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_j, 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_j 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.

Two tacts have been used to modify the BPP theory

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 $f(\tau)\exp(-\tau/\tau_{rot})$. 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–Hunt[2] approach for example makes use of a modulating correlation function obtained from Glarum's[3,4] defect diffusion model while the Chaban[5] approach makes use of an ordering parameter modulating term derived from the Isakovich–Chaban[6] 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 Meister[8] 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 paper[9] that the single translational relaxation theory of Torrey[10] does apparently predict the general frequency behavior of $1/T_1$ for glycerol. In their recent paper on magnetic relaxation in glycerol[7] 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 $1/T_{1\,rot}$. 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 Purcell[13] 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 ($\omega\tau\ll1$). $T_1(P)$ data has been taken by Benedek on glycerol, but as is pointed out in his thesis[14] 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 ($\omega\tau\ll1$)

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

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 ap-