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 $+70°C$ 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 Meister[33] 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 τ_{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 Meister[34] only in the strength factor $2\gamma^4\hbar^2 I(I+1)/5d_{intra}^6$.[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
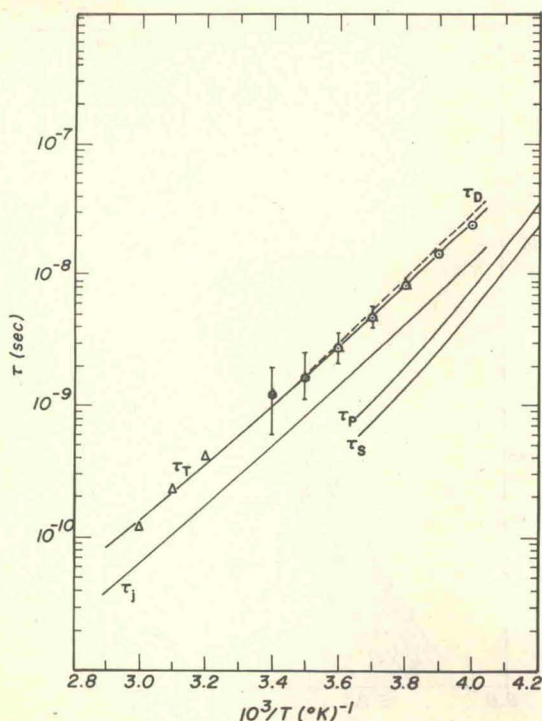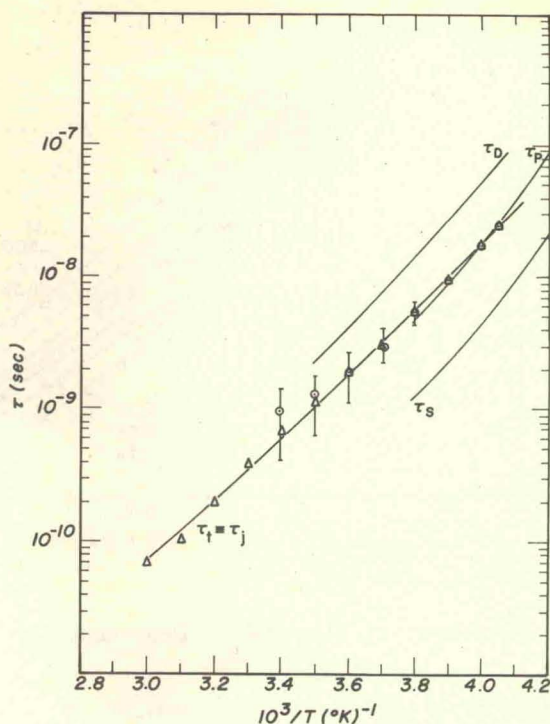
FIG. 12. Comparison of τ_t, τ_j with other relaxation times at atmospheric pressure, for 2-methylpentanediol 2,4. ⊙ From the T_1, T_2 fit; △ from T_1, D fit.

FIG. 11. Comparison of τ_t, τ_j with other relaxation times at atmospheric pressure for 1,3-butanediol. ⊙ From the T_1, T_2 fit; △ 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 $1/T_{1\,rot}$ 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 $1/T_{1\,rot}$ were made utilizing the above assumptions and the correlation times from quadrupolar data. It was observed that in the low temperature region the generated $1/T_{1\,rot}$ 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 $1/T_{1\,rot}$ was greater than $\approx 10\%$ of the measured data at the point of closest approach, i.e., this implies a $d_{intra} > 1.9$ 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.
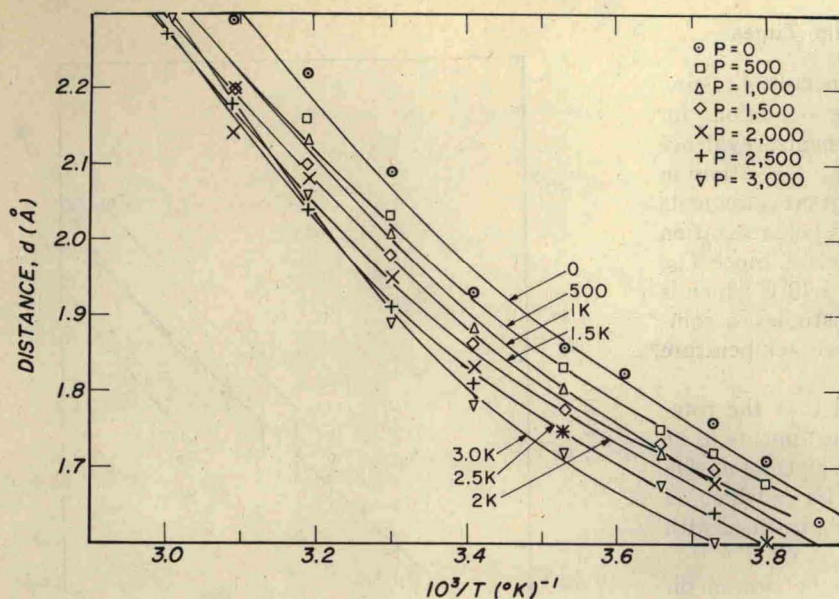
FIG. 13. Distance of closest approach vs $10/T(°K)^{-1}$ with pressure a parameter in glycerol.

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 $\alpha \geq 1/72$. 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.
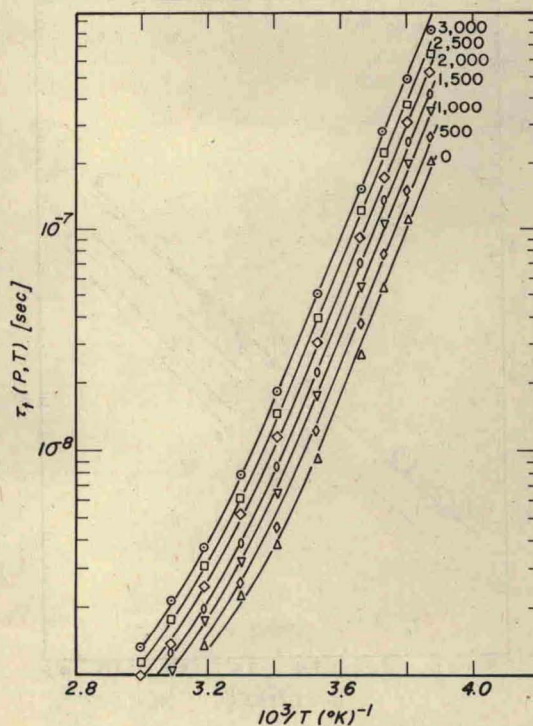

FIG. 14. τ_t vs $10^3/T(K°)^{-1}$ with pressure a parameter for glycerol using $\alpha = 0.005$.