A PULSED N.M.R. STUDY OF FLUORINE RELAXATION MECHANISMS IN TRIFLUOROTOLUENE

Thesis by

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ABSTRACT

Intermolecular dipole, intramolecular dipole, and spin-rotation coupling-relaxation mechanisms are studied in a pulsed n.m.r. investigation of trifluorotoluene in carbon disulfide. The viscosity dependence of each mechanism is examined and the relative contribution of each to the overall relaxation rate is estimated.

I. INTRODUCTION

The nuclear magnetic resonance spectroscopy of trifluorotoluene is complicated by fluorine relaxation through intramolecular and intermolecular dipole transfer, in addition to spin-rotational coupling. Many of the details of this latter coupling have been worked out, although the theoretical determination of good correlation times strains a theorist whose formulas deal with hard spheres rather than substituted toluene molecules. This investigation follows closely the work of Mr. Thomas E. Burke on the viscosity dependence of the longitudinal relaxation time, T_1.

T_1 characterizes the behavior of the z-component of the magnetization in a system described by the simple Bloch equation,

$$\frac{dM_z}{dt} = -\frac{(M_z - M_0)}{T_1}$$

Carrington expresses T_1 in terms of the off-diagonal matrix elements of V(t), the local potential of a spin in the system, as

$$T_1^{-1} = \frac{2}{\hbar^2}\int_{-\infty}^{\infty} \overline{V^*_{\alpha\beta}(t+\tau)\,V_{\alpha\beta}(t)}\,e^{i\omega_0 t}\,dt$$

where ω_0 is the frequency at which relaxation may occur. Theory exists to estimate the integrand, since it is found that the quantity $G(\tau)$, called the autocorrela-

tion function of f(t),

$$G(\tau) = f^*(t+\tau) f(t)$$

may be described for many physical processes by

$$G(\tau) = \overline{f^*(t) f(t)}\, e^{-|\tau|/\tau_c}$$

where τ_c is called the correlation time. This time may be interpreted as an approximate lifetime of a fluctuation in f. Debye's calculation of τ_c for hard spheres in a liquid,

$$\tau_c = \frac{4\pi\eta a^3}{3kT}$$

has proved to be extremely useful.[1]

Figure one, after that appearing in Hahn's famous descriptive article of 1953, indicates the principles of pulse n.m.r., or free induction decay. The general features of the experimental arrangement are the same as those used in continuous wave spectroscopy. The usual large, homogeneous magnetic field H_0, traditionally oriented in the plus-z direction on the drawing, is employed, while a smaller oscillating field, H_1, is applied in the x-direction. The magnitude of H_1 is greater than that employed for continuous wave experiments, but the distinctive characteristic of this perpendicular field is that it is applied only in pulses, of such duration to cause the net magnetization vector

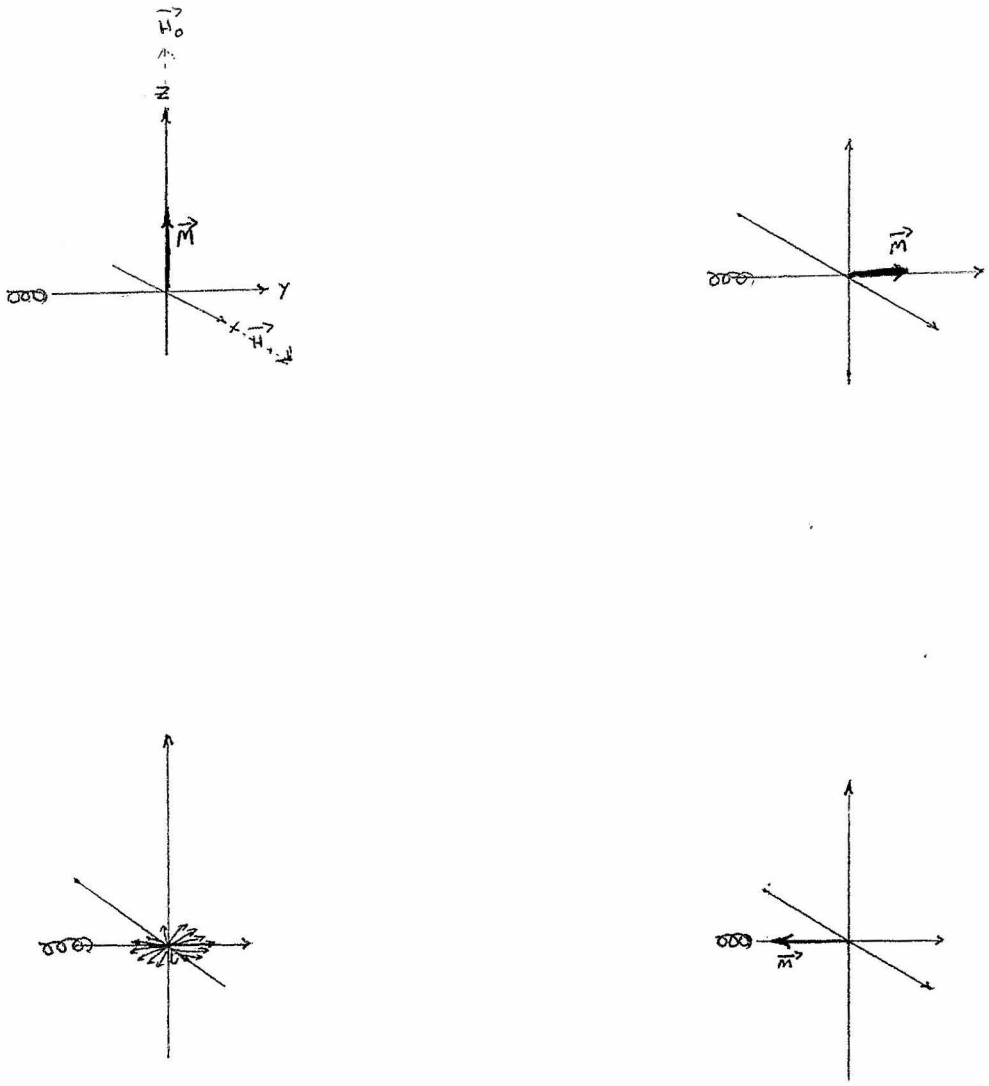


FIGURE 1

to precess from a direction perpendicular to the x-y plane to one parallel to it.

The oscillating field is sufficiently strong that the magnetization, which is an ensemble average of spins, does not lose coherence. After the pulse, called a "90-degree" pulse, the precessing spins lose this coherence; the frequency of each nucleus's precession is determined by its environment; inhomogeneity of H_o also causes small differences in frequency. What was a single vector precessing in the x-y plane immediately after the pulse is transformed to a "pancake" of magnetization.

A second pulse is applied after time τ. This pulse, of duration t_w, rotates the plane of magnetization vectors by 180 degrees about the x axis. Vectors of lower frequency, which had "lagged" behind faster vectors, now lead them, and at time 2τ the vectors regain coherence and are monitored by the receiver coil. If relaxation is occurring, successive measurements of the magnetization will show smaller and smaller values.[2]

The order of pulses is reversed in the present

experiment. A 180-degree pulse is first applied, sending M_o into the minus-z direction. After a variable interval τ, the 90-degree pulse rotates the magnetization into the -y direction where it is measured. Another measurement is performed once the sample has reached equilibrium again, after an interval of several times T_1.[3]

II. EXPERIMENTAL PROCEDURE

Figure 2 illustrates the experimental arrangement in block form. A positive square wave from the function generator triggers the Tektronix 162 waveform generator. The latter sends a positive sawtooth to the first of the identical Tektronix 163 pulse generators and a negative sawtooth to the second generator. The first pulse generator sends a control pulse of the proper length for the 180 degree pulse to the r.f. gate. When the sawtooth to the second generator reaches a preset value, that generator produces the 90 degree pulse, correctly delayed. The second generator also triggers the third generator, which sends a gating pulse to the hp 5245L counter. Together with the voltage-to-frequency converter, this counter samples the magnetization. A TSI 361 general purpose counter measures the 180 - 90 degree pulse interval.[4]

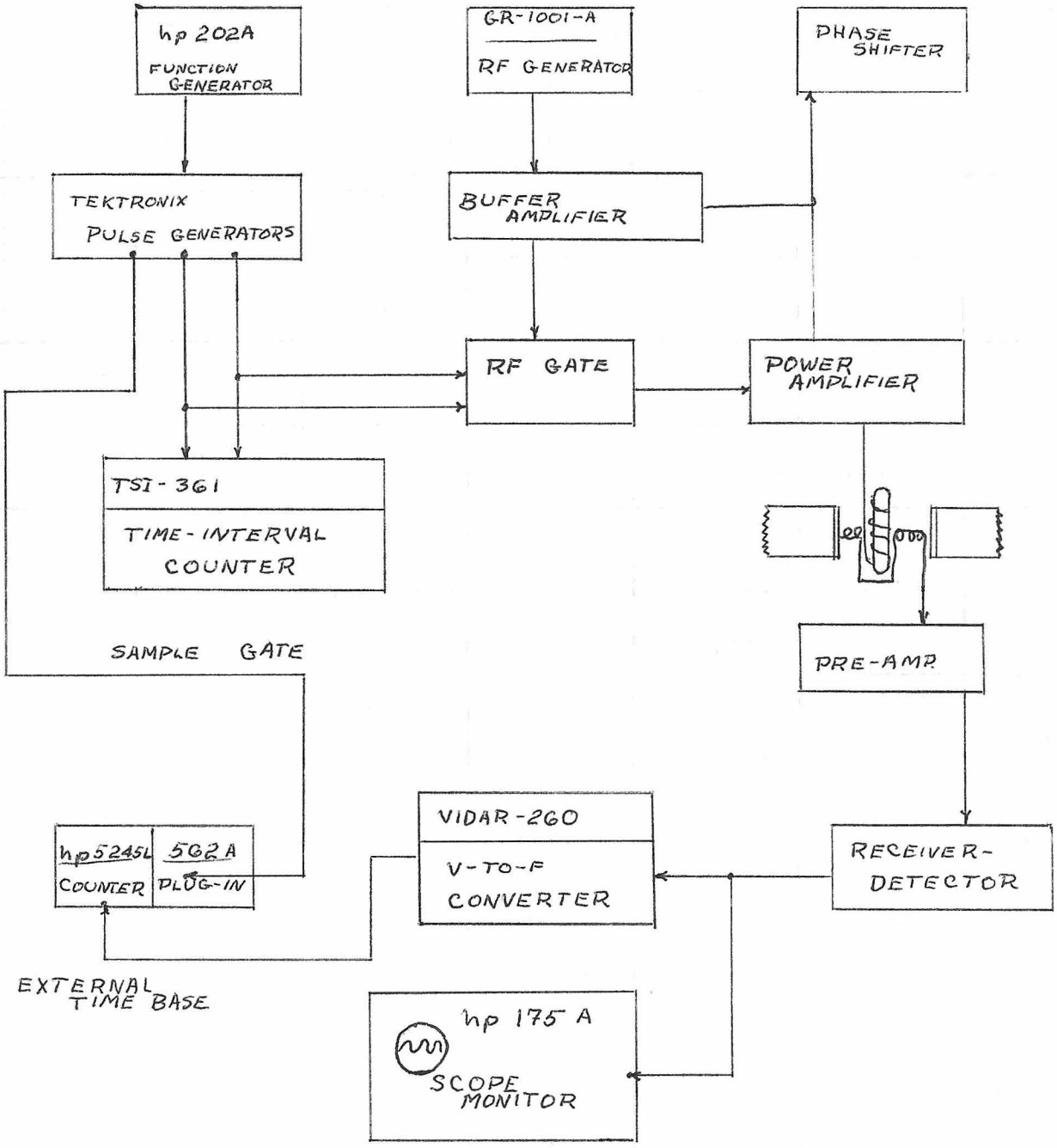

hp 202A
FUNCTION GENERATOR
GR-1001-A
RF GENERATOR
PHASE SHIFTER
TEKTRONIX
PULSE GENERATORS
BUFFER AMPLIFIER
RF GATE
POWER AMPLIFIER
TSI-361
TIME-INTERVAL COUNTER
PRE-AMP
SAMPLE GATE
hp5245L
COUNTER
562A
PLUG-IN
VIDAR-260
V-TO-F CONVERTER
RECEIVER-DETECTOR
EXTERNAL TIME BASE
hp 175 A
SCOPE MONITOR

FIGURE 2

Reagent grade carbon disulfide and trifluorotoluene were used in the investigation. Samples were allowed to equilibrate in a 25 degree water bath, after which their density was determined by weighing and their viscosity measured by a time-of-flow device calibrated by Mr. Burke to an expansion

$$\eta = a\rho t + b\rho/t$$

where η is the viscosity, ρ is the density, t is the time required for the fluid to pass between two marks, and a and b are empirically determined constants.

The samples were decanted into narrow-neck tubes, frozen with liquid nitrogen and pumped on a vacuum line for thirty minutes. After two more freeze-pump cycles the tubes were sealed with a torch. This process is believed to have been effective in removing dissolved oxygen, whose paramagnetic property is sufficient to change experimental T_1 values by a factor of two.[5]

In the determination of T_1, different intervals between the 180 and 90 degree pulses were chosen by varying the slope of the sawtooth trigger to the second pulse generator, and by varying the trigger level. Five readings of the magnetization were taken at each τ. Seventeen values of τ were used by the author

and thirty-five by Mr. Burke when he repeated the procedure. As a later discussion will show, proper choice of τ values was critical.

Although in fact the magnetization has the value $-M_0$ for $\tau=0$ and increases monotonically to $+M_0$, the digital readout gave only $|M_Z|$; for this reason, Mr. Burke wrote the Bloch equation in the following form for computation. Included is δ, the root-mean-square noise.

$$M_z = -M_0 + 2\delta + 2(M_0 - \delta)\exp(-t/T_1) \qquad t \leq \ln 2\, T_1$$

$$M_z = M_0 - 2(M_0 - \delta)\exp(-t/T_1) \qquad t \geq \ln 2\, T_1$$

The $M_Z(t_i)$ were put into a computer program, essentially a least squares fit, that evaluated T_1, M_0, and subject to the condition that

$$\frac{1}{n}\sum_{i=1}^{n}\left[M_z(t_i) - M_z\right]^2$$

be a minimum. The relaxation times were computed to be on the order of two seconds.

III. DISCUSSION

The most general expression for T_1 that includes well-studied relaxation mechanisms may be written

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)_{\substack{\text{intra-}\\ \text{dipole}}} + \left(\frac{1}{T_1}\right)_{\substack{\text{inter}\\ \text{dip.}}} + \left(\frac{1}{T_1}\right)_{\substack{\text{spin-}\\ \text{rot}}} + \left(\frac{1}{T_1}\right)_{\substack{\text{elec-}\\ \text{nuc.}\\ \text{dip}}} + \left(\frac{1}{T_1}\right)_{\sigma}$$

The fourth term, arising from the coupling of electron and nuclear spins, may be ignored if paramagnetic species have been eliminated, and in fact neither oxygen nor stray metal ions are expected to interfere in this experiment. The last term arises from the anisotropic chemical shift. Mr Burke computes that its contribution should be small; he also observes that independence of T_1 upon field strength supports the computation.

Expressions for the three terms remaining are available in the literature. When the viscosity is taken to be the variable of interest, the expression for T_1^{-1} may be written

$$\frac{1}{T_1} = A\eta + \frac{B}{\eta} + xC\eta$$

where x is the mole fraction of trifluorotoluene, and A,B, and C depend upon the solvent and the solute. The choice of carbon disulfide, a "magnetically inert" solvent, allows solute-solvent exchange to be minimized.

The intra-molecular dipole term, $A\eta$, may be written

$$A\eta = A'\tau_\theta$$

where τ_θ is the correlation time for the process. The subscript θ is used following the emphasis of Powles and Green upon the θ-dependence of intramolecular dipole relaxation in contrast to the ω-dependence of spin-rotation relaxation.

If fluorine-hydrogen coupling is ignored,

$$A' = \frac{3\gamma_F^4\hbar^2}{r_{FF}^6}$$

where γ_F is the gyromagnetic ratio of fluorine.[6]

The Debye result is used for τ_θ ,

$$\tau_\theta = \frac{4\pi}{3}\frac{\eta a^3}{kT}$$

The importance of Debye's derivation is enhanced by the fact that expressions for the correlation times corresponding to C and B have been derived only in terms of τ_θ . Abragam treats the case of intermolecular dipole-dipole relaxation, finding

$$\frac{(T_1^{-1})_{inter}}{(T_1^{-1})_{intra}} = \frac{3\pi N r_{FF}^6}{5a^3}$$

where N is the density of spins per cubic centimeter and requires a factor of two thirds for unlike spins.[7] Thus

$$C = \frac{6\pi^2\hbar^2\gamma_F^2\gamma_F^2}{5kT}\left(\frac{3\rho N_0}{M}\right) + \frac{4\pi^2\hbar^2\gamma_F^2\gamma_H^2}{5kT}\left(\frac{5\rho N_0}{M}\right)$$

The spin-rotation correlation time, τ_ω , is

not as well-documented as τ_θ . Powles and Green[8] give a simple diffusion argument to show that the two times are related by

$$\tau_\omega \tau_\theta = I/nkT$$

Hubbard[9] finds n to be six using a more complete method. This relationship indicates that τ_ω varies inversely with the viscosity, since τ_θ is known to be linear in η .

The "moment of inertia" of trifluorotoluene is taken to be the sum of the two larger moments. Also necessary in computing B is the spin-rotation coupling constant, C_α , and the moment of the CF_3 top, I_α . The final expression for B reduces to

$$B = \frac{8 C_\alpha^2 \, I \cdot I_\alpha}{9 h^2 \tau_\theta} .$$

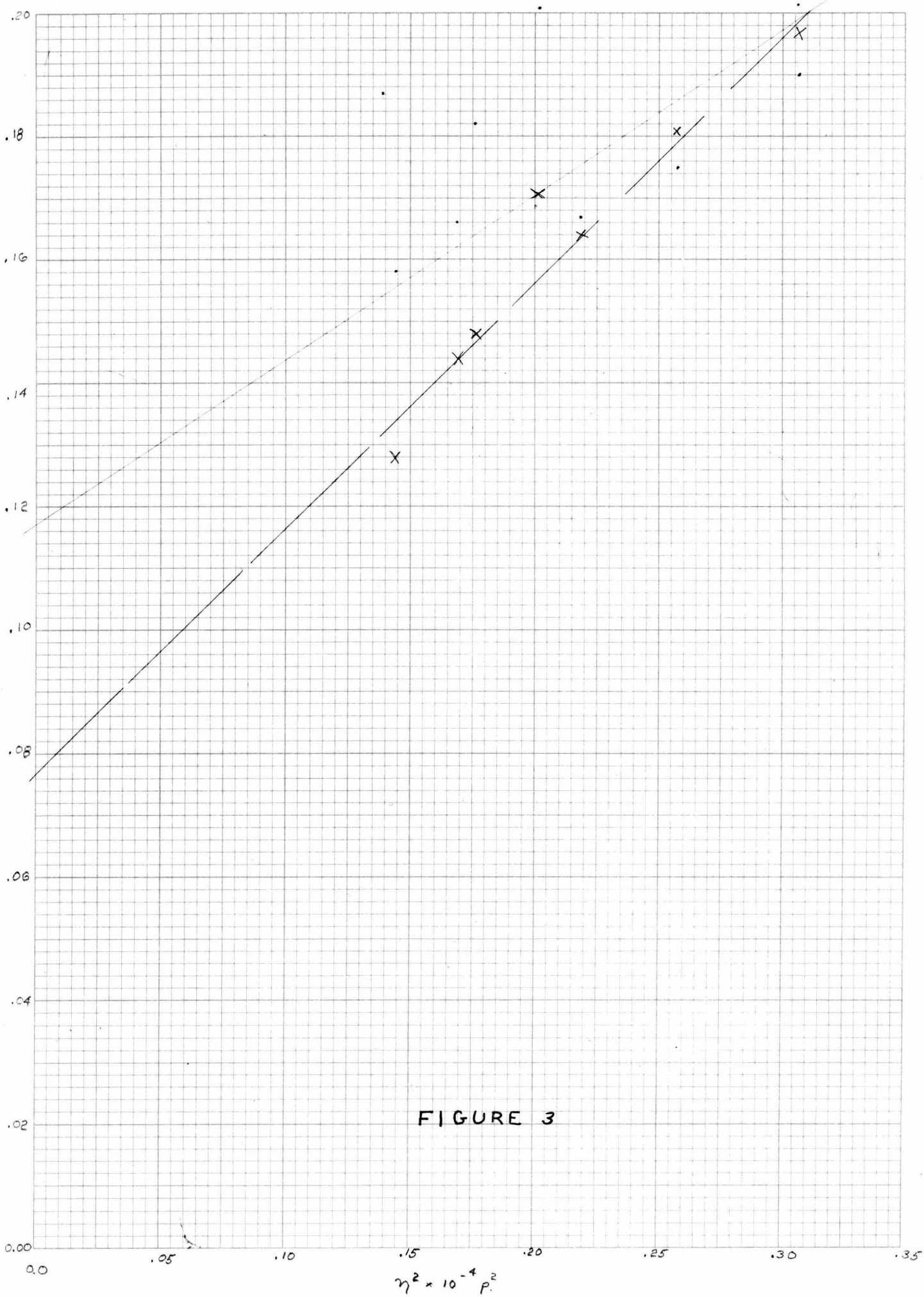
The general equation for T_1^{-1},

$$\frac{1}{T_1} = A\eta + \frac{B}{\eta} + C \times \eta$$

is inconvenient for determining A and B; multiplication by η gives an expression whose slope is A and intercept B when $\left(\frac{1}{T_1} - C\times\eta\right)$ is graphed as a function of η^2 (see Figure 3):

$$\eta\left(\frac{1}{T_1} - C\times\eta\right) = A\eta^2 + B$$

The theoretical intermolecular dipole coefficient C was calculated and used to "correct" each value of T_1^{-1}. C was found to be 6.36 $sec^{-1}poise^{-1}mole^{-1}l$.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$\eta^2 \times 10^{-4} P^2$

FIGURE 3

Each correction was ten per cent or less for each value of T_1^{-1}.

Two sets of T_1 values were used in the calculation, both from the same samples. The author used seventeen values of τ, the 180 - 90 degree pulse difference, while Mr. Burke took thirty-five τ values for each sample. The standard error in the author's results was roughly five times higher than Mr. Burke's error. The better accuracy of the latter's T_1's probably resulted from better distribution of the τ's as well as their greater number.

Two assumptions were made in the theoretical prediction of τ_θ. The first was that a, the "radius" of trifluorotoluene, could be determined from a hexagonal-packing model for spheres, in which

$$a^3 = .74 \frac{M}{\rho} \cdot \frac{3}{4\pi N_0}$$

The second assumption was that the fluorine-fluorine distance could be given by the distances and angles used for the moment of inertia calculation. The calculated value of τ_θ was $12.7 \pm 0.6 \times 10^{-12}$ sec. poise^{-1}. Mr. Burke's data agreed closely, giving $12.6 \pm .6 \times 10^{-12}$, while the author's data yielded $8.6 \pm .4 \times 10^{-12}$.

The predicted value of B, 3.95×10^{-3} poise sec., is higher than Mr. Burke's value of $.77 \pm .04 \times 10^{-3}$, or

the author's $1.17 \pm .05 \times 10^{-3}$. Such poor agreement is unexpected after the success of the prediction of τ_θ, but the expected crudeness of a theory that depends upon a hard sphere model suggests that the difference between the measured and predicted B values is nonetheless reasonable, that of the τ_θ values extraordinary. Since the theoretical expression for B depends upon τ_θ, the latter is bound to be better predicted than B, which suffers from inadequacies in two theories, not only one.

No attempt was made to check experimentally the intermolecular relaxation constant, C. Other values might have given a better linear fit in Figure 3, but C is too small to be determined accurately in this type of experiment. To estimate the relative importance of the three relaxation mechanisms, we may choose x = 1.0 and find (using Mr. Burke's experimental data)

$$\frac{1}{T_1} = A\eta + B/\eta + C\eta$$

$$.43 = .26 + .14 + .03$$

Thus the contribution of intramolecular dipole relaxation is about ten times that of its intermolecular analogue, and twice that of spin-rotational relaxation.

It is certainly possible that other relaxation

mechanisms do contribute in trifluorotoluene-carbon disulfide solutions. It is also possible that the theoretical models for τ_θ, B, and C contain errors. The experiments reported indicate, however, that the viscosity dependence of the theoretical expressions is correctly given. The findings are consistent both with the Debye model and with the more recent work of Powles and Green. It should be emphasized that no correlation times were actually measured; at the frequency employed (13.2 mc), whose associated time is of the order of 10^{-8} seconds, a correlation time of some 10^{-11} seconds may only be determined indirectly.

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