diffusion constants, as functions of temperature and pressure; D_{exptl}, experimentally measured diffusion constants.

Butanediol 1,3							2-Methlypentanediol 2,4						
Pressure (kg/cm²)							Pressure (kg/cm²)						
0.0	0.5	1.0	1.5	2.0	2.5	3.0	0.0	0.5	1.0	1.5	2.0	2.5	3.0
1.21					12.4	15.2	0.764				9.1	16.2	21.4
2.18					3.07	3.08	2.12				3.06	2.81	2.77
					2.05	1.69					2.78	1.96	1.43
10.6							23.5						
2.23			9.95	22.4	14.3	32.3	1.21			8.4	12.4	26.0	31.9
2.30			2.83	3.13	2.73	3.01	2.15			2.18	2.52	2.65	2.53
			2.17	1.18	1.41	0.755				3.83	2.05	1.08	0.803
6.4							15.2						
4.04		7.15	11.2	17.8	19.5	24.9	1.97		7.4	12.1	24.9	46.0	69.9
2.40		2.38	2.52	2.63	2.54	2.54	2.17		1.86	2.37	2.53	2.49	2.41
		2.15	1.54	1.05	0.892	0.700			4.44	2.01	1.03	0.540	0.381
3.85							9.60						
0.995	1.12	1.12	1.52	2.67	2.95	3.75	0.365	0.746	0.995	2.67	4.48	8.39	11.7
2.65	2.49	2.33	2.37	2.49	2.42	2.38	2.33	2.74	2.27	2.50	2.43	2.31	2.26
19.8	15.0	13.1	9.92	6.28	5.34	4.06		32.1	20.7	9.32	5.27	2.53	1.75
23.2							59.5						
1.24	1.62	1.78	2.49	4.18	4.97	6.23	0.995	1.12	2.24	4.97	8.58	15.3	20.5
2.44	2.37	2.28	2.30	2.36	2.31	2.24	2.70	2.47	2.42	2.40	2.29	2.14	2.13
12.9	9.41	7.92	5.76	3.60	2.91	2.18	29.3	20.1	10.8	4.64	2.45	1.20	0.882
14.0							36.0						
1.62	2.49	3.23	4.29	6.82	8.58	10.9	1.32	2.13	4.72	9.45	16.1	26.9	36.0
2.27	2.29	2.27	2.25	2.23	2.19	2.12	2.56	2.42	2.41	2.27	2.15	2.02	2.03
8.61	5.70	4.32	3.20	1.97	1.50	1.11	19.8	11.0	4.93	2.18	1.14	0.607	0.456
8.60							22.0						
2.83	4.29	5.72	7.96	11.8	14.4	18.9	1.99	3.73	8.99	17.0	28.1	45.5	59.9
2.27	2.24	2.24	2.18	2.11	2.05	1.99	2.49	2.39	2.30	2.11	2.02	1.91	1.91
4.91	3.17	2.37	1.61	1.02	0.787	0.567	12.5	6.15	2.35	1.05	0.582	0.320	0.224
5.20							13.0						
0.479	0.750	1.04	1.36	1.99	2.44	3.12	0.323	0.623	1.61	2.84	4.70	7.52	9.96
2.23	2.19	2.15	2.07	1.99	1.93	1.88	2.44	2.25	2.15	1.99	1.91	1.82	1.80
2.81	1.73	1.20	0.852	0.540	0.413	0.305	7.34	3.26	1.15	0.559	0.310	0.175	0.130
3.00							7.70						
0.858	1.27	1.74	2.29	3.18	4.10	5.25	0.535	1.33	2.66	4.78	8.06	13.0	17.1
2.18	2.10	2.04	1.96	1.88	1.81	1.75	2.36	2.22	2.00	1.87	1.77	1.69	1.67
15.0	9.38	6.43	4.52	3.00	2.17	1.57	41.6	14.9	6.04	2.93	1.56	0.880	0.654
18.0							45.0						
1.46	2.12	2.84	4.01	5.18	7.00	9.07	0.945						
2.08	2.00	1.91	1.86	1.75	1.68	1.60	2.25						
8.04	5.12	3.48	2.34	1.60	1.08	0.758	21.5						
							26.5						

the increasing uncertainty in the calculation as T_1/T_2 approaches unity is presented in Fig. 10 for glycerol where the results of the various fitting procedures are presented and the error bars on the T_1, T_2 fit points indicate this increasing uncertainty. The calculation using the ratio fit method was discontinued above 39.3°C for glycerol at atmospheric pressure and blank spaces will be noted in Table I. The values of τ_t are compared with the frequency of fit τ_t values in Fig. 10. As above, D is produced from τ_t, d and compared to the data of Fig. 8, which also contains the results of the frequency reduction.
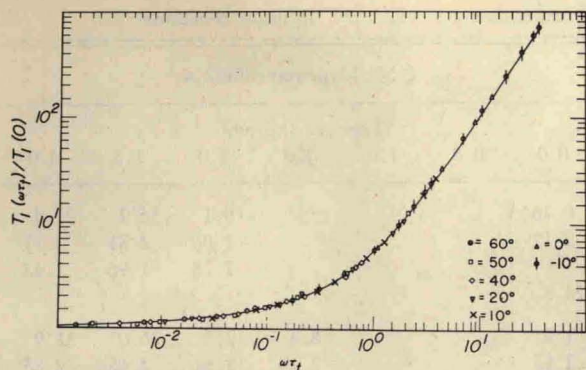
FIG. 9. Ratio $T_1 (\omega\tau_t)/T_1 (0)$ vs $\omega\tau_t$ fitted using $\alpha=10^{-5}$ and the data of Naock and Preissing.

As the figure shows the T_1, T_2 fit, produces D values for $10^3/T < 3.5°K^{-1}$ which are equal to those obtained from the frequency fit. Above $3.5°K^{-1}$ the curves begin to diverge. The reason for this discrepancy may reflect the onset of rotational contribution to the translational part which has a stronger frequency dependence than the translational or the fact that the Torrey theory does not truly represent the translational characteristics of $1/T_1$. Separation studies should provide some answers to this problem. But since this data is not available as yet, the discussion will be developed for the 30 MHz temperature data on the basis of the results of T_1, T_2 temperature fit, assuming the observed relaxation is translational in nature since this fit is consistent with the measured diffusion constants.

The errors bars of Fig. 10, on τ_t arise from the estimated $\pm5\%$ uncertainty in the glycerol T_1 and T_2 data. Since the error in the ratio T_1/T_2 increases as T_1 and T_2 come closer together the bars become large on the reduced values of τ_t with increasing temperature. To test the self-consistency of the method, the τ_t and d obtained from the 30 MHz T_1, T_2 data fit, are used to generate T_1 and T_2 for 20 MHz. The predicted T_1, T_2 values compare very well to the experimental values of Noack and Preissing, Drake, and Powles.

The range of the T_2 measurement is limited because of the onset of modulation on the T_2 echo train beyond about 35°C for all three liquids. Therefore a third reduction method, making use of T_1 data, which is not affected by modulation, and the self-diffusion constant D, which is limited by low rather than high temperatures, is used to extend the range of the reduction to recover τ_t. This method, called the T_1, D fit, provides another check on the other reduction methods in the high temperature overlap region. In the T_1, D fit, a value for τ_t and d are produced for each temperature which can be compared with overlapping values from the other reduction methods. Since D data is available only at atmospheric pressure, the results can only be compared there to those from other techniques. With the use of the T_1, T_2 fit and the T_1, D fit, the entire range

of our temperature data at atmospheric pressure can be reduced consistently.

Using the T_1, T_2 fit, the temperature data was reduced employing an $\alpha=0.07$ for BUT and $\alpha=0.2$ for MPD. The results are in good agreement with the diffusion constant values shown in Table I. Again using the iterated value of τ_t and d to produce T_1 for 10 and 20 MHz, a good fit to measured values is obtained for BUT and MPD.[32]

The ratio T_{1t}/T_{2t} at the T_1 minimum, which is theoretically a function of α, also provides a check on the fit to experimental data. In order to fit the diffusion constant for BUT and MPD values of $\alpha>0$ are necessary. While increasing α brings the fitted $D(T)$ curve closer to the data, α has an upper limit in order to be consistent with the theoretical prediction for T_1/T_2 at the minimum. The theoretical predictions of T_{1t}/T_{2t} for these liquids on the basis of $\alpha=0.005, 0.07, 0.2$ are 2.85, 2.35, and 1.9. The experimental ratios T_1/T_2 are approximately 3.6, 2.55, and 2.2, respectively, for glycerol, BUT, and MPD. Our estimate for the errors in these values is $\pm25\%$. Owing to the experimental uncertainty of the position of the T_1 minimum in temperature space, and the rapid falloff of the T_2 data in the region of the minimum, the values are in reasonable agreement with the theory.
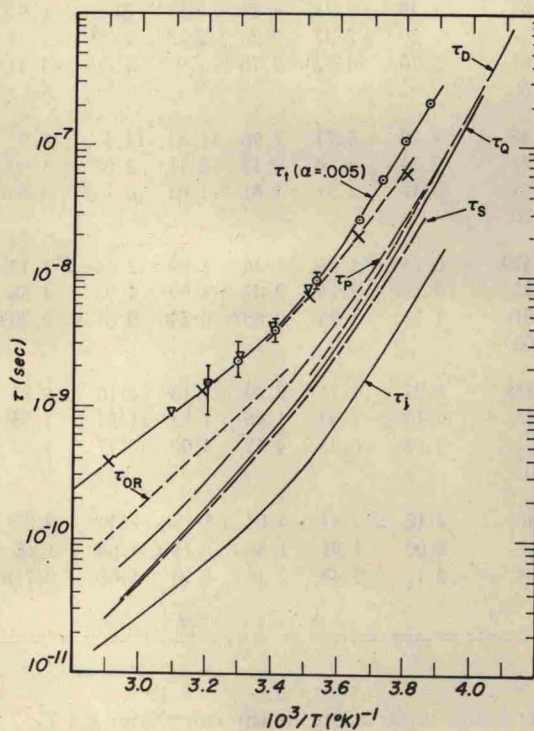

FIG. 10. The values of τ_t obtained from the three fitting procedures employed: $\odot$ from T_1, T_2 fit, x from $T_1(\omega)$ frequency fit, ∇ from T_1, D fit. The jump time τ_j is from Eq. (10). The other correlation times are drawn for comparison: τ_D dielectric, τ_Q quadrupolar, τ_p the mechanical volume at constant pressure τ_s mechanical shear, and τ_{oR} depolarized orientation.