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 Hubbard[18] 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 $\tau_{\text{rot}}/\tau_{\text{trans}}$. Employing reasonable estimates for these quantities leads to a correction of approximately 15%. Recently Harmon[38] 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 $1.9\pm 0.1\times 10^{-8}$ 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–Muller[17] formulation would lead to a maximum correction, for glycerol, in $1/T_1$ of a 2% or 3% increase.

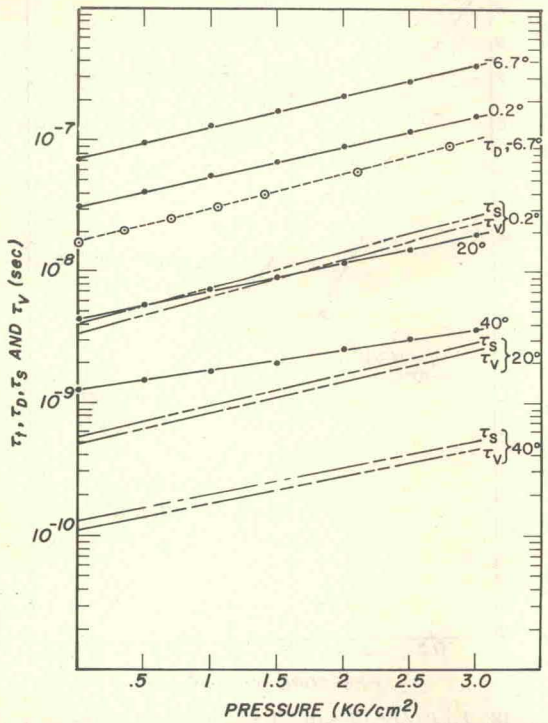

FIG. 15. Comparison of τ_t, τ_s, τ_v, and τ_D as functions of pressure with temperatures a parameter in glycerol. τ_t solid line, τ_s, τ_v, and τ_D as labeled.

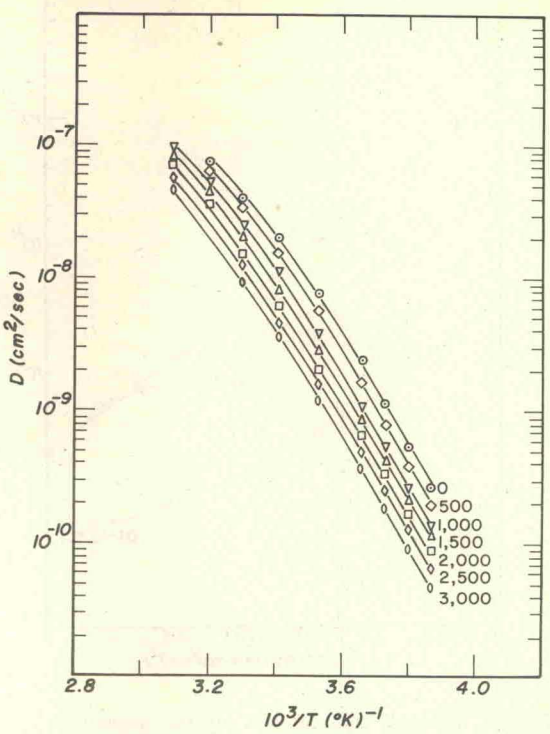

FIG. 16. Diffusion constant vs $10^3/T(°K)^{-1}$ with pressure as a parameter in glycerol.

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.

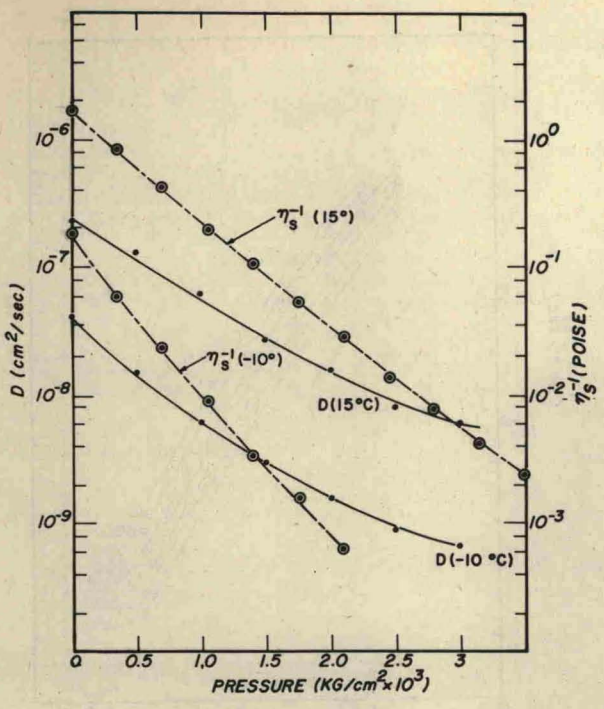

FIG. 17. Diffusion constant and inverse viscosity vs P with temperature a parameter in 2-methylpentanediol 2, 4. These diffusion constants were calculated from the best fit T_1, T_2, reduction as described in the text.

For glycerol, comparison of the pressure dependence of τ_t with τ_s and τ_v is possible in the temperature range -10–$+60$°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 includes $T_1(P)/T_1(1)$ for comparison. As mentioned above, Bull and Jonas[15] have shown for the mobile liquids acetone, benzene, and chlorobenzene, that $1/T_{1_{\text{inter}}} \propto 1/D \propto \eta$ 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 $T = 50$°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)

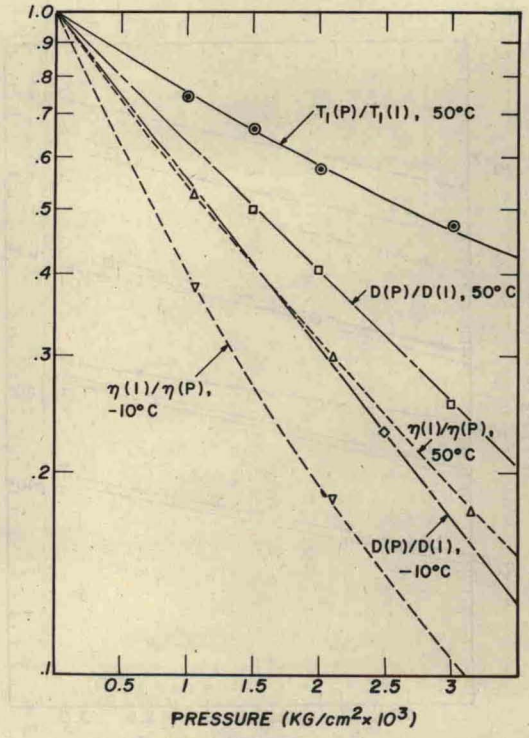

FIG. 18. $T_1(P)/T_1$ $(P=0)$, $D(P)/D(P=0)$, $\eta_s(P=0)/\eta_s(P)$ vs pressure at 50° and -10°C in glycerol. These diffusion constants were calculated from the best fit T_1, T_2, reduction as described in the text.