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Effect of Pressure on Viscosity of Higher Hydrocarbons and Their Mixtures

Edward M. Griest,* Wayne Webb, and Robert W. Schiessler†

Departments of Physics and Chemistry, The Pennsylvania State University, University Park, Pennsylvania

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Using the rolling-ball method the viscosity of seven pure hydrocarbons, having 25 or 26 carbon atoms, and three binary mixtures of them has been measured to 3450 bars at 37.8°, 60.0°, 98.8°, and 135°C. The compounds included isoparaffinic, cycloparaffinic, and aromatic types. The increase in viscosity with pressure was found to be strongly dependent on molecular structure. The viscosity-temperature coefficient $1/\eta(\partial\eta/\partial T)_p$ increased with increased pressure while the viscosity-pressure coefficient $1/\eta(\partial\eta/\partial P)_T$ decreased with increased temperature. The behavior of the binary mixtures corresponded within 5% over a range of 50–100 fold change in viscosity to that of the pure compounds equivalent to them in molecular weight and average molecular structure. This remarkable agreement is interpreted to mean that the viscosity of these compounds is some additive function of their constituent groups whether these groups are combined in the same or different molecules as long as the basic molecular symmetry is unchanged. The values of the Eyring theory $\Delta F_\pm$, $\Delta H_\pm{}^j$, $\Delta S_\pm$, and $\Delta V_\pm$ for these data are discussed. For the saturated compounds at constant temperature, an approximately linear relation was found between $\log\eta$ and $[(v/v_0)^4-(v/v_0)^2]$ where v is the specific volume and η the absolute viscosity.

I. INTRODUCTION

THE viscosity of liquid substances has been studied intensively for many years because of the importance of the data both to engineering applications and to the fundamental problem of the liquid state. While the analyses of Frisch, Eyring, and Kincaid[1,2] have led to progress in understanding the problem of viscous motion, Bridgman has pointed out that the theory still needs some essential modification in the physical ideas.[3] The most extensive studies of viscosity as a function of pressure both as regards pressure range and materials studied are those of Bridgman.[3,4] Starting with Eyring's equation, Muhkerjee[5] has derived a relation between viscosity and specific volume which agrees well with Bridgman's data on the halogenated benzenes. However, the final form of Muhkerjee's expression does not afford a direct test of the ideas used in its derivation because the essential expressions are not in the final working equation. It seems worthwhile then to secure further data on the viscosity of pure substances as a function of temperature and pressure and to study them for their relationship to other specific properties of the material.

A research group at The Pennsylvania State University has synthesized over 230 high purity hydrocarbons containing from 8 to 50 carbon atoms per molecule, and including a wide variety of structure types.[6] Most of the hydrocarbons are in the C_{25} to C_{30} region. Numerous physical properties have been determined for each compound for the purpose of relating these properties to the molecular structure.[6] Thus there exists in this supply of hydrocarbons related groups of intensively studied high purity liquids which afford a unique opportunity for investigating the effect of structural variables on viscosity. The study of these liquids under pressure offers the further advantage of varying the specific volume at constant temperature, thus permitting separation of the two physical variables in their effect on viscosity.

The object of the work reported in this paper has been to determine the effect of pressure on the viscosity of a structurally related group of pure high molecular weight hydrocarbons and some binary mixtures of them. The present paper reports the experimental data obtained and certain interesting conclusions which were derived from them.

II. APPARATUS AND EXPERIMENTAL PROCEDURE

A rolling-ball viscometer of the type originated by Flowers[7] and first applied by Hersey and Shore to pressure viscometry[8] was used. The apparatus employs the empirical principle that the velocity with which a sphere moves down an inclined tube filled with liquid is a function of the liquid viscosity.

A 10-ml sample was enclosed in a 1/4-in. bore steel tube and the time interval required for a 3/16-in. steel ball to roll from one end to the other was measured to the nearest 1/100 sec by means of an electric clock. Pressure was transmitted to the confined pure liquid through a flexible brass bellows filled with the sample and connected to the roll-tube. The pressure was measured by the resistance change of a coil of manganin wire immersed in the hydraulic fluid and kept at room temperature. The resistance of manganin

* Present Address: Research Laboratory, Corning Glass Works, Corning, New York.

† Present Address: Socony Mobil Laboratories, Paulsboro, New Jersey.

[1] Eyring, Frisch, Kincaid, J. Appl. Phys. 11, 75–80 (1940).

[2] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

[3] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 77, 115–128 (1949).

[4] P. W. Bridgman, Proc. Am. Acad. Arts Sci., 61, 57–99 (1926).

[5] A. K. Mukherjee, Trans. Indian Inst. Chem. Engrs. 2, 36–42 (1948).

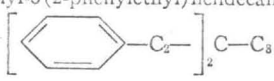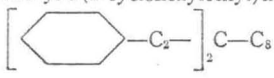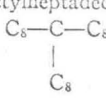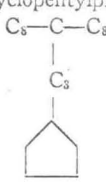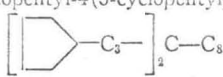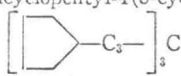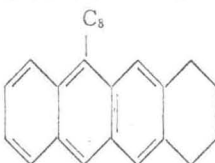[6] Schiessler *et al.* Ind. Eng. Chem. 47, 1660 (1955).

[7] A. E. Flowers, Proc. ASTM Bull. 14, 565 (1914).

[8] M. D. Hersey and H. S. Shore, Mech. Eng. 50, 221 (1928).

TABLE I. Structures and some pertinent properties of the seven pure hydrocarbons.

PSU No.	Structure[a] and name	Density[b] g/cc	$(1/\eta)(\partial\eta/\partial T)_p$[b] per °C	Melting point °C	Boiling point at 1 mm °C
18	1-Phenyl-3 (2-phenylethyl) hendecane	0.9094	0.0362	Below −60	197.0
19	1-Cyclohexyl-3 (2-cyclohexylethyl) hendecane	0.8548	0.0482	Glass −40	194.5
25	9-n-Octylheptadecane	0.7905	0.0306	−13.8	184.0
110	9 (3-Cyclopentylpropyl) heptadecane	0.8178	0.0324	−20.6	188.0
111	1-Cyclopentyl-4 (3-cyclopentylpropyl) dodecane	0.8469	0.0358	Approx. −40	193.0
113	1,7-Dicyclopentyl-4 (3-cyclopentylpropyl) heptane	0.8774	0.0432	−23.7	198.0
179	9-n-Octyl (1,2,3,4-tetrahydro) naphthacene	1.0122	0.1048	...	245.0

[a] Skeletal structures in which notation such as C_8 refers to straight chain of eight carbon atoms containing all appropriate hydrogens
[b] η is the absolute viscosity. The densities and also the slopes of the η vs T curves were determined at 37.8°C (100°F).

varies linearly with pressure.[9] The particular coil used in this work had a resistance of about 125 ohms at atmospheric pressure. The slope of the pressure resistance curve for this gauge, about 3.2×10^{-4} ohm/ bar, was determined using a deadweight gauge. Pressure changes could be measured to ±1 bar.

The viscometer was calibrated at 37.78°C and atmospheric pressure by filling with fourteen liquids of known viscosity and density and measuring the corresponding roll times. The calibration extended from 1.5 to 990 cp and above 10 cp was in accordance with

[9] P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, 1949), Chaps. 9, 12.

the linear equation

$$\eta = k(d_s - d_1)t + c, \qquad (1)$$

where η is the absolute viscosity, k and c constant depending on the dimensions of the apparatus, d_s and d_1 the densities of sphere and liquids, respectively, and t the roll time. Below 10 cp the viscosity was determined by reading directly from a calibration curve.

III. EXPERIMENTAL RESULTS

A study of the pressure-viscosity relation has been made on seven of the PSU hydrocarbons and three

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TABLE II.[a] A

PSU No.	Temp.[d] (°C)
18	37.8 60 98.9
19	37.8 60 98.9
25	37.8 60 98.9
110	37.8 60 98.9 135
111	37.8 60 98.9
113	37.8 60 98.9 135
179[a]	37.8 60 98.9 135

[a] The viscosity valu
are not as pure as 99
at 37.8°C 134.1 at 60°
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[b] Based on atmospi
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98.9°C, and PSU 1
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‡ The temperatures
and 275°F, respectively
[10] Cutler, McMickle
29, 727 (1958).

TABLE II.[a] Atmospheric pressure viscosity and relative viscosity[b] at elevated pressures[c] of seven pure hydrocarbons.

Boiling point at 1 mm °C	PSU No.	Temp.[d] (°C)	Atmos vis. (cp)	Pressure (bars)									
				345	689	1030	1380	1720	2070	2410	2760	3100	3450
197.0	18	37.8	11.47	1.64	3.67	4.30	6.93	10.9	16.9	26.2	40.4	61.1	93.3
		60	5.78	1.59	2.42	3.64	5.40	7.95	11.5	16.5	23.8	33.9	47.9
		98.9	2.50	1.55	2.16	2.93	3.91	5.28	7.05	9.35	12.4	16.1	20.9
194.5	19	37.8	28.66	2.20	4.47	8.62	16.3	30.6	55.0	95.3	167	. . .	. . .
		60	11.72	1.97	3.70	6.59	11.5	19.5	32.4	53.3	87.0	137	. . .
		98.9	4.06	1.80	2.89	4.58	7.19	11.0	16.6	24.9	36.4	53.4	77.3
184.0	25	37.8	7.06	1.64	2.66	3.91	5.72	8.16	11.46	15.7	21.3	28.6	37.8
		60	3.91	1.58	2.38	3.40	4.81	6.65	9.05	12.1	15.9	20.8	26.8
		98.9	1.87	1.52	2.16	2.96	3.97	5.10	6.63	8.44	10.7	13.4	16.6
188.0	110	37.8	9.43	1.62	2.61	4.08	6.19	9.16	13.4	19.0	26.5	36.6	49.8
		60	4.99	1.54	2.84	3.75	5.00	7.15	10.0	13.8	18.8	25.0	33.1
		98.9	2.26	1.51	2.23	3.45	4.08	5.40	7.12	9.33	12.1	15.6	19.8
		135	1.47	1.48	2.00	2.61	3.37	4.30	5.46	6.87	8.50	10.41	12.52
193.0	111	37.8	13.59	1.76	3.04	4.99	7.95	12.4	18.7	28.1	41.4	59.7	86.0
		60	6.79	1.67	2.68	4.21	6.38	9.40	13.7	19.5	27.3	38.1	52.4
		98.9	2.88	1.58	2.38	3.38	4.75	6.64	9.10	12.3	16.2	21.4	28.0
198.0	113	37.8	22.53	1.93	3.54	6.21	10.6	17.8	39.3	48.0	. . .	. . .	. . .
		60	10.16	1.78	3.04	5.04	8.07	12.6	19.7	29.8	44.8	66.3	96.7
		98.9	3.88	1.67	2.51	3.79	5.59	8.14	11.7	16.5	22.9	31.7	43.0
		135	2.13	1.61	2.35	3.32	4.54	6.20	8.45	11.3	15.0	19.7	. . .
245.0	179[a]	37.8	911.7	3.91	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
		60	135.3	2.78	7.92	22.4	. . .	. . .	. . .	. . .	. . .	. . .	. . .
		98.9	17.58	2.08	4.18	8.30	16.6	33.6	71.0	152	. . .	. . .	. . .
		135	5.93	1.74	2.94	5.02	8.40	14.2	23.8	40.6	69.5	120	208

[a] The viscosity values listed in Table II for PSU 179 were obtained on a sample that proved to have been slightly oxidized and therefore not as pure as were the others. The atmospheric values of the viscosities of the nonoxidized material were 839.7 at 37.8°C 134.1 at 60°C, 18.34 at 98.9°C. Scarcity of sample prevented obtaining a new high pressure run but the results of the mixture work reported herein suggest that the correct high pressure values can be obtained by multiplying the values entered by the ratio of the atmospheric values of the viscosities of the nonoxidized to the oxidized sample.

[b] Based on atmospheric pressure viscosity of water at 20°C being 1.0052.

[c] The pressure values correspond to 5000 psi intervals.

[d] The centigrade temperatures 37.8°C, 60°C, 98.9°C, and 135°C correspond to 100°F, 140°F, 210°F, and 275°F.

binary mixtures of them. The structures of the pure liquids and some pertinent physical properties of these compounds are shown in Table I. The first six hydrocarbons are closely related structurally while PSU 179 was included in order to obtain an indication of the effect of a radical difference in structure at the same molecular weight level. Viscosity measurements were made at 37.78°, 60°, and 98.9°C on PSU 18, PSU 19, PSU 25, and PSU 111. The other hydrocarbons and the mixtures were studied at 135°C,‡ in addition to the above temperatures. It will be recalled from the viscometer calibration equation that the liquid density at the pressure in question is a prerequisite to calculation of the viscosity. For PSU 18 at 37.78°, 60°, and 98.9°C, and PSU 19, PSU 25, and PSU 111 at 37.78° and 98.9°C the density had been experimentally determined over the pressure range used in the viscosity measurements.[10]

‡ The temperatures listed correspond to 100°, 140°, 210°, and 275°F, respectively.

[10] Cutler, McMickle, Webb, and Schiessler, J. Chem. Phys. 29, 727 (1958).

The Tait equation[11]

$$v_0 - v = C \log(B+P)/(B+P_0), \qquad (2)$$

where v_0 and v are are the specific volumes at the pressures P_0 and P, respectively, and C and B are constants characteristic of the liquid, was used to estimate the density of the remaining compounds to within 2%. The density of each mixture was assumed to be the same as that of the corresponding pure compound over the entire pressure range. This assumption has since been verified experimentally for the mixtures studied. A report of this $p-v-T$ work is given in reference 10.

The precision of the calculated viscosities is estimated to be ±1%. Below 5 cp the uncertainty of the rolling-ball viscosity values is estimated at ±4%, decreasing to ±2% at 10 cp and above. Another measure of the uncertainty is afforded by comparison of data on PSU 19, PSU 25, PSU 111, and a petroleum oil on which measurements were also made at 37.78°,

[11] P. G. Tait, Physics and Chemistry of the Voyage of H. M. S. Challenger (Stationery Office, London), Vol. II, Part IV, S. P., LXI (1888).

and 98.9°C by ASME Pressure-Viscosity Project at Harvard University.[12,13] The agreement varies from sample to sample, and also with temperature, being somewhat poorer at the low viscosities. However, with three of the samples at 37.8°C and with one sample at 98.9°C, the two methods agree to within 2–3% up to 1500 cp. For the remainder, the discrepancies are of the order 2–6%. About 2–3% of this difference may probably be accounted for by changes in the samples caused by oxidation during the measurements at Harvard.

Table II lists the values read from graphs of the viscosities in centipoises plotted against the pressure.

IV. DISCUSSION

Although pressure causes the viscosity of hydrocarbon liquids to increase monotonically without exception, the magnitude of the effect varies widely depending on the type of compound. All the liquids used in this work contained 25 or 26 carbon atoms per molecule. In spite of this similarity in molecular weight, an extreme range in viscosity was experienced between the isoparaffin, PSU 25, and the fused-ring aromatic-naphthenic compound, PSU 179, which at 2412 bars and 98.9°C increased to 8.4 and 152 times their respective atmospheric viscosities, an 18-fold difference.

The changes in viscosity due to structural variations which are observed at atmospheric pressure have been found to be enhanced by increasing external pressure. Thus in the series PSU 25, PSU 110, PSU 111, and PSU 113 wherein the five outermost carbon atoms in each normal octyl group of PSU 25 are progressively replaced by cyclopentyl rings at 37.8°C the ratios of atmospheric viscosities are 1:1.34:1.92:3.18 while at 3450 bars (50 000 psi) the ratios have changed to 1:1.84:4.14:12.9. Table II shows that the relative increase in viscosity with pressure increases with the atmospheric viscosity for substances of similar ring structure. This seems to be generally true.[9]

The effect of changing the type of ring structure is shown in Table II. There it is seen that the dicyclohexyl compound, PSU 19, increases viscosity 77-fold whereas the dicyclopentyl, PSU 111, increases viscosity only 28-fold when the pressure is increased from atmospheric to 3450 bars at 98.9°C. Also, PSU 18, the diphenyl compound analogous to PSU 19 increases its viscosity only 21-fold for similar pressure changes. The viscosity of the fused ring compound PSU 179 increased 208-fold for the same pressure change but at 135°C. Note that the effect of raising the temperature is to reduce the

[12] "Viscosity and density of over forty lubricating fluids of known composition at pressures up to 150 000 psi and temperatures to 425°F," Vol. I and II, Report of the American Society of Mechanical Engineers Research Committee on Lubrication, 29 West 39th, New York, New York.
[13] Bradbury, Mark, and Kleinschmidt, Trans. Am. Soc. Mech. Engrs. 73, 667 (1951).

TABLE III. Effect of pressure on temperature coefficient of viscosity, $(1/\eta)(\partial\eta/\partial T)_p$, at 60°C.

PSU No.	$(1/\eta)(\partial\eta/\partial T)_p$, (°C^{-1})		% increase
	1 atmos	2760 bars	
25	0.0229	0.0335	46
110	0.0266	0.0344	29
111	0.0275	0.0427	55
113	0.0304	0.0518	70
19	0.0340	0.0608	79
18	0.0270	0.0481	78

relative change in viscosity for a given pressure increase.

A large change in molecular weight produces a considerably smaller effect. For example, at 3450 bars PSU 25, a C_{25} compound, shows a 33-fold increase over its atmospheric viscosity while isopentane increases only 6.3-fold under similar conditions. As previously observed by Bridgman,[4] the viscosity-temperature coefficient, $1/\eta(\partial\eta/\partial T)_p$, increases at high pressures. For these high molecular weight compounds the increase is of the order of 40–80% over 2760 bars at 60°C. Table III shows the variation of this quantity for six of the pure liquids. Of the compounds containing two cyclic groups, the cyclohexyl, PSU 19, and the phenyl, PSU 18, show corresponding changes in the viscosity-temperature coefficient with pressure, increasing about 1.4 times as much as the cyclopentyl compound, PSU 111, and 1.7 times the isoparaffin, PSU 25. Within their own group, the compounds containing cyclopentyl rings again exhibit an increasing effect with the progressive cyclization, PSU 110, PSU 111, and PSU 113.

The mixtures, 25_2-113_1, 25_1-113_2, and 25_1-90_2 (the subscripts refer to the relative number of moles of each component) were studied primarily for comparison with a single chemical compound having the same molecular weight and the same average molecular structure. That is, the physical mixtures listed in Table IV correspond to the individual compounds listed with them which in this connection will be referred to as "chemical" mixtures.

In previous work in this laboratory, R. W. Schiessler and co-workers found the physical properties of these physical and "chemical" mixtures at atmospheric pressure to be remarkably similar, in many cases agreeing nearly within the error of measurement.[14] Most notable is the agreement in viscosity, which averages 2% for paraffinic-naphthenic mixtures and about 7% for compositions containing aromatic rings, for temperatures ranging from 0°C to 98.9°C.

Table V summarizes the results obtained for viscosities of the mixtures as a function of pressure at several temperatures. The greatest divergence of the ratio of the viscosity of the pure compound to that of

[14] Schiessler et al., Proc. Am. Petrol. Inst. 26, III, 254 (1946).

No.

25_2-113_1

25_1-113_2 C$_8$—C

25_1-90_2 C$_8$—C

physical mixtu
PSU 110 at 13
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very low and
is least for sh

TABLE V. C

Mixture at °C

$(25)_2+(113)_1$
37.8°C

60

98.9

135

$(25)_1+(113)_2$
37.8°C

60

98.9

$(25)_1+(90)_2$
60°C

98.9

a Ratio of visc
chemical mixture

TABLE IV. Physical mixtures and corresponding chemical mixtures.

No.	1 mole	2 mole	Chemical mixture	PSU No.
$25_2 - 113_1$	cyclopentyl—C_3—C—C_3—cyclopentyl, with C_3—cyclopentyl branch	C_8—C—C_8, with C_8 branch	C_8—C—C_8, with C_3—cyclopentyl branch	110
$25_1 - 113_2$	C_8—C—C_8, with C_8 branch	cyclopentyl—C_3—C—C_3—cyclopentyl, with C_3—cyclopentyl branch	C_8—C—C_3—cyclopentyl, with C_3—cyclopentyl branch	111
$25_1 - 90_2$	C_8—C—C_8, with C_8 branch	cyclohexyl—C_2—C—C_2—cyclohexyl, with C_2—cyclohexyl branch	C_8—C—C_2—cyclohexyl, with C_2—cyclohexyl branch	19

physical mixture (C/P) is 5% except for one case, PSU 110 at 135°C and 345 bars. This single discrepancy is doubtless due to the fact that the viscosity here was very low and the accuracy of the rolling-ball method is least for short roll times. The average discrepancy was only 3%. This agreement is truly noteworthy when it is remembered that the viscosity of both the mixtures and the corresponding pure compounds increase 5000 to 10 000 percent. *The coincidence of the viscosity values indicates that with molecules of this size*

TABLE V. Comparison of the viscosities of chemical compounds and corresponding physical mixtures at elevated pressures.

Mixture at °C	Atmos	345	689	1030	1380	1720	2070	2410	2760	3100	3450	(bars)
$(25)_2+(113)_1$												
37.8°C	9.43	15.1	25.1	38.8	60.3	89.0	127	181	253	348	475	viscosity (cp)
	1.00	1.01	0.98	0.99	0.97	0.97	0.99	0.99	0.99	0.99	0.99	ratio C/P[a]
60	4.99	7.84	12.1	18.0	26.3	37.5	52.4	72.0	97.9	129	171	viscosity (cp)
	1.00	0.98	0.97	0.96	0.95	0.95	0.95	0.96	0.96	0.97	0.96	ratio C/P[a]
98.9	2.28	3.37	4.95	6.92	9.48	12.6	16.7	21.8	28.2	36.1	45.6	viscosity (cp)
	0.99	1.01	1.02	1.01	0.97	0.97	0.97	0.97	0.97	0.97	0.98	ratio C/P[a]
135	1.47	1.96	2.79	3.76	4.98	6.42	8.21	10.2	12.8	15.7	19.3	viscosity (cp)
	1.00	1.11	1.05	1.02	0.99	0.98	0.97	0.99	0.98	0.98	0.95	ratio C/P[a]
$(25)_1+(113)_2$												
37.8°C	13.66	24.3	42.0	68.2	108	167	253	376	552	798	1140	viscosity (cp)
	0.99	0.98	0.98	0.98	1.00	1.00	1.00	1.02	1.02	1.02	1.03	ratio C/P[a]
60	6.79	11.5	18.4	28.8	43.2	63.7	92.8	132	185	258	351	viscosity (cp)
	1.00	0.98	0.99	0.99	1.00	1.00	1.00	1.00	1.00	1.00	1.01	ratio C/P[a]
98.9	2.90	4.54	6.82	9.60	13.6	18.8	25.7	34.7	46.3	60.9	79.2	viscosity (cp)
	0.99	1.00	1.00	1.01	1.01	1.02	1.02	1.02	1.01	1.02	1.02	ratio C/P[a]
$(25)_1+(90)_2$												
60°C	12.27	23.7	44.2	79.1	140	236	393	650	1060	...	...	viscosity (cp)
	0.96	0.95	0.97	0.97	0.96	0.97	0.97	0.99	0.99	...	...	ratio C/P[a]
98.9	4.16	7.21	11.8	19.0	29.7	46.0	69.8	103	154	224	326	viscosity (cp)
	0.98	0.99	0.97	0.96	0.96	0.95	0.95	0.97	0.95	0.95	0.93	ratio C/P[a]

[a] Ratio of viscosity of pure compound or chemical mixture to viscosity of physical mixture. For example the ratio of viscosity of chemical mixture PSU 110 to physical mixture 25_2-113_1 at 37.8°C and 689 bars is 24.6/25.1=0.98.

that have the same basic symmetry, the viscosity is an additive function of the parts of the molecule, independent of whether these parts are in the same or different molecules.

Since the chief external effect of the increase in pressure is the decrease in specific volume, a qualitative explanation of the variation of the effect of pressure on viscosity among different compounds may be related to their diminished free volume. The intermolecular forces, which are related to the chemical type, are known to vary inversely as a high power of the intermolecular radii and the work required to move the liquid molecules past one another, that is the viscosity, must rise sharply as this distance decreases.[15] While the rigidity of a molecule would not be expected to be a rapidly varying function of pressure, the effect of a given degree of rigidity would become increasingly important at high pressure. If the molecule be able to deform easily (with a small change in internal energy) then adaptation to a variety of hole shapes is possible within a short time and a low viscosity is evidenced.

It has been known for many years that the viscosity of a substance could be described over a short temperature range by the equation

$$\eta = \exp(B/RT),$$

when η is the absolute viscosity and A and B are characteristic of the substance.[16,17] Because of the practical and theoretical importance of viscosity, many attempts have been made to obtain a general expression for it as a function of temperature and pressure. One of the best known theoretical approaches is that of Eyring and his co-workers.§ The equation they suggest for expressing the viscosity as a function of pressure is

$$\eta = N/V (2\pi mkT)^{\frac{1}{2}} v_f^{\frac{1}{3}} \exp \frac{\Delta E_{\mathrm{Vis}} + PV/n'}{RT},$$

where v_f is a "free volume," ΔE_{Vis} an energy associated with viscous flow, n' a numeric in the range 6–8, and the other symbols have their usual significance. This equation was tested with the data of the research reported herein. Agreement as to direction of variation and order of magnitude was found *but no choice of the parameters reproduced the data quantitatively.*

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[15] R. W. Schiessler, Ph.D. dissertation, The Pennsylvania State University (1944).

[16] E. N. da C. Andrade, Phil. Mag. **17**, 497, 698 (1934).

[17] J. de Guzman, Anales soc. espan. fis. y quím. **11**, 353 (1913).

§ Reference 2 summarizes the work of Eyring and his co-workers and contains a complete bibliography of their work published up to the time of the publication of reference 2.

[18] A. Bondi, Ann. N. Y. Acad. Sci. **53**, 870 (1951).

[19] A. Bondi, J. Chem. Phys. **14**, 591 (1946).

[20] E. Brunner, J. Chem. Phys. **17**, 346 (1949).

[21] Brunner has criticized the appearance of Planck's constant in an equation for a nonquantum phenomenon and suggested a different pre-exponential coefficient. Bondi in reference 18 expresses preference for the form suggested by Brunner. Both forms contain the volume in the denominator and since to fit the data the other factor must be empirically determined anyway, we choose to use the form suggested in reference 2.

TABLE VI. $\Delta F_{\pm}$, Free energy of activation for viscous flow (kcal/mole).

Sample	°C	Atmos	1034	2067	3101
PSU 25	37.8	5.54	6.35	6.99	7.54
C_8—C—C_8	60.0	5.56	6.33	6.95	7.48
C$_8$	98.9	5.69	6.44	7.00	7.49
PSU 18	37.8	5.73	6.60	7.42	8.20
C_8—C—C_2—	60.0	5.69	6.51	7.26	7.95
C$_2$	98.9	5.76	6.51	7.13	7.72
PSU 111	37.8	5.95	6.86	7.65	8.35
C_5—C—C_5	60.0	5.87	6.79	7.54	8.20
C$_3$	98.9	5.95	6.80	7.50	8.11
PSU 110	37.8	5.70	6.53	7.24	7.85
C_8—C—C_8	60.0	5.70	6.48	7.16	7.74
C$_3$	98.9	5.80	6.58	7.17	7.72
	135	5.99	6.75	7.31	7.82
PSU 113	37.8	6.18	7.28	8.22	
$\left[\mathrm{C}_3\right]C_3$	60.0	6.11	7.15	8.03	8.81
	98.8	6.13	7.07	7.88	8.59
	135	6.27	7.18	7.90	8.57
PSU 19	37.8	6.36	7.65	8.78	
C_8—C—C_2—	60.0	6.23	7.44	8.47	9.41
C$_2$	98.9	6.19	7.27	8.19	9.04
	135	6.30	7.32	8.13	8.90

A less specific form of the Eyring equation is[18-21]

$$\eta = (Nh/V)\exp(\Delta F_{\pm}/RT) = (Nh/V)\exp\frac{\Delta H_{\pm} - T\Delta S_{\pm}}{RT},$$

(3)

viscous flow

ure (bars)	2067	3101
34		

35	6.99	7.54
33	6.95	7.48
44	7.00	7.49

50	7.42	8.20
51	7.26	7.95
51	7.13	7.72

36	7.65	8.35
79	7.54	8.20
30	7.50	8.11

53	7.24	7.85
38	7.16	7.74
38	7.17	7.72
5	7.31	7.82

| 8 | 8.22 | |

5	8.03	8.81
7	7.88	8.59
8	7.90	8.57
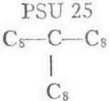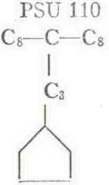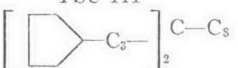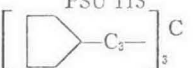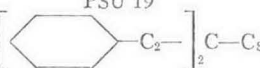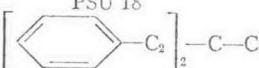
5	8.78	
4	8.47	9.41
7	8.19	9.04
2	8.13	8.90

$$\Delta H_{\pm} - T\Delta S_{\pm} \over RT,$$ (3)

on is[13-21]

TABLE VII. Values of $\Delta H_{\pm}{}^{j} \equiv R[\partial(\ln Z)/\partial(1/T)]_v$ at 71.1°C (160°F).

$\Delta H_{\pm}{}^{j}$ (kcal/mole)

Density gm/cm³	PSU 25 C_8—C—C_8 | C_8	PSU 110 C_8—C—C_8 | C_3	PSU 111	PSU 113	PSU 19	PSU 18
0.790	2.23	2.13				
0.800	2.57					
0.810	2.60	2.13				
0.820	3.08	2.35				
0.830	3.25	2.43				
0.840	3.70	2.51			2.66	
0.850	3.92	2.98	2.62		3.03	
0.860	4.43	3.32	2.76		3.41	
0.870	4.70	3.74	2.97	2.98	3.96	
0.880	5.06	4.13	3.12	3.39	4.30	
0.890		4.36	3.60	3.92	4.83	
0.900		4.60	4.11	4.12	5.24	
0.910			4.26	4.64	6.01	2.99
0.920			4.70	5.23	6.34	3.36
0.930			5.09	5.61	7.12	3.53
0.940				6.11		4.00
0.950				6.57		4.03
0.960				7.01		4.69
0.970						5.30
0.980						5.93
0.990						6.50

where

$$\Delta F_{\pm} = RT \ln(\eta V/Nh) \tag{4}$$

$$\Delta H_{\pm} = R \frac{\partial(\ln Z)}{\partial(1/T)_p} = \frac{\partial(\Delta F_{\pm}/T)}{\partial(1/T)_p} \tag{5}$$

$$\Delta S_{\pm} = -\left(\frac{\partial(\Delta F_{\pm})}{\partial T}\right)_p. \tag{6}$$

In these equations $\Delta F_{\pm}$ is the Eyring free energy of activation for viscous flow, $\Delta H_{\pm}$ the enthalpy of activation for viscous flow, $\Delta S_{\pm}$ the entropy of activation associated with the flow and Z the kinematic viscosity, equal to η/d.

The values of $\Delta F_{\pm}$ were computed from the data of Table II and Eq. (4) in order to compute $\Delta H_{\pm}$ and $\Delta S_{\pm}$, and a quantity $\Delta H_{\pm}^i$ to be discussed later in this paper. Table VI is an abbreviated list of the values of $\Delta F_{\pm}$; a complete list is not given since $\Delta F_{\pm}$ gives no information not contained in Table II. From Table VI it is seen that the variation of $\Delta F_{\pm}$ with temperature is small at any fixed pressure indicating approximate conformance to the De Guzman or Andrade type of equation even at high pressures.[16,17] It should be noted that although the viscosity is always a decreasing function of temperature that $\Delta F_{\pm}$ is not. In fact $\Delta F_{\pm}$ exhibits minimums in some cases, e.g., PSU 110. Using the data of Schiessler, Whitmore, and co-workers for the heats of vaporization the ratios $E_{vap}/\Delta F_{\pm}$ were calculated and found to vary from 3.9 to 4.5 at atmospheric pressure. These values agree with those previously observed.[2]

The several differential coefficients used in the Eyring theory have significance independent of the particular theory used since they describe the variation of the viscosity with the variable of differentiation. The enthalpy of activation, $\Delta H_{\pm}$, has been computed by Lowitz for the compounds reported here and for others whose viscosities as a function of pressure have been studied in this laboratory. The results of these studies are reported in another paper.[22] An analysis of $\Delta H_{\pm}$ into two parts has been made by Eyring et al.[2] One part, $\Delta H_{\pm}^i \equiv R[\partial(\ln Z)/\partial(1/T)]_v$ has been interpreted as representing the energy to move a molecule into a vacancy which has already been created. The second part of $\Delta H_{\pm}$ called $\Delta H_{\pm}^h$ and equated to the difference between $\Delta H_{\pm}$ and $\Delta H_{\pm}^i$ has been interpreted as the energy required to form the hole.[2,18,19,23] Values of $\Delta H_{\pm}^i$ have been determined at intervals of 0.01 g/cm³ in the density for six of the compounds. The ranges of pressures and temperatures, shown in Table II, were such that ten densities were available for four compounds and nine densities for two compounds. The derivatives were obtained by measuring the slopes of

curves $\ln Z$ *versus* T at constant density. Although the values of $\Delta H_{\pm}^i$ were determined for at least seven different temperatures for each compound, only those for one temperature, 71.1°C (160°F) are listed in Table VII. These are typical of the others obtained. In every case $\Delta H_{\pm}^i$ increases with density at constant temperature as would be expected (see Table III), since this represents an isothermal increase in pressure from atmospheric to 3300 bars. When the data at all temperatures are examined, it is found that the increase in $\Delta H_{\pm}^i$ ranges from a factor of 1.9 to 3.1 with 2.2 representing a rough average. On the average, the cyclohexyl, PSU 19, has the highest factors while the dicyclopentyl, PSU 111, has the lowest. One might expect the branched paraffin, PSU 25, to have the lowest if $\Delta H_{\pm}^i$ represents the work to move into a vacancy. At temperatures other than that of Table VII one observes similar behavior but the magnitudes of the ratios of the maximum to the minimum values may be in a different order from those of Table VII. This seems difficult to correlate with an interpretation of $\Delta H_{\pm}^i$ as an energy to move into a vacancy.

It might seem logical to compare the values of $\Delta H_{\pm}^i$ at equal densities and equal temperatures. With $d = 0.8800$ at $T = 7.1°C$ the order of increasing magnitude of $\Delta H_{\pm}^i$ is PSU 18, 111, 113, 110, 19, and 25. It would seem reasonable to suppose the "hole" size to be about equal under these conditions yet *the simplest structure (and the structure with greatest freedom of intramolecular and intermolecular rotation) shows the greatest $\Delta H_{\pm}^i$ value*. The smallest value of the density available for PSU 18 was 0.9100 but even so and in spite of its two phenyl rings its $\Delta H_{\pm}^i$ value is still the lowest for these conditions. It should be noted that while PSU 25 is at the highest pressure for this density that PSU 110 is at a higher pressure than PSU 19 and PSU 111 is at a higher pressure than PSU 113.

When all of the data for $\Delta H_{\pm}^i$ are examined one finds that for fixed density levels and increasing temperatures there are 13 instances of monotonic decrease of the $\Delta H_{\pm}^i$ values, 19 of decrease to constant value, 4 of no significant change, and 22 minimums occurring. The minimums were not very marked, however.

$\Delta S_{\pm}$, the Eyring theory entropy of activation, was calculated at two temperatures and four pressures by use of the Gibbs-Helmholtz equation and the values of $\Delta H_{\pm}$ and $\Delta F_{\pm}$ already calculated. The values obtained from $\Delta S_{\pm}$ are listed in Table VIII. From Table VIII it is immediately apparent that $\Delta S_{\pm}$ increases with an increase of pressure. An examination of the changes in the relative viscosity with temperature at the higher pressures compared with corresponding changes at lower pressures, Table II, would lead one to expect this result. Table VIII shows that there is always a decrease of $\Delta S_{\pm}$ with an increase in temperature, with the magnitude of this decrease usually being greater at the higher pressures. The quantity $\Delta S_{\pm}$ is seen to be very structure dependent with the larger

[22] Lowitz et al. submitted for publication to J. Chem. Phys.
[23] References 17 and 18 represent a study by Bondi of the several differential coefficients of the Eyring theory using the extensive data, mostly at atmospheric pressure, found in the literature for many compounds, including lubricating oils.

Pressure (bars)	PSU 23 60°C	9
1	−1.62	
1030	−0.60	
2070	+0.30	
3100	+0.93	

values being as
the diphenyl P
the tricyclopent
is greatly enhan
indicates.

The behavior
general with th
energy associate
with $\Delta H_{\pm}$, is c
$\Delta H_{\pm}$, and they i

The quantity
in the Eyring t
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observed parall
$(\Delta H_{\pm} - \Delta H_{\pm}^i)$
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fact that $(\partial \ln Z$
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axis. At any gi
temperature of
sures above 20
course, the sam
as do the origi
60°C, when th
3000 bars, $\Delta V_{\pm}$
18, 32% for the
dicyclohexyl P
paraffin PSU 2
differences in Δ
having the highe

It should be
$[(1/\eta)(\partial\eta/\partial P)]$
at higher pressu

[24] Further studie
wider range of ten
the near future.

TABLE VIII. $\Delta S_\pm = 1/T[\Delta H_\pm - \Delta F_\pm]$ for six high-purity hydrocarbons.

Pressure (bars)	PSU 25 60°C	98.9°C	PSU 110 60°C	98.9°C	PSU 111 60°C	98.9°C	PSU 113 60°C	98.9°C	PSU 19 60°C	98.9°C	PSU 18 60°C	98.9°C
1	−1.62	−4.46	−0.41	−3.19	+0.08	−2.76	+1.68	−2.08	+3.70	−1.12	+0.35	−2.96
1030	−0.60	−4.29	+0.71	−3.76	1.15	−1.62	4.33	−0.97	7.60	−1.20	2.93	−1.96
2070	+0.30	−3.27	+2.05	−2.84	3.03	−0.51	4.50	+1.03	11.41	+3.78	6.19	+0.08
3100	+0.93	−1.65	+3.17	−0.97	5.65	+0.48	8.49	+3.41	14.70	+7.38	10.60	+3.01

values being associated with the more rigid molecules the diphenyl PSU 18, the dicyclohexyl PSU 19, and the tricyclopentyl PSU 113. The effect of this rigidity is greatly enhanced by higher pressures, as Table VIII indicates.

The behavior of $\Delta S_\pm$ for these compounds agrees in general with the pattern indicated by Bondi.[18,19] The energy associated with $T\Delta S_\pm$, while not as great as with $\Delta H_\pm$, is certainly not negligible compared with $\Delta H_\pm$, and they increase together.[24]

The quantity $\Delta V_\pm \equiv RT(\partial \ln Z/\partial P)_T$ is interpreted in the Eyring theory as a volume characteristic of the flow process. In the derivative Z is the kinematic viscosity. This relationship is a consequence of the definition of $\Delta F_\pm$ as $RT \ln(\eta V/Nh)$. Bondi[19] has observed parallel relationships between $\Delta V_\pm/V$ and $(\Delta H_\pm - \Delta H_\pm{}^i)$ for a number of compounds. Since $\Delta V_\pm$ is found to be but a small fraction of the molecular volume, V, he concludes that long chain molecules flow segment-wise. Of course, the mixture data of the present paper and that cited earlier[6] furnish more direct evidence of segmental flow. The values of $\Delta V_\pm$ were calculated for the compounds studied in this paper. These values will not be reproduced here since all the significant information follows from Table II and the fact that $(\partial \ln Z/\partial P)_T$ does not differ significantly from $(\partial \ln Z/\partial P)_T$. The values of $\Delta V_\pm$ decrease with increasing pressure in all cases reported here as the curves of $\ln Z$ vs P are concave toward the pressure axis. At any given pressure, $\Delta V_\pm$ decreases when the temperature of the isotherm is increased, for all pressures above 200 bars. The values of $\Delta V_\pm$ show, of course, the same characteristic structural dependence as do the original data in Table II. For example at 60°C, when the pressure is increased from 165 to 3000 bars, $\Delta V_\pm$ decreases 24% for the diphenyl PSU 18, 32% for the tricyclopentyl PSU 113, 34% for the dicyclohexyl PSU 19, and 41% for the branched paraffin PSU 25. The higher pressures enhance the differences in $\Delta V_\pm$ at all temperatures with PSU 19 having the highest value and PSU 25 the smallest value.

It should be pointed out that the pressure coefficient $[(1/\eta)(\partial \eta/\partial P)]_T$ might become an increasing function at higher pressures than those employed in this work

for others have found the $\ln \eta$ vs P becomes convex toward the pressure axis in many cases when the pressures are carried to 10 000 bars.[12] The magnitude of $\Delta V_\pm$ varies from 10% to 16% of the molar volume at 165 bars and 37.8°C and from 5% to 9% at 3000 bars and 135°C. The largest values are associated with the dicyclohexyl, PSU 19, and smallest values with the monocyclopentyl, PSU 110, in each case.

As was previously stated no choice of the parameters of the Eyring equation was found that reproduced the data of this report quantitatively. An empirical equation was therefore sought that would do so. It seemed reasonable to try to adapt the semiempirical equation

$$\eta = A \exp(B/RT) \qquad (7)$$

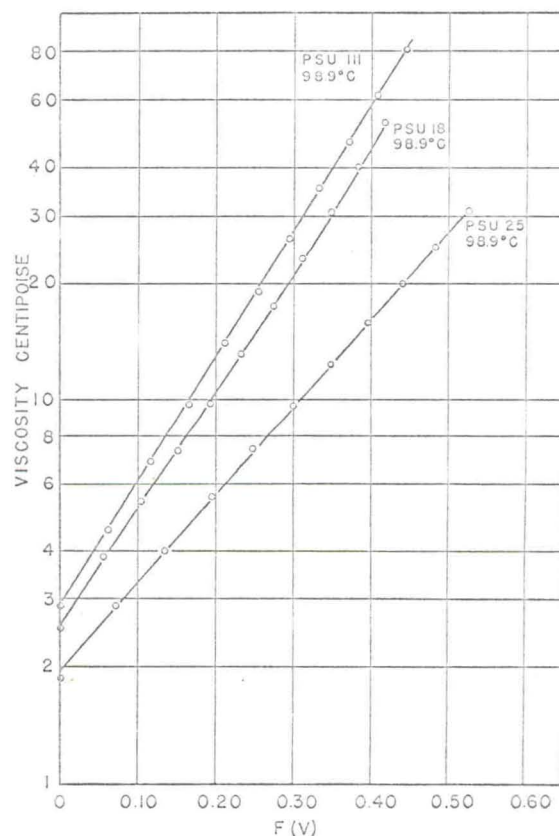discussed previously, to the pressure data as this

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[24] Further studies of $\Delta S_\pm$ data on more compounds and over a wider range of temperature will be submitted for publication in the near future.

FIG. 1. Absolute viscosity versus $F(v) = [(v_0/v)^4 - (v_0/v)^2]$ for PSU 25, 18, and 111 at 98.9°C.
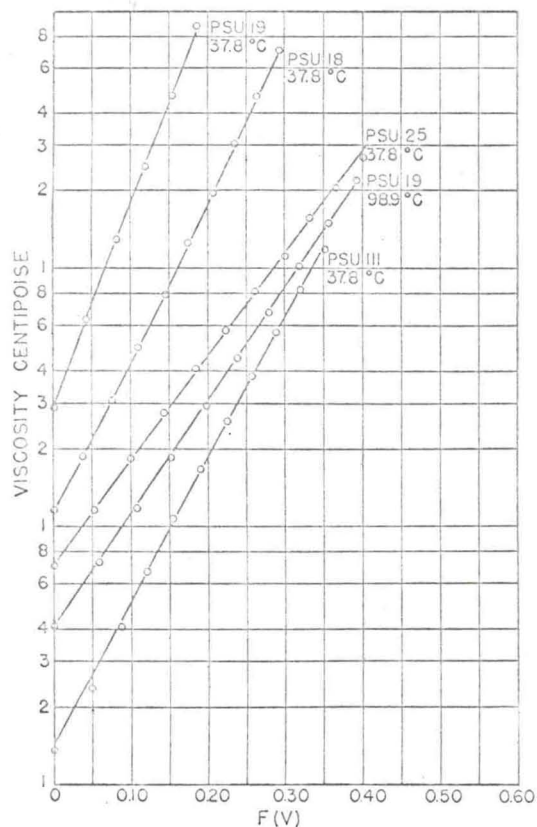
FIG. 2. Absolute viscosity *versus* $F(v) = [(v_0/v)^4 - (v_0/v)^2]$ for PSU 18, 19, 25, and 111 at 37.8°C and PSU 19 at 98.9°C. The first cycle is 10–100 cp for the PSU 111 curve and is 1–10 cp for all other curves.

equation is known to describe the viscosity variation with temperature over short temperature ranges. A and B in Eq. (7) are parameters characteristic of the liquid and both are functions of the specific volume. Letting the subscript null refer to atmospheric pressure and assuming constant temperature, Eq. (7) leads to the

relationship

$$\mathrm{Log}(\eta/\eta_0) = (B - B_0)/(2.303RT), \qquad (8)$$

when η and B refer to values at elevated pressures, the variation of A with pressure having been neglected. It is necessary to seek a suitable form for expressing B as a function of the specific volume or the pressure. Among the several approximation functions tried, the best results were obtained by assuming

$$B(v) = b/v^4 - a/v^2 \qquad (9)$$

and

$$b = av_0^2. \qquad (10)$$

The form of (9) was suggested from the Lennard-Jones intermolecular potential function $\phi = C_1 r^{-6} + C_2 r^{-12}$. It can be objected this function is valid only for spherical molecules but it has been successfully extrapolated in other instances.[18,19] With the use of (9) and (10) Eq. (8) becomes

$$\log(\eta/\eta_0) = (K/T)[(v_0^4/v^4) - (v_0^2/v^2)]. \qquad (11)$$

To test the agreement of Eq. (11) with the data, curves were plotted on $\log\eta$ *versus* $[(v_0^4/v^4) - (v_0^2/v^2)] \equiv F(v)$.

Figures 1 and 2 show the agreement between the resulting Eq. (11) and the experimental viscosities. In terms of viscosity the points for each of the three nonaromatic hydrocarbons, PSU 19, PSU 25, and PSU 111, at 37.8° and 98.9°C fall on straight lines with an average deviation of 2% and a maximum deviation of 8%, but PSU 18, the compound containing two phenyl groups, exhibits a definite curvature which is greater at the higher temperature. Evidently the stronger forces existing between aromatic molecules require a more exact expression than the form of the expression (9), or the Lennard-Jones function, to describe their variation with intermolecular distance.

[25] J. E. Lennard-Jones, Proc. Roy. Soc. (London) A106, 46 (1924).