrupolar-relaxation times as a function of temperature on deuterated glycerol as well as low frequency proton spin-lattice relaxation measurements also provide supporting evidence. The nuclear correlation time τ_c , the mean time between diffusive jumps τ_i , and the distance of closest approach d are produced from a fit of the T_1 and T_2 data to the translational relaxation theory. The values τ_c and τ_i are compared to the corresponding times obtained from dielectric, ultrasonic and light scattering experiments.

I. INTRODUCTION

Proton nuclear magnetic resonance relaxation studies have been employed through various models to yield information about the dynamical motions of molecules in hydrogen bonded (associated liquids). These analyses are made under severe assumptions concerning the contributions of the inter- and intramolecular relaxation processes. In the case of these particular types of liquids there are at present no experimental studies available which would provide direct information on the magnitude of these separate contributions. Attempts are presently being made using selective deuteration techniques to overcome the difficulties of separation which are caused by hydroxyl exchange effects. The unambiguous interpretation of spin-spin $(1/T_2)$ and spin-lattice $(1/T_1)$ relaxation remains problematic. Previous temperature studies have avoided this problem by assuming that the rotational process is the dominant relaxation effect and that the intermolecular contribution to the NMR relaxation times is negligible. The validity of such an assumption does not rest on any solid theoretical or physical reasoning but is intuited from arguments concerning the value of the self diffusion constant and the geometry of the molecule.

It is obvious, however, under the assumption of rotational predominance, when one tries to explain the temperature data in highly viscous associated liquids, that the simple rotational theory of Bloembergen, Pound, and Purcel (BPP)¹ fails to explain the quantitative behavior of T_1 or T_2 experimentally observed.⁰¹

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in an attempt to provide a quantitative description of the data for viscous liquids. One approach has been to modify the single Debye spectrum $\tau/(1+\omega^2\tau^2)$ proposed by BPP, by introducing a distribution of correlation times $g(\tau)$. This procedure is *ad hoc* since no theoretical model is given to justify the use of a particular distribution function, other than its usefulness in representing the T_1 , T_2 data or other types of data for the liquid under study (dielectric, ultrasonic, etc.) and so provide a measure of the correlation time.

The other type of modification proposed is the introduction of a hybridized autocorrelation function $K(\tau)$, which is the product of the single rotational exponential correlation function and a modulating correlation function derived from a physical model of the form $f(\tau) \exp(-\tau/\tau_{\rm rot})$. The hybrid correlation function accounts for the "effective distribution" of rotational times needed to bring the BPP theory into quantitative agreement with the data. The Powles-Hunt² approach for example makes use of a modulating correlation function obtained from Glarum's^{3,4} defect diffusion model while the Chaban⁵ approach makes use of an ordering parameter modulating term derived from the Isakovich-Chaban⁶ order diffusion model. Both approaches consider diffusion effects as important in modifying the fundamental relaxational behavior implied in using the rotational correlation function.

Recently Noack and Preissing (NP)7 have made extensive T_1 frequency and temperature measurements (0.45-117 MHz, -20°-+70°C) on glycerol. Noack and Preissing considered many of the currently used distributions of correlation times and have shown that none of these can account for the observed T_1 frequency dependence. While some distributions can explain the upper limiting $\omega^{3/2}$ frequency dependence of T_1 (as the Powles-Hunt and Chaban models do also), none of these theories can account for the entire frequency behavior. The Powles model, besides introducing a number of unknown parameters, fails to fulfill the so called "temperature compatibility test" of Noack and Preissing which requires that the theoretical ratio of the zero frequency limits of T_1 at two different temperatures be in the same ratio as the measured low frequency values at these temperatures. The log-Gaussian distribution used by Favret and Meister⁸ on glycerol to reduce data at 10 and 20 MHz has been shown by Noack and Preissing to fail this relationship even though choice of different width parameters allows a at at other frequencies.

Recently the Chaban theory has been analyzed extensively in this laboratory using the data of Noack and Preissing as well as unpublished data taken in our laboratory, and shown to be inadequate in explaining the frequency data or extended temperature data.

Noack and Preissing have noted in an earlier paper⁹ that the single translational relaxation theory of Torrey¹⁰ does apparently predict the general frequency behavior of $1/T_1$ for glycerol. In their recent paper on

magnetic relaxation in glycerol⁷ they have made use of some of the features of this theory. However, they have chosen not to follow a strict physical interpretation of the translation model, and have rather, only made use of the mathematical properties of the intensity function arising from the translational model, to construct a so called "diffusion distribution function", $g(\tau/\tau_0)$. This distribution function is interpreted as representing a Debye type spectrum and is combined with the BPP rotational constant to produce a hybrid formula for $1/T_{1 \text{ rot}}$. Here τ_0 is interpreted as an average rotational, rather than a translational correlation time, which intrinsically follows from the use of the translational model. The hypothesis behind this interpretation again is that rotational motions are the dominant relaxation process in liquids of this type.¹¹

In view of the origins of the theory of translational relaxation theory, it is more consistant to use a strict interpretation of the translational relaxation model of Torrey (and as recently revised by Kruger).¹² The data presented in this work as well as data from other sources is treated under the hypothesis that translation rather than rotation represents the dominant relaxation process for NMR in viscous liquids.

For the most part, all relaxation studies have been done as a function of temperature and frequency. Relatively few pressure dependent studies, which provide a means of studying density dependent effects alone, have been done. In the present work, NMR measurements have been made on three highly viscous associated liquids as a function of pressure as well as temperature in an effort to provide a greater understanding of relaxation effects in such liquids.

Since the first investigation of the pressure dependence of the nuclear relaxation time T_1 by Benedek and Purcell¹³ relatively few NMR pressure studies on any liquids have been made. Most studies have been made on mobile liquids well out of the dispersion region $(\omega\tau \ll 1)$. $T_1(P)$ data has been taken by Benedek on glycerol, but as is pointed out in his thesis¹⁴ this data is questionable as representative of the pure liquid and has not been published. Benedek reported that the sample used contained about 5% water, and probably did not remain free of pressure fluid contamination during the experiment.

Benedek's results for mobile liquids indicated that the relative value $T_1(P)/T_1(1)$ as a function of pressure does not follow that of D(P)/D(1) or $\eta(1)/\eta(P)$, the relative diffusion constant and the inverse relative viscosity normalized to atmospheric pressure.

Such a relationship is expected on the basis of the BPP theory in the motional narrowing region ($\omega \tau \ll 1$)

$$1/T_1 = (C_1 \tau_{\rm rot} / r^6) + (C_2 N / dD), \qquad (1a)$$

where C_1 and C_2 are quantum mechanical constants, r is interproton distance, τ_{rot} is the rotational correlation time, N is the spin density, d is distance of closest approach of two nuclei. By including the Debye relation, $\tau_{\rm rot} \propto \eta/T$, and the Stokes Einstein relation, $D \propto T/\eta$ where T is the temperature

$$1/T_1 \propto \eta/T \propto D. \tag{1b}$$

Benedek's studies show that: (1) $T_1(P)/T_1(1)$ is higher than that predicted. (2) D(P)/D(1) and $\eta(1)/\eta(P)$ do not have the same pressure dependence.

Bull and Jonas¹⁵ have recently shown that the reason for the discrepancy (besides the paramagnetic impurity effects in Benedek's samples) arises because the simple Debye theory for τ_{rot} is incorrect. It has been pointed out that T_1 must first be separated into its inter and intra parts before a comparison with D(P) or $\eta(P)$ can be made. Consequently Bull and Jonas have reported a deuterated-protonated separation study as a function of pressure in several mobile liquids to study the inter and intra parts as a function of pressure. They have found that $1/T_{1 \text{ inter}}(P)$ roughly follows the predictions of the BPP theory for D(P) and $\eta^{-1}(P)$ and $1/T_{1 \text{ intra}}$ digresses from the predictions of Eq. (1b).

The above considerations have motivated and guided this study. The chief concerns of this work are: (1) to critically evaluate the translational relaxation theory with all available data; (2) to study the effect of pressure and temperature on the nuclear magnetic spinlattice and spin-spin relaxation times T_1 and T_2 in three highly viscous associated liquids: glycerol; 1,3butanediol; and 2-methyl-2, 4-pentanediol (BUT, MPD for short), also to infer from these macroscopic times the pressure and temperature dependence of the microscopic nuclear correlation time, τ_t , and its association with the translational diffusion constant; and (3) as a secondary objective to compare the nuclear correlation time as a function of temperature and pressure (T, P)with microscopic relaxation times obtained from other types of studies.

II. THEORY

The correct formulation of the Torrey translational relaxation theory taking into account the Kubo-Tomita¹⁶ correction has been given elsewhere^{12,17} and will only be briefly reviewed here for the sake of clarity.

Under the conditions of isotropic motion the autocorrelation function for the mth term of dipole-dipole interaction Hamiltonian, which provides the major contribution to the proton spin-lattice and spin-spin relaxation in the liquids under consideration, is given by

$$K^{(m)}(\tau) = C^{(m)} N \iiint \rho \exp\{-(2\tau/\tau_j) [1 - A(\rho)]\}$$

$$\times J_{5/2}(\rho r) J_{5/2}(\rho r_0) r^{-3/2} r_0^{-3/2} \rho(r_0) d\rho dr dr_0 \qquad (2)$$

$$X J_{5/2}(pr) J_{5/2}(pr_0) r^{-3/2} r_0^{-3/2} p(r_0) dp dr dr_0$$

with m=0, 1, 2 and

$$C^{(0)} = 48\pi/15, \quad C^{(1)} = 8\pi/15, \quad C^{(2)} = 32\pi/15.$$
 (2')

N is the total number of spins, $J_{5/2}(\rho r)$ is the Bessel

function of order 5/2, $p(r_0)$ describes the initial physical distribution of the spins, $A(\rho)$ depends on the model for diffusive motion, and τ_i is the average time between flights defined in terms of the average squared flight distance and the translational self-diffusion constant $\tau_j \equiv \langle r^2 \rangle / 6D.$

With a model for $p(r_0)$, $K^{(m)}(\tau)$ can be further reduced without giving an explicit form for $A(\rho)$. Torrey has assumed an initial probability distribution of the form

$$p(r_0) = n/N, r_0 \ge d,$$

= 0 $r_0 < d,$ (3)

that is, a uniform probability of finding n spins/cc in the volume element dr_0 beyond a distance of closest approach, d. It has also been assumed in this formulation that the spins under consideration are at the center of the diffusing molecules upon which the spins ride. Hubbard's formulation¹⁸ considers these off center spin effects in the extreme narrowing limit. Harmon and Muller¹⁷ have recently included the effects of a nonuniform spin density and off center spins by using the radial distribution function and the Hubbard correction in the low frequency limit of the Torrey theory. Since incorporation of these effects is presently intractible in the general frequency theory presentations here, these effects will be considered separately below. For now a uniform probability density will be assumed. Then, from Eq. 2,

$$K^{(m)}(\tau) = C^{(m)}(n/d^3) \int d\rho [J_{3/2}(\rho d)/\rho] \\ \times \exp(-(2\tau/\tau_j)[1 - A(\rho)]), \quad (4)$$

$$J^{(m)}(\omega) = C^{(m)} \tau_j(n/d^3) \int d\rho [J_{3/2}(\rho d)/\rho] \\ \times \{1 - A(\rho)/[1 - A(\rho)]^2 - \frac{1}{4}(\omega \tau_j)^2\}.$$
(5)

At this point it is convenient to introduce the concept of correlation time for the translational model. Kubo¹⁹ defined this time for the case of nonexponential relaxation functions²⁰ as

$$\tau_c \equiv \int_0^\infty \frac{K(\tau)}{K(0)} d\tau.$$
 (6)

This τ_c is identified as the fundamental microscopic time associated with the diffusion of spins giving rise to the relaxation of these spins, i.e.,

$$\tau_{c} \equiv \tau_{\rm NMR} \equiv \tau_{t} = \frac{3}{2} \tau_{j} \int_{0}^{\infty} \frac{d\rho}{\rho} \frac{J_{3/2}(\rho d)}{[1 - A(\rho)]}.$$
 (7)

The final solution of the theory under the above assumption then reduces to giving a physical model for $A(\rho)$ or equivalently its Fourier transform $P_1(r)$. Kruger¹² has shown that an $A(\rho) = (1 + D\tau_j \rho^2)^{-1}$ arising from Torrey's thermally activated diffusion model

(9)

gives rise to a $J^{(m)}(\omega)$ of the form

$$J^{(m)}(\omega) = C^{(m)}(n/d^3)^2_{3f_t}(\alpha, \omega \tau_t) \tau_t, \qquad (8)$$

where $f_t(\alpha, \omega \tau_t)$ is defined by Kruger as

$$\begin{aligned} x, y) &\equiv 3(1/5+\alpha) \left(v \left[1 - (u^2 + v^2)^{-1} \right] \\ &+ \exp(-2v) \cos 2u \left\{ v \left[1 + (u^2 + v^2)^{-1} \right] + 2 \right\} \\ &+ \exp(-2v) \sin 2u \left\{ u \left[1 - (u^2 + v^2)^{-1} \right] \right\} \right) (1/y^2), \end{aligned}$$

where

and

$$y \equiv \omega \tau_i,$$
 (9)

$$\binom{n}{v} = (2\alpha^{1/2})^{-1} [q(1\mp q)]^{1/2}, \qquad (9'')$$

$$q = \{1 + [1 + (5\alpha)^{-1}]^2 (1/y^2)\}^{-1/2}.$$
 (9''')

Here $\alpha = \langle r^2 \rangle / 12d^2$ and from Eq. (7)

In

$$\tau_t = (d^2/5D)(1+5\alpha) = (d^2/5D) + \frac{1}{2}\tau_j.$$
(10)

Using the Kubo-Tomita¹⁶ correction for Bloembergen's $1/T_1$, $1/T_2$ expressions and Eqs. (8) and (2'), the following expressions can be obtained

$$1/T_{1t} = (C_t/\omega) [f_t(\alpha, y) + 4f_t(\alpha, 2y)]y, \qquad (11)$$

$$1/T_{2t} = (C_t/\omega) [\frac{3}{2} + \frac{5}{2} f_t(\alpha, y) + f_t(\alpha, 2y)] y, \quad (12)$$

where

$$C_t = \frac{2}{5}\pi\gamma^4\hbar^2(n/d^3),$$

and the $\lim_{y\to 0} f(\alpha, y) = 1$ has been used to specify $J^{(0)}(0)$ in the $1/T_2$ equation.

It is of considerable interest to consider the limiting forms of $1/T_{1\nu}$ $1/T_{2\iota}$ for large and small values of α and $\omega \tau_{j}$.

III. LIMITING CASES OF THE KRUGER FORMULAS FOR $1/T_{1_t}$

A. Diffusive Limit $(\alpha \rightarrow 0)$

In this limit the mean jump length squared is very small compared to the distance of closest approach. This implies that $\frac{1}{2}\tau_j \ll d^2/5D$ so that $\tau_t \rightarrow d^2/5D$. In this case it is easy to show that in this limit, Eq. (9) reduces to

$$f_{t}(\alpha=0, y) = \frac{3}{5} \left(\left[u - (2u)^{-1} \right] + \left\{ \left[u + (2u)^{-1} + 2 \right] \right. \\ \left. \times \cos 2u + \left[u - (2u)^{-1} \right] \sin 2u \right\} \exp(-2u) \right) (1/y^{2}),$$
(13)

where $u = v = x/2 \equiv \frac{1}{2} (\omega d^2/D)^{1/2}$.

This result yields a normalized intensity function which is equivalent to that obtained by Noack and Preissing⁷ and Abragam²¹ for a $P(r, r_0, \tau)$ given by Fick's law. This same result can be derived using the Torrey formalism by choosing $A(\rho) = 1 - \langle r^2 \rangle \rho^2/6$, the first two terms of an expansion of $A(\rho)$ in powers of ρ^2 .

This result then is interpreted as the limit of the

random flight theory when $\langle r^2 \rangle$ and τ_j are small. The resulting $1/T_1$ expression for the $\alpha=0$ case has the following limiting forms:

$$1/T_{1t} = [6(5)^{1/2}/25] \pi \gamma^4 \hbar^2 (n/d^3) (\omega^{3/2} \tau_t^{1/2})^{-1},$$

 $\alpha = 0, \quad \omega \tau_j \gg 1, \quad (14a)$

 $+ [4\tau_t/(1+4\omega^2\tau_t^2)] \},$ (15)

$$= 2\pi\gamma^4 \hbar^2 (n/d^3) \tau_i, \qquad \alpha = 0, \quad \omega \tau_j \ll 1. \quad (14b)$$

B. Jump Limit $(\alpha \rightarrow \infty)$

In this case $A(\rho) \rightarrow 0$ so that Eq. (5) directly gives a single correlation time spectrum which yields the following:

$$1/T_{1t} = (2\pi/5)\gamma^4\hbar^2(n/d^3)\{[\tau_t/(1+\omega^2\tau_t^2)]$$

where

 $\tau_t = \tau_j/2, \qquad (d^2 \ll \langle r^2 \rangle).$

This result is formally identical to BPP rotational formula with a different strength factor.

It is noted from these limiting case discussions on α that the important differences of the processes, i.e., $1/T_1(\alpha=0) \propto \omega^{-3/2}$ and $1/T_1(\alpha \rightarrow \infty) \propto \omega^{-2}$, only become evident at values of $\omega \tau \ge 1$. This indicates the necessity of high frequency measurements. It is further noted that $1/T_1$ for $\omega \tau_j \ll 1$ is independent of the value of α since from Eqs. (4), and (6), $J_{\omega \tau_j \ll 1}(\omega) = 16\pi n \tau_t / 45d^3$ so that $1/T_1(\omega \tau_j \ll 1) = 2\pi n \gamma^4 \hbar^2 \tau_t / d^3$ for all α . In the $\omega \tau_j \ll 1$ limit a distinction between rotational and translational contributions is extremely difficult if the temperature dependences of $\tau_{\rm rot}$ and τ_t are similar since $1/T_1 \operatorname{rot}(\omega \tau_{\rm rot} \ll 1) = 2\gamma^4 \hbar^2 \tau_{\rm rot} / 5d_{\rm intra}^6$.

IV. EXPERIMENTAL PROCEDURE

A hydrostatic oil generating system capable of attaining 3500 kg/cm² with control to ± 10 kg/cm² was constructed with standard high pressure equipment. The oil was separated from the sample vessel by a piston type separator cell. CS₂ was used as the intermediate transmitting fluid. Measurement of the pressure was accomplished by direct reading of a Heise type "c" (0-3500 kg/cm²) Bourdon gauge whose guaranteed accuracy is 1% of full scale. The pressure vessel used was constructed of 304 stainless steel (2 in. o.d., $\frac{1}{2}$ in. i.d.) and fitted with high pressure thermocouple and electrical feedthroughs. Details of this system will be presented in a future work.

The sample cell used to transmit the pressure to the liquid under investigation is identical to that described by Stejskal, Brooks, and Weiss^{22,23} and was found useable through the range of the measurements $(-30-+70^{\circ}\text{C}, 0-3000 \text{ kg/cm}^2)$. It was found useful to only fill the sample cell to 85% of its total capacity to allow for expansion of the liquid at elevated temperatures.

The temperature of the high pressure bomb and sample holder were maintained by a liquid bath set

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between the pole faces of the magnet. The bath was proportionally controlled to $\pm 0.1^{\circ}$ C.

The NMR spin echo instrumentation used for T_1 , T_2 measurement which has been described elsewhere,²⁴ was modified to allow measurements at 30 MHz. A calibrated LEL 30 MHz receiver was used to detect and amplify the NMR signal. The gain was ≈ 110 dB with a 2 MHz bandwidth. The NMR coil consisted of 12 turns of #22 tinned copper wire with a 0.30 in. intercoil spacing. The application of pressure did not upset the tuning beyond the range of fine control, and usually adjustment for pressure was unnecessary beyond 500 kg/cm².

The glycerol is Fisher certified grade (99.9% minimum purity). The 1,3-butanediol (BUT) and 2-methyl-2,4-pentanediol (MPD) are Matheson gas chromatoguality reagent grades (gas chromatography certified 0.1% impurities). These samples were used without further purification.



FIG. 1. T_1 as a function of temperature with pressure a parameter at 30 MHz for glycerol. The \times represents atmospheric data taken from Connor, Ref. 27.

Before the NMR measurements were undertaken, viscosity measurements over the temperature range of interest were made on each sample liquid. Comparison of the glycerol viscosities with values from the Handbook of Physics and Chemistry for 100% glycerol and measurements on 99.95% glycerol,²⁵ indicated that less than 0.1% water was present in the sample used. Comparisons of viscosities for BUT and MPD were made with values in the literature.²⁶

Sample liquids are loaded into the NMR sample cell in a glove box under an atmosphere of ultra purity N_2 gas. In addition, to establish a reference point for sample purity checks during the experiment, a temperature run at atmospheric pressure is made for each liquid before the sample is subjected to any other pressures.

The pressure dependences of T_1 and T_2 are determined by keeping each sample at constant temperature while varying the pressure. T_1 and T_2 are measured



FIG. 2. T_1 as a function of temperature with pressure a parameter at 30 MHz for 1,3-butanediol.

every 500 kg/cm² from 0-3000 kg/cm² and the pressure is slowly returned to atmospheric pressure before changing the temperature. T_1 and T_2 are then measured at the next desired temperature and the results compared with the atmospheric temperature reference run. If their values are within $\pm 5\%$ of the reference, the sample is assumed to be uncontaminated and the next pressure run is initiated. This procedure is repeated after each pressure run to insure that no progressive contamination takes place. If a deviation of greater than 5% from the reference data is detected the measurement is disregarded and a fresh sample is loaded and run.

 T_1 measurements for the entire temperature and pressure range of each liquid were made using a $180^{\circ}-90^{\circ}$ pulse pair sequence.

 T_2 measurements for the range $10^{-1}-3\times10^{-4}$ sec. for all sample liquids were made by the Carr-Purcell technique using one 90° pulse followed by thirty-two 180° pulses. Below 3×10^{-4} sec the 90° decay tail was exponential allowing measurement of T_2 from a plot of the decay tail directly without homogeneity correction.



FIG. 3. T_1 as a function of temperature with pressure a parameter at 30 MHz for 2-methyl-2, 4-pentanediol.



FIG. 4. T_2 as a function of temperature with pressure a parameter at 30 MHz for glycerol.

V. EXPERIMENTAL RESULTS AND ANALYSIS

A. Data

The behavior of T_1 and T_2 as functions of $10^3/T$ with pressure as a parameter is presented for all three liquids in Figs. 1–6. Figure 1, for glycerol, also contains T_1 data from Connor²⁷ who has measured $T_1(T)$ at 30 MHz from -77 to $+160^{\circ}$ C. Our atmospheric pressure fits very well with the temperature data of Noack and Preissing who have also made $T_1(T)$ measurements at eight frequencies (0.45-117 MHz) in the same temperature range as our data $(-20+70^{\circ}C)$. Unfortunately no comparable T_2 data is available. To our knowledge the only other reliable T_2 data over a wide temperature range is the data of Powles²⁸ at 21.5 MHz who measured T_1 and T_2 from -50 to $+83^{\circ}$ C, and the unpublished T_1 , T_2 data of Drake²⁹ at 20 MHz taken at this laboratory. Noack and Preissing do present T_2 measurements at 10, 20, and 40 MHz but their temperature range is very small $(0+21^{\circ}C)$ and is confined to the region of the T_1 minimum where the slope of T_2



FIG. 5. T_2 as a function of temperature with pressure a parameter at 30 MHz for 1,3-butanediol.

changes rapidly with temperature. The Noack and Preissing values of T_2 are 15%-20% higher than those of Powles or Drake whose values differ by less than 10%. Our 30 MHz T_2 's have therefore been compared to those of the latter and agree with this data.

The following observations are made on the basis of these figures: (1) The T_1 minima for all three liquids studied, shift toward higher values of temperature with increasing pressure; the largest shifts occur for MPD. (2) The magnitudes of T_2 at constant temperature shift downward with increasing pressure. As is found above for T_1 , the shifts are largest for MPD. (3) The slopes of the high and low temperature T_1 vs $^{\circ}K^{-1}$ asymptotes for each pressure appear to be close to parallel. (4) The T_1 (minimum) values for glycerol and butanediol exhibit a downward trend with increasing pressure of about 4% and 8% over the pressure range.



FIG. 6. T_2 as a function of temperature with pressure a parameter at 30 MHz for 2-methyl-2, 4-pentanediol.

B. Fitting Procedure

The results of translational relaxation theory were used to analyze the T_1 and T_2 data. The extensive frequency and temperature data for glycerol allows a test of the self-consistency of fitting the data to the translational theory. Two independent methods were used: one based on frequency measurements at selected temperatures depending on T_1 only, the other based on the use of both T_1 and T_2 at fixed frequency (30 MHz).

The T_1 frequency reduction at fixed temperatures makes use of a two parameter least squares fitting computer program, which, by successive iteration, minimizes the quadratic mean error (qme) of $T_1(\omega)$ data points. The data for these computations are obtained from the $T_1(T)$ data of NP⁷ and the atmospheric pressure values of $T_1(T)$ measured in this study at 30 MHz. A value for the translational correlation time τ_t and the distance of closest approach d are obtained at each of the selected temperatures. α is obtained by fitting the Noack and Preissing lowest temperature $T_1(\omega)$ data $(0-20^{\circ}C)$ first, and then kept constant for higher temperatures. It is found that for values of $\alpha \leq 0.005$ the over-all qme to the $T_1(\omega)$ data is <5% for all temperatures and is lowest (1%-3%) at the high temperatures. If values of $\alpha > 0.005$ are used the individual high frequency T_1 data points at the low temperatures do not fit within the estimated experimental error to the data ($\approx \pm 10\%$). Hence we have chosen $\alpha = 0.005$ as the limit to our fit and these results are used in the following discussion. It should be noted that according to the above analysis if $\alpha \rightarrow 0$ the asymptotic behavior of T_1 will lead to a frequency dependence $\approx \omega^{3/2}$ which is the reported experimental result of Noack and Preissing for the -10, $-20^{\circ}CT_{1}(\omega)$ curves. Use of $\alpha = 0.005$ predicts a gradual curvature for $T_1 \[\omega; \tau_t =$ const]. This small curvature however is still consistent with the data within the relative error of the frequency data available.

Figure 7 presents the Noack and Preissing data, the solid lines represent the Torrey (Kruger) function generated for the correlation time τ_t and distances of closest approach d determined for best fit to the data at each temperature. The representation of the data is found to be very good over the entire range of measurement.

From the τ_t and d values produced by the fit, a value of the self-diffusion constant D can be generated for each temperature by using Eq. (10). The value of the D obtained from the fit can then be compared to actual experimental values³⁰ given in Fig. 8. The results of these calculations over this frequency and temperature range provide strong evidence of the validity of the Torrey translational diffusion model.

Referring to the choice of $A(\rho)$ in Sec. III.A of the



FIG. 7. Spin-lattice relaxation in glycerol as a function of frequency. The data points are taken from NP⁷. The solid lines represent the Torrey (Kruger) function generated for the correlation time τ_t and distances of closest approach d, determined from best fit reduction as discussed in the text.



FIG. 8. Diffusion constant as a function of temperature at atmospheric pressure in glycerol; experimental and fitted values. See Ref. 30.

theory and substituting into Eq. (5), $\tau = (2\rho^2/D)^{-1}$, $\tau_0 = d^2/2D$ it can be shown that the $J_1(\omega)$ used by Noack and Preissing³¹ is proportional to the $J_{t,\alpha=0}(\omega)$ in the Torrey theory. The proportionality constant is $(2/5b^6)/(8\pi/15d^3)$. However, the ratio $T_1(\omega\tau_0)/T_1(0)$ which NP use to demonstrate their fit is independent of the rotational constant. Therefore the reasonable success of their frequency fit must also be regarded then as representing the usefulness of the translational model. Noack and Preissing's relatively poorer fit at low values of $\omega\tau_0$ (high temperature) probably is due to the fact that the *d* used in their procedure must be kept within certain bounds to be physically consistent with the hybrid interpretation of $J_t(\omega)$.

No restriction of d is made in our fits. Using the two parameter fitting procedure on τ_t and d described above, $T_1(\omega\tau_t)/T_1(0)$ can be produced as a function of $\omega\tau_t$ for the $\alpha = 0$ limit to compare with the fit of Noack and Preissing; in this limit $\tau_t = d^2/5D$. The results are shown in Fig. 9 which can be compared to Noack and Preissing.⁷

The second method of reduction makes use of T_1 and T_2 temperature data at $\omega = \text{const}$ (30 MHz) and allows an independent check on the results of the frequency data reduction; and also provides a two parameter fit to the data. This T_1 , T_2 reduction is used to analyze all the temperature and pressure data taken for glycerol, MPD and BUT. In this method the ratio of T_{1t}/T_{2t} from translational theory is fitted to match the ratio of (T_1/T_2) data for each temperature (for each pres-

TABLE I. The reduced par	ameters: τ , translational	correlation time; d, dist	tance of closest approach;	D _{cale} , translational
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		Glycerol ^a						
		Pressure (lrg/am ²)					TERMIN TU.	
T (°C)	a the state of the	0.0	0.5	1.0	1.5	2.0	2.5	3.0
60.2	τ (×10 ⁻¹⁰ sec)	5.30			8.5	9.6	11.3	13.5
	$d \; (\times 10^{-8} \mathrm{cm})$	2.41			2.29	2.27	2.28	2.31
	$D_{\text{cale}} (\times 10^{-7} \text{ cm}^2/\text{sec})$ $D_{\text{exptl}} (\times 10^{-7} \text{ cm}^2/\text{sec})$	2.10			1.40	1.30	1.00	0.800
40.4	- (>(10=10 coc)	0 5	07	11.0	12 5	15.0	19.0	21 5
49.4	$d(\times 10^{-8} \text{ cm})$	2 30	2 22	2 22	2 18	2 16	2 15	21.5
	$D_{\rm rel}$ (×10 ⁻⁷ cm ² /sec)	2.00	1.15	0.960	0.820	0.660	0.540	0.420
	D_{exptl} (×10 ⁻⁷ cm ² /sec)	1.20			0.010	0.000		A TO DEC
39.3	$\tau ~(\times 10^{-10} \text{ sec})$	13.0	15.0	18.0	21.0	26.0	31.3	39.0
	$d \ (\times 10^{-8} \text{ cm})$	2.18	2.12	2.10	2.08	2.05	2.03	2.03
	D_{cale} (×10 ⁻⁷ cm ² /sec)	0.780	0.660	0.540	0.420	0.330	0.260	0.200
	$D_{\text{exptl}} (\times 10^{-7} \text{ cm}^2/\text{sec})$	0.670						
30.0	τ (×10 ⁻⁹ sec)	2.10	2.60	3.25	3.95	5.00	6.10	7.80
	$d ~(\times 10^{-8} { m cm})$	2.07	2.02	2.00	1.97	1.95	1.92	1.91
	$D_{\text{cale}} (\times 10^{-8} \text{ cm}^2/\text{sec})$	4.30	3.40	2.60	2.00	1.50	1.20	0.90
	$D_{\text{exptl}} \; (\times 10^{-8} \; \text{cm}^2/\text{sec})$	3.60						
21.0	τ (×10 ⁻⁹ sec)	3.80	5.00	6.50	8.20	10.3	13.1	17.0
	$d \; (\times 10^{-8} \; \mathrm{cm})$	1.97	1.93	1.90	1.88	1.86	1.83	1.80
	$D_{\rm cale}~(\times 10^{-8}~{\rm cm}^2/{\rm sec})$	2.10	1.60	1.15	0.860	0.640	0.500	0.380
	$D_{\text{exptl}} (\times 10^{-8} \text{ cm}^2/\text{sec})$	1.80						
12.6	τ (×10 ⁻⁹ sec)	7.80	10.8	14.0	18.0	23.0	30.0	39.5
	$d \ (\times 10^{-8} \text{ cm})$	1.98	1.85	1.82	1.81	1.79	1.76	1.73
	$D_{\rm cale}$ (×10 ⁻⁸ cm ² /sec)	0.940	0.680	0.480	0.355	0.270	0.210	0.160
	$D_{\text{exptl}} (\times 10^{-8} \text{ cm}^2/\text{sec})$	0.830						
4.6	τ (×10 ⁻⁹ sec)	18.0	25.0	33.0	42.0	54.0	70.0	93.0
	$d \ (\times 10^{-8} \ {\rm cm})$	1.82	1.79	1.76	1.75	1.73	1.71	1.67
	$D_{\rm cale}~(\times 10^{-8}~{\rm cm^2/sec})$	0.385	0.270	0.190	0.145	0.110	0.085	0.064
	$D_{\text{exptl}} (\times 10^{-8} \text{ cm}^2/\text{sec})$							
-2.8	τ (×10 ⁻⁸ sec)	4.30	5.90	7.90	10.0	13.0	16.6	22.0
1 12 12 E (5)	$d \ (\times 10^{-8} \text{ cm})$	1.76	1.73	1.70	1.70	1.68	1.65	1.62
	$D_{\rm calc}$ (×10 ⁻⁸ cm ² /sec)	0.150	0.105	0.074	0.058	0.048	0.033	0.025
	$D_{\text{exptl}} (\times 10^{-8} \text{ cm}^2/\text{sec})$							
-10.0	τ (×10 ⁻⁸ sec)	10.3	14.0	19.0	24.0	31.0	40.0	53.0
as all Stalk as	$d \ (\times 10^{-8} \ {\rm cm})$	1.70	1.68	1.64	1.65	1.63	1.60	1.58
and the state of the state	D_{cale} (×10 ⁻⁹ cm ² /sec)	0.580	0.400	0.280	0.220	0.165	0.130	0.090
	$D_{\rm exptl} ~(\times 10^{-9} ~{\rm cm^2/sec})$							
-16.8	τ (×10 ⁻⁸ sec)	24.0	33.0	44.0	58.0	74.0	94.0	120.0
	$d \ (\times 10^{-8} \text{ cm})$	1.64	1.64	1.58	1.62	1.57	1.55	1.55
	D_{cale} (×10 ⁻⁹ cm ² /sec)	0.225	0.150	0.100	0.086	0.060	0.048	0.034
	D_{exptl} (×10 ⁻⁹ cm ² /sec)							
		A CONTRACT				La series and the		and the second second

^a Data from graphs (Figs. 13, 14, 16).

sure). Since T_{1t}/T_{2t} from Eqs. (11) and (12) is only a function of τ_t , d is eliminated. This allows τ_t to be determined directly and then d is produced from the T_1 relationship [Eq. (11)]. As in the previous method, the value of α is kept constant for all temperatures. The values τ_t and d are then used to produce T_{2t} which is

compared to the value of T_2 experimentally measured. It should be observed that as the motional narrowing region is approached in these liquids at higher temperatures and lower pressure the ratio of T_1/T_2 approaches unity and the precision of the T_1 , T_2 fit calculation becomes increasingly poor. An example which indicates

NMR RELAXATION IN HYDROGEN BONDED LIQUIDS

Butanediol 1,3							2-Meth	lypentane	ediol 2,4				
	Pressure (kg/cm ²)				Pressure (bg/am2)								
0.0	0.5	1.0	1.5	2.0	2.5	3.0	0.0	0.5	1.0	1.5	2.0	2.5	3.0
1.21					12.4	15.2	0.764				9.1	16.2	21.4
2.18					3.07	3.08	2.12				3.06	2.81	2.77
10.6					2.05	1.69	22 E				2.78	1.96	1.43
10.0							23.5						
2.23			9.95	22.4	14.3	32.3	1.21			8.4	12.4	26.0	31.9
2.30			2.83	3.13	2.73	3.01	2.15			2.18	2.52	2.65	2.53
6.1			2.17	1.18	1.41	0.755	15.0			3.83	2.05	1.08	0.803
0.4							15.2						
4.04		7.15	11.2	17.8	19.5	24.9	1.97		7.4	12.1	24.9	46.0	69.9
2.40		2.38	2.52	2.63	2.54	2.54	2.17		1.86	2.37	2.53	2.49	2.41
2 95		2.15	1.54	1.05	0.892	0.700	0.60		4.44	2.01	1.03	0.540	0.381
5.65							9.00						
0.995	. 1.12	1.12	1.52	2.67	2.95	3.75	0.365	0.746	0.995	2.67	4.48	8.39	11.7
2.65	2.49	2.33	2.37	2.49	2.42	2.38	2.33	2.74	2.27	2.50	2.43	2.31	2.26
19.8	15.0	13.1	9.92	0.28	5.34	4.00	50 5	32.1	20.7	9.32	5.27	2.53	1.75
23.2							39.3						
1.24	1.62	1.78	2.49	4.18	4.97	6.23	0.995	1.12	2.24	4.97	8.58	15.3	20.5
2.44	2.37	2.28	2.30	2.36	2.31	2.24	2.70	2.47	2.42	2.40	2.29	2.14	2.13
12.9	9.41	7.92	5.76	3.60	2.91	2.18	29.3	20.1	10.8	4.64	2.45	1.20	0.882
14.0	Ť.						30.0						
1.62	2.49	3.23	4.29	6.82	8.58	10.9	1.32	2.13	4.72	9.45	16.1	26.9	36.0
2.27	2.29	2.27	2.25	2.23	2.19	2.12	2.56	2.42	2.41	2.27	2.15	2.02	2.03
8.61	5.70	4.32	3.20	1.97	1.50	1.11	19.8	11.0	4.93	2.18	1.14	0.607	0.456
8.60							22.0						
2.83	4.29	5.72	7.96	11.8	14.4	18.9	1.99	3.73	8.99	17.0	28.1	45.5	59.9
2.27	2.24	2.24	2.18	2.11	2.05	1.99	2.49	2.39	2.30	2.11	2.02	1.91	1.91
4.91	3.17	2.37	1.61	1.02	0.787	0.567	12.5	6.15	2.35	1.05	0.582	0.320	0.224
5.20							13.0						
0 479	0 750	1 04	1 36	1 00	2 44	3 12	0 323	0 623	1 61	2 84	4 70	7 52	9.96
2.23	2.19	2.15	2.07	1.99	1.93	1.88	2.44	2.25	2.15	1.99	1.91	1.82	1.80
2.81	1.73	1.20	0.852	0.540	0.413	0.305	7.34	3.26	1.15	0.559	0.310	0.175	0.130
3.00							7.70						
0 050	1 27	1 74	2 20	2 10	4 10	5 25	0 525	1 22	2 66	1 70	0.06	12 0	17 1
2 18	2 10	2 04	1.29	1 88	4.10	1.75	2 36	2 22	2.00	1.70	1 77	1 69	1 67
15.0	9.38	6.43	4.52	3.00	2.17	1.57	41.6	14.9	6.04	2.93	1.56	0.880	0.654
18.0							45.0		1.1				
					-								
1.46	2.12	2.84	4.01	5.18	7.00	9.07	0.945						
2.08	5 12	3 49	2 24	1.75	1.08	0.759	2.25						
0.04	5.12	3.48	2.34	1.00	1.08	0.158	21.5						
							20.5						

diffusion constants, as functions of temperature and pressure; Dexpel, experimentally measured diffusion constants.

the increasing uncertainty in the calculation as T_1/T_2 approaches unity is presented in Fig. 10 for glycerol where the results of the various fitting procedures are presented and the error bars on the T_1 , T_2 fit points indicate this increasing uncertainty. The calculation using the ratio fit method was discontinued above 39.3°C for glycerol at atmospheric pressure and blank spaces will be noted in Table I. The values of τ_t are compared with the frequency of fit τ_t values in Fig. 10. As above, *D* is produced from τ_t , *d* and compared to the data of Fig. 8, which also contains the results of the frequency reduction.



FIG. 9. Ratio $T_1 (\omega \tau_t)/T_1$ (0) vs $\omega \tau_t$ fitted using $\alpha = 10^{-5}$ and the data of Naock and Preissing.

As the figure shows the T_1 , T_2 fit, produces D values for $10^3/T < 3.5^{\circ} K^{-1}$ which are equal to those obtained from the frequency fit. Above $3.5^{\circ} K^{-1}$ the curves begin to diverge. The reason for this discrepancy may reflect the onset of rotational contribution to the translational part which has a stronger frequency dependence than the translational or the fact that the Torrey theory does not truly represent the translational characteristics of $1/T_1$. Separation studies should provide some answers to this problem. But since this data is not available as yet, the discussion will be developed for the 30 MHz temperature data on the basis of the results of T_1 , T_2 temperature fit, assuming the observed relaxation is translational in nature since this fit is consistent with the measured diffusion constants.

The errors bars of Fig. 10, on τ_t arise from the estimated $\pm 5\%$ uncertainty in the glycerol T_1 and T_2 data. Since the error in the ratio T_1/T_2 increases as T_1 and T_2 come closer together the bars become large on the reduced values of τ_t with increasing temperature. To test the self-consistence of the method, the τ_t and d obtained from the 30 MHz T_1 , T_2 data fit, are used to generate T_1 and T_2 for 20 MHz. The predicted T_1, T_2 values compare very well to the experimental values of Noack and Preissing, Drake, and Powles.

The range of the T_2 measurement is limited because of the onset of modulation on the T_2 echo train beyond about 35°C for all three liquids. Therefore a third reduction method, making use of T_1 data, which is not affected by modulation, and the self-diffusion constant D, which is limited by low rather than high temperatures, is used to extend the range of the reduction to recover τ_t . This method, called the T_1 , D fit, provides another check on the other reduction methods in the high temperature overlap region. In the T_1 , D fit, a value for τ_t and d are produced for each temperature which can be compared with overlapping values from the other reduction methods. Since D data is available only at atmospheric pressure, the results can only be compared there to those from other techniques. With the use of the T_1 , T_2 fit and the T_1 , D fit, the entire range of our temperature data at atmospheric pressure can be reduced consistently.

Using the T_1 , T_2 fit, the temperature data was reduced employing an $\alpha = 0.07$ for BUT and $\alpha = 0.2$ for MPD. The results are in good agreement with the diffusion constant values shown in Table I. Again using the iterated value of τ_t and d to produce T_1 for 10 and 20 MHz, a good fit to measured values is obtained for BUT and MPD.³²

The ratio T_{1t}/T_{2t} at the T_1 minimum, which is theoretically a function of α , also provides a check on the fit to experimental data. In order to fit the diffusion constant for BUT and MPD values of $\alpha > 0$ are necessary. While increasing α brings the fitted D(T) curve closer to the data, α has an upper limit in order to be consistent with the theoretical prediction for T_1/T_2 at the minimum. The theoretical predictions of T_{1t}/T_{2t} for these liquids on the basis of $\alpha = 0.005, 0.07, 0.2$ are 2.85, 2.35, and 1.9. The experimental ratios T_1/T_2 are approximately 3.6, 2.55, and 2.2, respectively, for glycerol, BUT, and MPD. Our estimate for the errors in these values is $\pm 25\%$. Owing to the experimental uncertainty of the position of the T_1 minimum in temperature space, and the rapid falloff of the T_2 data in the region of the minimum, the values are in reasonable agreement with the theory.



FIG. 10. The values of τ_t obtained from the three fitting procedures employed: \odot from T_1 , T_2 fit, x from $T_1(\omega)$ frequency fit, \bigtriangledown from T_1 , D fit. The jump time τ_i is from Eq. (10). The other correlation times are drawn for comparison: τ_D dielectric, τ_Q quadrupolar, τ_p the mechanical volume at constant pressure τ_s mechanical shear, and τ_{oR} depolarized orientation.

C. Comparison with Quadrupolar Times

In addition to the self-diffusion constant measurements and the self-consistency of the reductions for temperature and frequency measurements, evidence for the predominance of translational relaxation in glycerol has been made possible by recent measurements of the spin-lattice and spin-spin quadrupole relaxation times T_{1Q} and T_{2Q} in perdeuterated glycerol. Since T_{1Q} , T_{2Q} have been measured from -20 to $+70^{\circ}$ C which is the same range as the present proton studies, a comparison of the relaxation times and their temperature dependences may be made.

Drake and Meister³³ have indicated that the rotational motion of the glycerol- d_8 molecule appears to be the predominant relaxation process in glycerol- d_8 . On this basis they have calculated a value for $\bar{\tau}_Q$ which on the basis of previous studies can then be identified with $\tau_{\rm rot}$ for protonated glycerol.

The formulas required to represent the proton dipole-dipole rotational relaxation differ from the expressions for the quadrupole relaxation employed by Drake and Meister³⁴ only in the strength factor $2\gamma^4 \hbar^2 I (I+1)/5 d_{intra}^{6.35}$ In this expression the parameter d_{intra} (average proton separation) is unknown, although reasonable estimates can be made for it. However, even without specific knowledge of the magnitude of d_{intra} it is observed that, for calculations at 30 MHz



FIG. 11. Comparison of τ_i , τ_j with other relaxation times at atmospheric pressure for 1,3-butanediol. \odot From the T_1 , T_2 fit; \triangle from T_1 , D fit.



FIG. 12. Comparison of τ_i , τ_j with other relaxation times at atmospheric pressure, for 2-methylpentanediol 2, 4. \odot From the T_1 , T_2 fit; \triangle from T_1 , D fit.

[assuming Drake and Meister's Eq. (2) and (7)],³³ these rates do not have the same asymptotic behavior at the low temperatures (long correlation times). Since T_{1Q} and T_{2Q} have only been measured for 5 MHz, the exact frequency behavior of $1/T_{1 \text{ rot}}$ for glycerol will have to await further measurements to ensure this comparison. However it seems sufficient to compare temperature dependences of these rates at 30 MHz to demonstrate the reasonableness of the hypothesis that the rotational contribution is small.

Calculations of the $1/T_{1 \text{ rot}}$ were made utilizing the above assumptions and the correlation times from quadrupolar data. It was observed that in the low temperature region the generated $1/T_{1 \text{ rot}}$ had a significantly different temperature dependence than the data and that the measured diffusion constants could not be recovered employing the Torrey (Kruger) translational model if $1/T_{1 \text{ rot}}$ was greater than $\approx 10\%$ of the measured data at the point of closest approach, i.e., this implies a $d_{\text{intra}} > 1.9$ Å to satisfactorily reduce the data.

Since no data is presently available to verify the actual magnitude of the rotational contribution in any of the liquids studied here as a function of temperature or pressure, the reduction is carried out under the assumption that the rotational contributions for all three liquids can be neglected.





D. Discussions of Temperature Dependence of Correlation Times

Figures 10-12 show the variation of τ_t , τ_j and other microscopic relaxation times, as a function of temperature at atmospheric pressure.^{36,37} In glycerol the temperature dependences of all the times are similar from +12°C to lower temperatures while τ_t and τ_j vary less at higher temperatures. In BUT the variation of τ_t and τ_j is slower than the other times throughout the range of the data while in MPD the variation of τ_t follows that of τ_p and τ_s quite closely throughout the temperature range, varying more than τ_D below -10°C.

The ratio of τ_t/τ_j [which from Eq. (10) is constant for a given α] indicates which limit more closely governs the translational part of $1/T_1$ for a particular liquid. In glycerol $\tau_t/\tau_j \approx 22$, so that $1/T_{1t}$ has a translational behavior close to the diffusive limit (i.e., $\alpha \rightarrow 0$), while the translational motion in BUT and MPD is closer to the jump limit (i.e., $\alpha \rightarrow \infty$). The latter association is a result of the behavior of $1/T_{1t}$ for $\alpha > 0$. Kruger's calculations indicate that the onset of the ω^2 dependence of $1/T_{1t}$ occurs within a decade in $\omega \tau_t$ of the T_1 minimum for $\alpha \ge 1/72$. This implies that the α values of 0.07 and 0.2 are in this limit.

Further comparison of τ_j to τ_D , τ_s , or τ_v , which may be governed by both rotational and translational motions, does not at present seem fruitful since the relative contributions of these two separate motions to the dielectric, shear, and volume relaxation processes is unknown.

The variation of d vs temperature and pressure for all three liquids is given in Table I and Fig. 13 for glycerol as an example. The figure shows that d decreases with decreasing temperature and increasing pressure and becomes less than a molecular diameter. The d values are smaller than expected from the Torrey definition of d. However, if d is considered a measure of the closest distance between two protons on neighboring molecules, the magnitudes are not unreasonable. The magnitude of the decrease of d with temperature and pressure is not understood at present.



FIG. 14. τ_t vs $10^3/T(K^\circ)^{-1}$ with pressure a parameter for glycerol using $\alpha = 0.005$.

E. Effects of Off-Center Spins and Nonuniform Spin Density

There are two possible effects which the theory has not taken into account which would change the effective values of τ_t and d, and perhaps produce a value for d higher than predicted. The first effect formulated by Hubbard¹⁸ for $\omega \tau \ll 1$ takes into account the fact that the spins are off the center of the molecule they "ride" and hence their motion with respect to the center of mass, modifies the effective intermolecular interaction. The relationship developed by Hubbard involves estimates of the distance from the off-center spin to the center of the molecule, the molecular radius and the ratio $\tau_{\rm rot}/\tau_{\rm trans}$. Employing reasonable estimates for these quantities leads to a correction of approximately 15%. Recently Harmon³⁸ has measured T_1 vs ω in glycerol from 1–6 MHz at 22.9°C and found that T_1 vs $\omega^{1/2}$ is linear. He calculates a value for $D^{-3/2}$ $(1+\delta)$ of $1.9\pm$ 0.1×10^{-8} which is plotted as an effective diffusion constant in Fig. 8. As can be seen in Fig. 8, this value is within 10% of the experimentally measured quantity indicating that the factor $(1+\delta)$ is less than 15% and probably of the order of a few percent.

The second effect is introduced from a consideration of the nonuniform spin-density through the use of the radial distribution function. Using the Harmon-Muller¹⁷ formulation would lead to a maximum correction, for glycerol, in $1/T_1$ of a 2% or 3% increase.



FIG. 15. Comparison of τ_t , τ_s , τ_v , and τ_D as functions of pressure with temperatures a parameter in glycerol. τ_t solid line, τ_s , τ_v , and τ_D as labeled.



FIG. 16. Diffusion constant vs $10^3/T(^{\circ}K)^{-1}$ with pressure as a parameter in glycerol.

These corrections therefore do not appear to be significant for glycerol. It is assumed that the relative effects will be similar for BUT and MPD.

F. Discussion of Pressure Dependence of Correlation Times and Diffusion Constants

In reducing the pressure data, the same values of α used at atmospheric pressure were used. The temperature dependences of the correlation times τ_t with pressure as a parameter are presented in Fig. 14 for glycerol and Table I. All three liquids exhibit a non-Arrhenius temperature dependence for most of the range of measurement, with significant curvature at the higher temperatures. The slope of τ_t vs temperature for each liquid is essentially independent of pressure i.e., $\tau_t(T)$ for the various pressures are parallel. The relative ratio of $\tau_t(P_1)/\tau_t(P_2)$ increases for the liquids in the order glycerol (5), BUT (7), MPD (30) over the pressure range 0–3 kbar.

Table I shows the variation of τ_t vs pressure for various temperatures. Glycerol is also presented in Fig. 15 for observation. For glycerol $\ln \tau_t$ with pressure has an Arrhenius behavior, with a slope which decreases as the temperature increases. In the case of the other two liquids, BUT and MPD, the $\ln \tau_t$ vs pressure is non-Arrhenius and have a decreasing slope with increasing pressure. In these cases in contrast to glycerol the slopes are independent of temperature.



FIG. 17. Diffusion constant and inverse viscosity vs P with temperature a parameter in 2-methylpentanediol 2, 4. These diffusion constants were calculated from the best fit T_1 , T_2 , reduction as described in the text.

For glycerol, comparison of the pressure dependence of τ_t with τ_s and τ_v is possible in the temperature range $-10-+60^{\circ}$ C. The relaxation times τ_s and τ_v were determined from viscosity and relaxational moduli data available in the literature.^{39,40} The only dielectric pressure data available that overlaps the τ_t measurements presented here is for glycerol at -6.7° C.⁴¹ The slope of τ_D is 8% greater and that of τ_s is 25% greater than that of τ_t (as well as τ_j owing to the fact that α is constant).

The behavior of the diffusion constant D as a function of temperature with pressure as a parameter is given in Table I and for glycerol in Fig. 16. As noted for τ_t , D reflects the same general characteristics. Again a non-Arrhenius behavior is found for all three liquids, glycerol, BUT, and, to a lesser extent, MPD.

The pressure dependence of the diffusion constants are given in Table 1 and for MPD are presented in Fig. 17. The diffusion constant is found to be log linear with pressure for both glycerol and BUT, while MPD exhibits a curvature which has decreasing slope with increasing pressure. Glycerol appears to have a temperature independent slope for $\ln D$ vs pressure while both BUT and MPD exhibit an increasing slope with temperature decrease.

The behavior of the diffusion constant relative to atmospheric pressure D(P)/D(1) and the inverse of $\eta(P)/\eta(1)$ as functions of pressure for glycerol at 50 and -10° C are shown in Fig. 18. This figure also in-

cludes $T_1(P)/T_1(1)$ for comparison. As mentioned above, Bull and Jonas¹⁵ have shown for the mobile liquids acetone, benzene, and chlorobenzene, that $1/T_{l_{inter}} \propto 1/D \propto \eta$ as a function of pressure. From Fig. 18 $T_1(P)/T_1(1)$ for glycerol 50°C, the highest temperature for which T_1 and D data is available, does not follow the pressure dependence of either D or η^{-1} . The lack of correspondence can be attributed to the fact that the value of $\omega \tau_t \cong 0.2$ at $T = 50^{\circ}$ C is not sufficiently small so that the limiting case $1/T_{1(\omega_{\tau}\ll 1)} \propto 1/D$ would not be applicable. The lack of correspondence, however, between the pressure variation of D and η_s^{-1} for both glycerol and MPD (Figs. 18 and 17) must be regarded as fundamental to the physical process since the fit at this temperature is entirely consistent with the frequency data. The failure of the simple notion that $D \propto 1/\eta$, is not surprising, however, since in viscous hydrogen bonded liquids, cooperative effects are expected to control the individual process affecting these quantities more drastically than in mobile liquids.

VI. CONCLUSIONS

Under the assumption that intramolecular contributions to T_1 and T_2 can be neglected in comparison to the intermolecular contribution, the relaxation theory of Torrey has been shown to be reasonably successful in explaining the frequency dependence (for glycerol)



FIG. 18. $T_1(P)/T_1$ (P=0), D(P)/D(P=0), $\eta_s(P=0)/\eta_s(P)$ vs pressure at 50° and -10° C in glycerol. These diffusion constants were calculated from the best fit T_1 , T_2 , reduction as described in the text.

and the temperature dependence of T_1 and T_2 data available for glycerol, BUT and MPD. Reduction of both types of data, for glycerol, give identical results for temperatures above 12°C with some discrepancy at lower temperatures. The recovery of the self-diffusion constant at atmospheric pressure supports the use of the temperature reduction.

Comparison of $1/T_{1 \text{ rot}}$ in perdeuterated glycerol to $1/T_1$ data indicates that the rotational contribution must be less than 10% in the region of the T_1 minimum to allow a reasonable fit to the translational part of $1/T_{1}$.

The above results represent a reversal of previous notions concerning the strength of rotational and translational relaxation processes in viscous liquids and underline the importance of considering translational diffusive effects.

 $\ln \tau_t$ vs T is found to be non-Arrhenius for all three liquids. $\ln \tau_t$ vs P is linear in glycerol. $\ln D$ vs P is linear in glycerol and BUT. In MPD and glycerol, for which $\eta_s(P)$ has been measured, D is not proportional to η_s^{-1} .

A good fit to both temperature and pressure NMR data is possible with fixed values of α for each of the three liquids studied through the complete temperature and pressure range of the measurements.

The fitted values of d are less than a molecular diameter. However, if d is considered a measure of the closest distance between protons on neighboring molecules, the magnitudes obtained are not unreasonable.

The effects of off-center spins and a nonuniform distribution of intermolecular spins in accordance with the radial distribution functions is found to be negligible (at least at low $\omega \tau$) in $1/T_{1 \text{ inter}}$ for glycerol.

Comparison of τ_i and τ_j with other times available in literature, does not indicate any apparent relationships though the temperature dependences of all τ 's are similar. This may indicate that motions other than translational motions may be involved in the processes measured by these times.

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and τ_v were calculated from viscosity data mentioned in Ref. 26. The following empirical formulas for η_{θ} were used to calculate τ_v , τ_p in glycerol and τ_s , τ_v , τ_p in BUT and MPD.

MPD $\eta_8 = \exp[-3.315 + 1.74 \times 10^8 / (T + 273)^8]$

BUT $\eta_8 = \exp[-1.3776 + 1.5744 \times 10^8 / (T + 273)^3]$

GLY $\eta_8 = \exp\{2.30258[-0.724+0.98\times10^8/(T+273)^3]\}$.

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