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RELATIVE VISCOSITY

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and Cappi and Bett.[12] The present n-pentane data at 30°C are bracketed by the results from these earlier investigations [7, 12] each of which had a reported accuracy of ±1 %.

High pressure viscosity measurements were made on benzene at 30 and 50°C and on cyclohexane and carbon tetrachloride at 50°C using an unpolished quartz crystal with a fundamental frequency of approximately 30 kHz. Because of the rougher surface of this crystal, the value of K_1 was affected more by the change in kinematic viscosity of the medium than for polished crystals. Although these results showed slightly more experimental scatter, the smoothed values agreed to ±0.5 % with the polished crystal data.

At present the theory of the viscosity of liquids has not developed sufficiently to enable meaningful comparisons between theory and experiment to be made for molecules as complex as those presented here. It is, however, of interest to compare briefly the results expected on the Enskog theory. According to Enskog [14] the viscosity of a dense fluid η can be written in terms of the value of the corresponding dilute fluid η_0 at the same temperature by the equation:

$$\frac{\eta V}{\eta_0 b_0} = \frac{1}{y} + 0.8 + 0.76y, \tag{7}$$

where $b_0 = 2\pi N\sigma^3/3$ with σ the molecular diameter and $y = (pV/NkT) - 1$. It follows that the relative change in viscosity as a function of pressure is

$$\frac{\eta_p}{\eta_1} = \frac{V_1 y_1}{V_p y_p}\left(\frac{1 + 0.8y_p + 0.76y_p^2}{1 + 0.8y_1 + 0.76y_1^2}\right). \tag{8}$$

To obtain some relevance of hard-sphere theory to experiment for real systems Michels and Gibson [15] suggested replacing the pressure by the kinetic pressure $T(\partial p/\partial T)_V$, so that $y = V/R(\partial p/\partial T)_T^{-1}$. If this is done for the present results, table 4 shows poor agreement with experiment even for the simplest member of the present series CCl_4. The results for n-pentane, e.g., show that as the pressure increases the discrepancy becomes worse, being approximately a factor of 5 at 7000 bar. No other

TABLE 4.—COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF η_p/η_1 FOR CCl_4 AT 30°C

P (bar)	1	250	500	750	1000	1250
η_p/η_1 expt.	1	1.250	1.530	1.842	2.186	2.563
η_p/η_1 calc.	1	1.037	1.075	1.108	1.179	1.269

theory without a number of adjustable parameters at present seems capable of producing the steep pressure dependence of viscosity that actually occurs for even moderately complex organic liquids such as are reported here.

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