

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)		
	1 atmos	2760 bars	% increase
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 C₂₅ 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, 25₂-113₁, 25₁-113₂, and 25₁-90₂ (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 ₁₁

25 ₁ -90 ₂ C ₈ -C ₁₁
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physical mixture
PSU 110 at 135°C
is doubtless due to
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

* Ratio of viscosity of pure compound to that of chemical mixture