between the pole faces of the magnet. The bath was proportionally controlled to ±0.1°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. 2. T_1 as a function of temperature with pressure a parameter at 30 MHz for 1,3-butanediol.
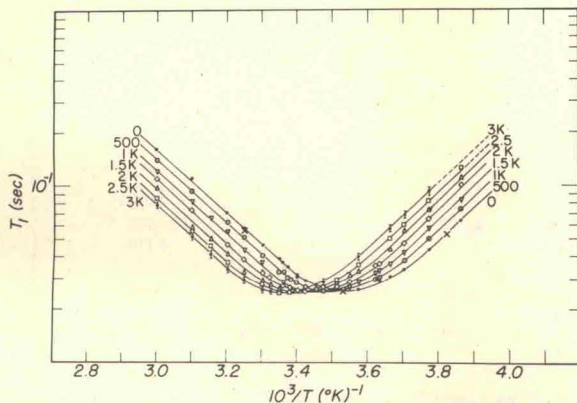

FIG. 1. T_1 as a function of temperature with pressure a parameter at 30 MHz for glycerol. The × represents atmospheric data taken from Connor, Ref. 27.

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
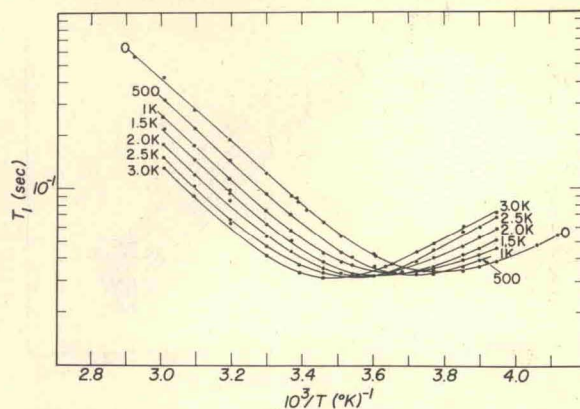
every 500 kg/cm² from 0–3000 kg/cm² and the pressure is slowly returned to atmospheric pressure before changing the temperature. T_1 and T_2 are then measured at the next desired temperature and the results compared with the atmospheric temperature reference run. If their values are within ±5% of the 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°–90° pulse pair sequence.

T_2 measurements for the range 10^{-1}–3×10^{-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.
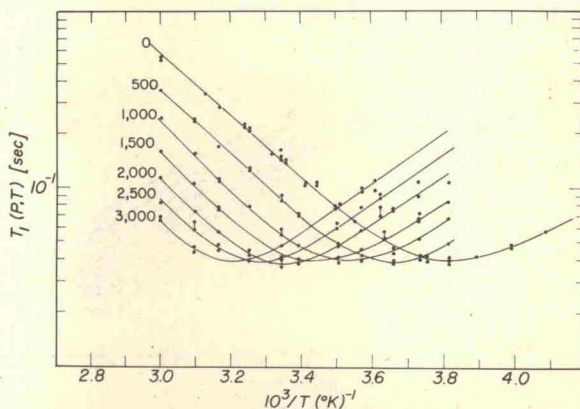

FIG. 3. T_1 as a function of temperature with pressure a parameter at 30 MHz for 2-methyl-2,4-pentanediol.
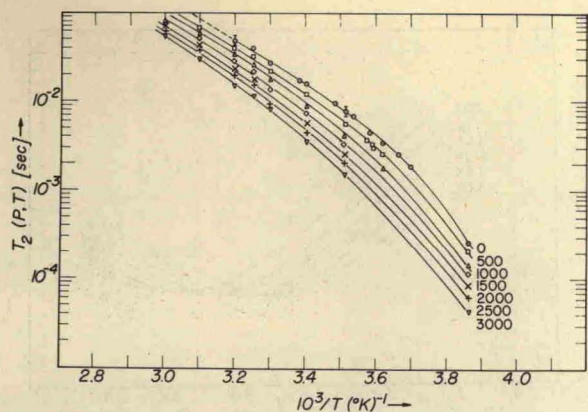
FIG. 4. T_2 as a function of temperature with pressure a parameter at 30 MHz for glycerol.

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 Connor[27] who has measured $T_1(T)$ at 30 MHz from -77 to $+160°C$. 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 ($-20-+70°C$). 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 Powles[28] at 21.5 MHz who measured T_1 and T_2 from -50 to $+83°C$, and the unpublished T_1, T_2 data of Drake[29] 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 ($0-+21°C$) and is confined to the region of the T_1 minimum where the slope of T_2
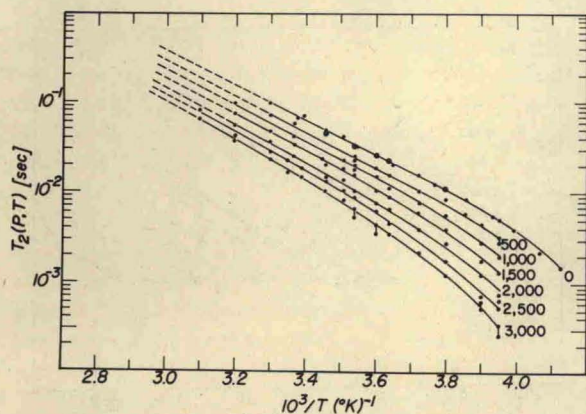

FIG. 5. T_2 as a function of temperature with pressure a parameter at 30 MHz for 1,3-butanediol.

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 °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.
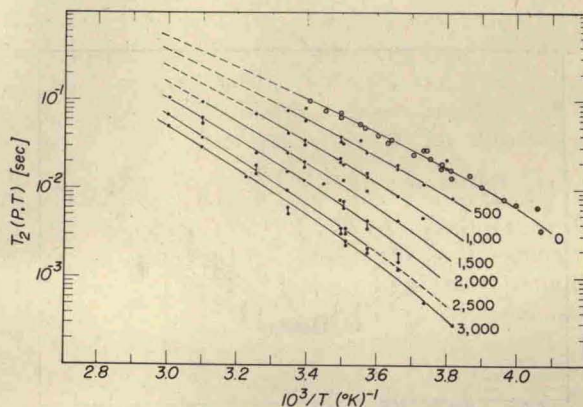

FIG. 6. T_2 as a function of temperature with pressure a parameter at 30 MHz for 2-methyl-2,4-pentanediol.

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 NP[7] 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