

The effects of pressure on the density, dielectric constant, and viscosity of several hydrocarbons and other organic liquids

D. W. BRAZIER AND G. R. FREEMAN

Chemistry Department, University of Alberta, Edmonton, Alberta

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The effects of pressures up to 4 kbar on the density, dielectric constant, and viscosity of *n*-pentane, *n*-hexane, *n*-octane, cyclopentane, methylcyclohexane, and 2,2-dimethylbutane (DMB) were measured at 30 °C. The pressure effects on the viscosities of *n*-hexane and *n*-octane were also determined at 0 and 60°. The densities of diethyl ether and cyclopentanone and the dielectric constant of carbon tetrachloride at high pressures are also recorded. The densities of the hydrocarbons increased by 20–30%, and the dielectric constants increased by 11–16% as the pressure was increased from 1 to 4000 bars at 30°, but the viscosities increased by 695–2352% over the same pressure range. Carbon tetrachloride froze at 1500 bars at 30°, and cyclopentanone froze at 3500 bars at about 20°. In agreement with earlier work on other liquids, the value of the Clausius–Mosotti function $(\epsilon - 1)V/(\epsilon + 2)$ for the present compounds decreased slightly with increasing pressure. The viscosity at a given pressure decreased slightly with increasing temperature, and temperature effect increased with increasing pressure. In general, the smaller the compressibility of the liquid, the greater was the effect of pressure on the viscosity; DMB was an exception because its viscosity increased abnormally rapidly with pressure. Molecular structure and liquid structure have greater influences on the pressure dependence of viscosity than on that of density or dielectric constant.

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Introduction

As part of an investigation of the effect of pressure on the radiation induced conductance of liquid hydrocarbons (1), it was necessary to measure the variation of the density, dielectric constant, and viscosity of the liquids. The hydrocarbons used in the conductance study were *n*-pentane, *n*-hexane, *n*-octane, cyclopentane, methylcyclohexane, and 2,2-dimethylbutane. These and several other compounds were used in the present work. Values of pressure coefficients of physical properties of many liquids have been reported earlier (2–9).

Experimental

High Pressure System

The high pressure system is described briefly in ref. 1 and in detail in ref. 10. The pressure vessel temperature was controlled to within $\pm 0.5^\circ$ over the range 0–60 °C.

Materials

The *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, cyclopentane, methylcyclohexane, and 2,2-dimethylbutane were Phillips Research Grade and were purified as described earlier (1). Phillips Research Grade benzene was purified by repeated partial recrystallization. Eastman Spectroscopic Grade carbon tetrachloride and diethyl ether were used as supplied. Dodecane, tetradecane (both from Eastman Organic Chemicals), and octadecane (Matheson, Coleman and Bell) were also used as supplied. Eastman White Label cyclopentanone was distilled twice through a 45 cm column packed with glass helices, retaining the middle 50% each time.

A series of viscometric standard oils, which were mixtures of high boiling straight chain hydrocarbons, were obtained from the Cannon Instrument Co. This company also supplied the precalibrated Ubbelohde viscometers. Silicone oils from Dow Corning Co. were also used during the calibration of the rolling ball viscometer. The viscosities of the silicone oils were measured with the Ubbelohde viscometers.

Density Measurements

The change of liquid volume with pressure was measured using a bellows dilatometer (3, 11). A detailed description of the apparatus is given elsewhere (10). The internal volume of the dilatometer was 20 ml. The change of volume of the bellows was measured with a slide wire, using the potential ratio technique (11). The dilatometer operation was calibrated at atmospheric pressure, using a special apparatus (10).

Dielectric Constant Measurements

The dielectric constants of the hydrocarbons were measured at pressures up to 4 kbar in the cell shown in Fig. 1. Pressure was transmitted to the cell interior by a teflon piston and cylinder of the type described by Jamieson (12). The leads from the cylindrical platinum electrodes through the Supramica plug (Fig. 1) were cemented with Armstrong Epoxy Resin cement. Samples of the latter cement, cured for 4 days at 80°, were placed in contact with the hydrocarbon liquids for 4 months and no change in the dielectric constants of the liquids was observed.

Capacitance measurements were made with a General Radio Impedance Bridge, Model 1608-A. The bridge was calibrated with an accuracy of ± 0.02 pF. The capacitance measurements were conducted at 1 kc. The total system capacitance at 30° and atmospheric pressure was determined with a series of standard dielectrics between the cell plates. The standards used were air ($\epsilon = 1.0005$),

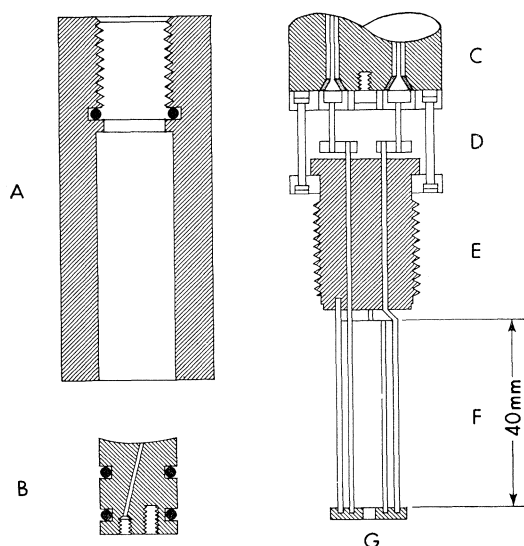


FIG. 1. Dielectric constant cell (not to scale): A, teflon cylindrical cell walls; B, teflon piston with "O" ring seals; C, pressure vessel closure piston; D, stainless steel and teflon cell holder; E, Supramica Ceramoplastic plug; F, cylindrical platinum electrodes (0.25 mm thick); G, teflon cap.

cyclohexane ($\epsilon = 2.023$), carbon tetrachloride ($\epsilon = 2.239$), benzene ($\epsilon = 2.274$), and diethyl ether ($\epsilon = 4.335$). The total capacitances at atmospheric pressure ranged from 40 to 70 pF. A calibration graph was plotted of total capacitance vs. dielectric constant of the liquid in the cell.

Viscosity Measurement

A rolling ball viscometer (13, 14) was used to measure the viscosities of the liquids at pressures up to 4 kbar. The principle of operation was to measure the amount of time required for a ball to roll a given distance down a tilted tube full of liquid. A steel ball, 6.35 mm diameter, and a precision bore quartz tube, 7.99 ± 0.01 mm internal diameter, were used. The roll tube with ball-detector coils is illustrated in Fig. 2. The roll tube was inserted in a tiltable pressure vessel.

Full details of the viscometer construction and operation are given elsewhere (10). Briefly, the roll tube and detector device were placed within a cylindrical stainless steel holder that contained a bellows section for the transmission of pressure. Electrical connections to the interior of the holder, through end plate H (Fig. 2), were made with Latronics Corp. metal to ceramic terminal seals. The detector coils, in slots E, were each 100 turns of 30 gauge magnet wire (Belden Wire Co.). The coils were wound in series.

The electrical circuit and timing device used in conjunction with the detector coils are described in ref. 10. The time required for the ball to roll between the two detector coils was measurable with a precision of $\pm 0.3\%$.

All the components of the viscometer and holder were cleaned in a Soxhlet extractor before being assembled. The solvent used was either hexane or the hydrocarbon to

be investigated. Soldered components underwent a preliminary extraction with water.

The assembled viscometer and holder were tested for leaks on a vacuum line, then filled by a technique similar to that used for the filling of the conductance cells (10).

The viscometer was calibrated with a series of liquids of known viscosity. The calibration plot for 30°C is shown in Fig. 3. The variables of the system were correlated with the expression (14)

$$[1] \quad \eta = \kappa(\rho_s - \rho_L)t$$

where η is the viscosity, κ is the viscometer coefficient, ρ_s and ρ_L are the densities of the ball and the liquid, respectively, and t is the roll time. The variation of ρ_s with

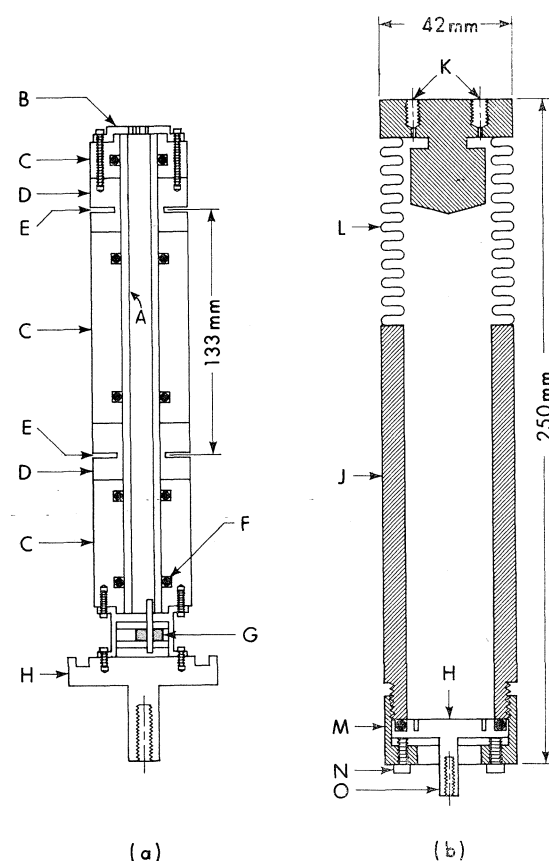


FIG. 2. (a) Viscometer roll tube assembly (not to scale): A, quartz roll tube; B, perforated cap; C, aluminium cylinder section, slotted on the outside to allow liquid to flow to the bottom of the cell holder; D, Lucite detector coil bobbin; E, detector coil slot; F, "O" ring; G, electro-magnet; H, stainless steel base plate.

(b) Viscometer roll tube holder (not to scale): Constructed of stainless steel; H, base plate; J, cylinder; K, filling apertures in cap, to be closed by needle valve type screws; L, bellows; M, compression screw cap; N, compression screw (8 in all); O, tapped stem, to fix viscometer to pressure vessel closure piston.

TABLE I
Pressure dependences of relative volumes of several hydrocarbons at 30 °C

Pressure (bars)	Relative volume						
	<i>n</i> -Pentane	<i>n</i> -Hexane	<i>n</i> -Heptane	<i>n</i> -Octane	Cyclo- pentane	Methyl- cyclohexane	2,2-Dimethyl- butane*
1	1.000	1.000	1.000	1.000	1.000	1.000	1.000
500	0.930	0.941	0.945	0.953	0.947	0.956	0.935
1000	0.889	0.905	0.909	0.921	0.914	0.928	0.900
1500	0.859	0.877	0.882	0.898	0.888	0.906	0.872
2000	0.836	0.858	0.863	0.879	0.867	0.888	0.853
2500	0.821	0.841	0.848	0.863	0.850	0.872	0.837
3000	0.804	0.826	0.834	0.848	0.837	0.858	0.823
3500	0.791	0.814	0.823	0.837	0.825	0.846	0.812
4000	0.778	0.803	0.813	0.827	0.815	0.836	0.802
4500	0.767	0.796	—	—	0.807	0.828	—
Molar volume (cm ³) at 1 bar	117.03	132.46	148.38	164.53	95.32	129.08	134.9
Density (g/cm ³) at 1 bar	0.6165	0.6505	0.6753	0.6942	0.7357	0.7606	0.639

*Estimated from data in ref. 3.

pressure and temperature was negligible; $\rho_s = 7.78 \pm 0.02$ g/cm³ under all conditions used. Values of ρ_L were taken from Table I.

The variation of $(\rho_s - \rho_L)t$ with η was determined at several temperatures in the range 0–60 °C for each of the two angles of inclination. The values of $(\rho_s - \rho_L)t$ plotted in Fig. 3 were obtained for 30 °C by graphical interpolation. Similar plots were made for 0 and 60 °C. The values of η were taken from ref. 15 or were measured with an Ubbelohde viscometer. All of the standards used, except the two cyclic hydrocarbons, fell on a smooth curve at each temperature (Fig. 3). The cause of the deviation of the cyclic compounds is unknown, but it may have to do with an effect of liquid structure on eddy currents. The flow of liquid past the ball in the tube was probably

turbulent, indicated by the fact that the value of κ was viscosity dependent under the present conditions (see ref. 14).

The viscosities of the hydrocarbons under pressure at 30 °C were obtained by evaluating $(\rho_s - \rho_L)t$ and reading the corresponding values of $\log \eta$ from Fig. 3. It was assumed that the calibration plot obtained at atmospheric pressure was valid at higher pressures, the change in the roll time arising only from the increased viscosity. This assumption is reasonable because the dimensions of the ball and of the roll tube were reduced by only 0.1 and 0.3 %, respectively, at 4.5 kbar.

Results and Discussion

Pressure Dependence of Density

The pressure–volume relationships were determined for *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, cyclopentane, and methylcyclohexane at 30° and pressures up to 4.5 kbar. The results are reported as relative volumes, i.e. the ratio of the volume at pressure p to that at 1 bar, and are listed in Table I. The absolute densities and molar volumes at 1 bar are also given.

There was no hysteresis in the measurements. The value of the potential ratio obtained from the dilatometer at atmospheric pressure after a pressure cycle agreed with the value obtained before the pressure was applied, to within 0.1%. At least two runs were done for each compound, and the results were averaged. The reproducibility of the relative volumes measured from one experiment to the next was $\pm 0.25\%$ at 4000 bars, and was better at lower pressures.

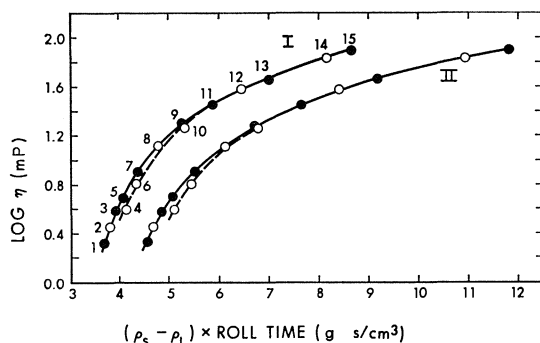


FIG. 3. Viscometer calibration plot, 30 °C: I, 30° angle of inclination; II, 20° angle. The liquids used were: 1, *n*-pentane; 2, *n*-hexane; 3, 2,2-dimethylbutane; 4, cyclopentane; 5, *n*-octane; 6, methylcyclohexane; 7, *n*-decane; 8, *n*-dodecane; 9, *n*-tetradecane; 10, Dow silicone oil (2 cts); 11, Cannon standard oil S3; 12, *n*-octadecane; 13, Dow silicone oil (5 cts); 14, Cannon standard oil S6; 15, Dow silicone oil (10 cts).

TABLE II
Pressure dependences of relative volumes of diethyl
ether and cyclopentanone

Pressure (bars)	Relative volume	
	Diethyl ether (30°)	Cyclopentanone (25°)
1	1.000	1.000
500	0.939	0.964
1000	0.893	0.938
1500	0.866	0.899
2000	0.842	0.884
2500	0.824	0.872
3000	0.811	0.860
3500	0.799	0.850
4000	0.786	0.841
Molar volume (cm ³) at 1 bar	105.61	89.2
Density (g/cm ³) at 1 bar	0.7018	0.943

Pressure-volume measurements on 2,2-dimethylbutane were not done. The relative volumes of this compound at 30° at different pressures were estimated graphically from Bridgman's data (3), and are listed in Table I.

Table II lists the relative volumes measured for diethyl ether at 30° and cyclopentanone at 25°. These measurements are related to other studies in this laboratory. It was also noted that if the temperature of cyclopentanone at 3500 bars was lowered to 20°, the sample froze. This tends to support the interpretation (16) that the rapid decrease in the radiation yield of isomerization of

cyclopentanone to 4-pentenal, as the pressure was increased from 3000 to 5000 bars at about 25°, was due to the solidification of the sample.

Where comparison with other literature values is possible (3, 5, 6), the present results agree with them to within 0.2%. The only exception was *n*-pentane, for which the present result at 4 kbar was 1% higher than that estimated graphically from Bridgman's data at 0, 50, and 95° (3).

Pressure Dependence of Dielectric Constant

The total capacitance of the system was determined as a function of pressure with a given liquid in the cell, and the dielectric constant was read directly from the calibration graph. The sensitivity of the system was approximately 10 pF per unit change in dielectric constant. The agreement between the total capacitance values before and after a pressure cycle was usually within 0.5%, unless a phase change had occurred. The cell became distorted if the sample froze in it. The change in cell capacitance caused by the decrease in the electrode dimensions with increasing pressure amounted to an error of 0.06% in the measured capacitance at 4 kbar. This was calculated using the volume compressibility of platinum, which is (2)

$$[2] \quad \beta = 3.6 \times 10^{-7} - 3.6 \times 10^{-12} p$$

where p is the pressure in kg/cm² (1 bar = 1.02 kg/cm²).

Values of the relative dielectric constant, i.e. the

TABLE III
Pressure dependences of relative dielectric constants at 30°

Pressure (bars)	Relative dielectric constants						
	<i>n</i> -Pentane	<i>n</i> -Hexane	<i>n</i> -Octane	Cyclo- pentane	Methylcyclo- hexane	2,2-Dimethyl- butane	Carbon tetrachloride
1	1.000	1.000	1.000	1.000	1.000	1.000	1.000
500	1.045	1.036	1.026	1.037	1.028	1.039	1.034
1000	1.074	1.060	1.047	1.060	1.047	1.068	1.055
1500	1.096	1.078	1.064	1.079	1.063	1.087	1.069§
2000	1.114	1.094	1.077	1.094	1.074	1.102	—
2500	1.129	1.107	1.087	1.108	1.089	1.116	—
3000	1.142	1.118	1.096	1.121	1.099	1.128	—
3500	1.153	1.129	1.106	1.133	1.108	1.139	—
4000	1.163	1.138	1.113	1.144	1.116	1.149	—
Dielectric con- stant* at 1 bar	1.83†	1.875†	1.935‡	1.96†	2.01†	1.86†	2.217†

*Estimated from reported values or from the square of the refractive index. The latter values are reported to only three significant figures. The source references are cited.

†See ref. 21.

‡See ref. 22.

§Freezes at 1500 bars at 30°; see ref. 23.

TABLE IV
Pressure dependence of relative viscosity of *n*-hexane and *n*-octane

Pressure (bars)	Relative viscosity					
	<i>n</i> -Hexane			<i>n</i> -Octane		
	0°	30°	60°	0°	30°	60°
1	1.00	1.00	1.00	1.00	1.00	1.00
500	1.63	1.58	1.61	1.70	1.62	1.56
1000	2.20	2.18	2.24	2.43	2.26	2.23
1500	2.91	2.81	2.82	3.30	3.12	2.95
2000	3.67	3.44	3.45	4.38	4.09	3.73
2500	4.54	4.35	4.17	6.25*	5.28	4.62
3000	5.70	5.30	4.98	—	6.83	5.79
3500	7.01	6.47	5.69	—	8.85	7.58
4000	8.63	7.75	6.82	—	11.64	9.95
$\eta(\text{cP})$ at 1 bar	0.381	0.285	0.223	0.712	0.487	0.359

*Freezes above 2500 bars.

ratio of the dielectric constant at pressure p to that at 1 bar, are listed for *n*-pentane, *n*-hexane, *n*-octane, cyclopentane, methylcyclohexane, 2,2-dimethylbutane, and carbon tetrachloride at 30° in Table III. The absolute values of the dielectric constant at atmospheric pressure are also given.

The present results for *n*-pentane and *n*-hexane agree with those of earlier workers (8, 9). Our values of the relative dielectric constant at 30° and 2 kbar for *n*-pentane and *n*-hexane are 1.114 and 1.094, respectively, whereas those estimated from the literature are 1.113 (8) and 1.096 (9), respectively.

The Clausius-Mosotti (C.M.) function is

$$[3] \quad \frac{\epsilon - 1}{\epsilon + 2} V = \frac{4}{3} \pi N \alpha$$

where ϵ is the dielectric constant, V is the molar volume of the liquid, N is Avogadro's number, and α is the molecular polarizability. This function is frequently used to describe the relationship between the molar volume, or density, and the dielectric constant of a medium. It is usually assumed that the C.M. function is independent of the density of the medium, but plots of the left-hand side of eq. [3] against the densities of liquids at high pressures have slightly negative slopes (see Fig. 4 and refs. 2, 7-9). Two possible explanations of the negative slope are (a) that the form of the C.M. function is incorrect at high densities (17), and (b) that the molecular polarizabilities decrease with increasing pressure (18, 19). Both (a) and (b) may contribute to the observed effect.

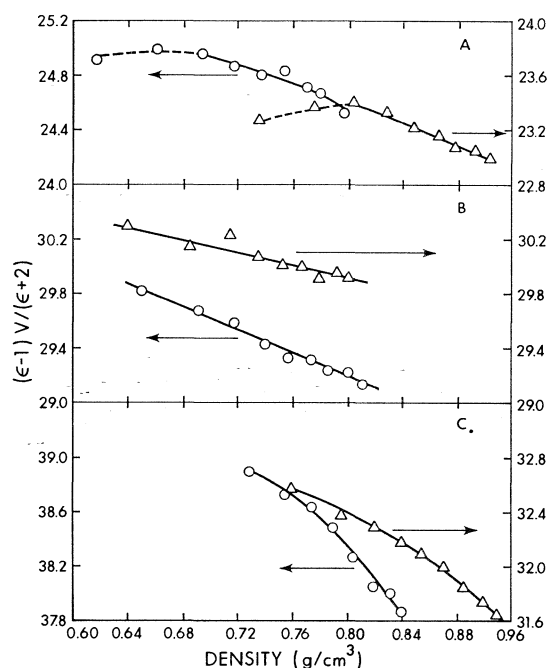


FIG. 4. Clausius-Mosotti function plotted against density at 30°C. A: \circ , *n*-pentane; Δ , 2,2-dimethylbutane. B: \circ , *n*-hexane; Δ , cyclopentane. C: \circ , *n*-octane; Δ , methylcyclohexane; \circ , left hand scale; Δ , right hand scale.

Pressure Dependence of Viscosity

The relative viscosities, i.e. values of the ratio of the viscosity at pressure p to that at 1 bar at the same temperature, of *n*-hexane and *n*-octane at 0, 30, and 60 °C are listed in Table IV. The relative viscosity increased greatly as the pressure was

TABLE V
Pressure dependence of relative viscosity of *n*-pentane, cyclopentane, methylcyclohexane, and 2,2-dimethylbutane at 30°

Pressure (bars)	Relative viscosity			
	<i>n</i> -Pentane	Cyclopentane	Methylcyclohexane	2,2-Dimethylbutane
1	1.00	1.00	1.00	1.00
500	1.53	1.64	1.67	2.00
1000	2.08	2.36	2.50	3.03
1500	2.73	3.00	3.59	4.44
2000	3.47	3.87	5.18	6.05
2500	4.17	4.64	7.10	8.33
3000	5.00	5.62	10.30	12.06
3500	5.93	6.90	14.23	16.57
4000	6.95	8.10	18.41	23.52
η (cP) at 1 bar	0.216	0.390	0.641	0.330

increased from 1–4000 bars; it decreased slightly as the temperature was increased from 0–60°. The temperature effect increased with increasing pressure.

The absolute values of the viscosities at 1 bar are given at the bottom of Table IV.

The relative viscosities of *n*-pentane, cyclopentane, methylcyclohexane, and 2,2-dimethylbutane at 30° and pressures up to 4000 bars are listed in Table V. The absolute viscosities at 1 bar are also given.

The present 30° data for *n*-pentane, *n*-hexane, *n*-octane, and methylcyclohexane may be compared with results of Bridgman (2). The present results for hexane and octane are 6% lower than Bridgman's at 4000 bars, but the discrepancy decreases with decreasing pressure. The cause of the difference is not known. The present result for pentane is 1% lower and that for methylcyclohexane is 2% lower than Bridgman's at 4000 bars.

Although the relative volumes of similar organic compounds are similar at a given pressure, the relative viscosities of the compounds at a pressure of several thousand bars vary over a wide range (2). In the current work the relative volumes of the hydrocarbons at 4000 bars were all in the range from 0.836 to 0.778, whereas the relative viscosities at this pressure varied from 6.95 to 23.5. With the exception of 2,2-dimethylbutane, which has been exceptional throughout this work (1), the relative viscosity at 4000 bars increases with the relative volume at that pressure (Fig. 5). A "large" value of the relative volume at a high pressure implies a small compressibility of the liquid. Thus, when comparing several similar

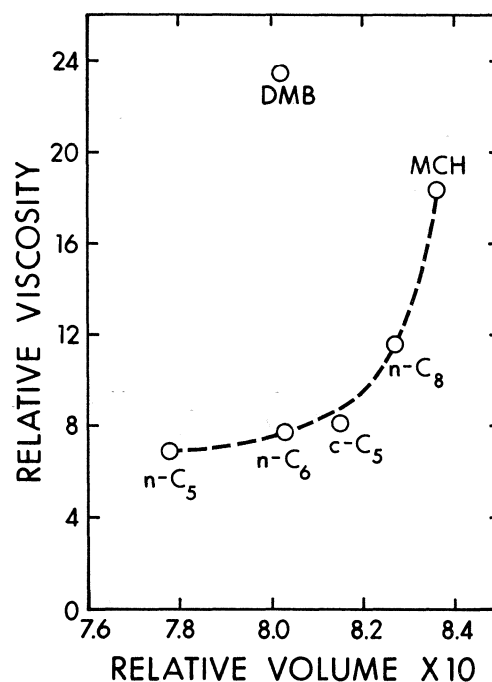


FIG. 5. Relative viscosity vs. relative volume for several hydrocarbons at 4000 bars and 30 °C. DMB is 2,2-dimethylbutane and MCH is methylcyclohexane.

liquids, a large relative viscosity is linked to a small compressibility; both of these properties are probably linked to a close molecular packing in the liquid.

The abnormally high value of the relative viscosity of 2,2-dimethylbutane (Fig. 5) supports the observation of Bridgman (2) that the vis-

cosity-pressure effects are largest for those liquids with the most complicated molecules. For example, isocompounds showed larger viscosity increases than did the isomeric normal compounds (2). It is clear that molecular structure and liquid structure have great influences on the magnitude of the effect of pressure on viscosity.

The free volume theory of liquids adequately describes the pressure and temperature dependences of the viscosities of the liquids *n*-pentane, *n*-hexane, and *n*-octane, provided one assumes that the "limiting specific volume" increases with increasing temperature and decreases with increasing pressure in ways similar to the changes in the specific volume of a solid (20). The theory was applied only to liquids whose viscosities were not described by the Arrhenius equation (20). The theory utilizes empirical constants which cannot be evaluated for the other hydrocarbons used in the current work, due to lack of appropriate data. It would be especially interesting to attempt to apply the theory to 2,2-dimethylbutane.

Acknowledgments

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