

Study of the Compressions of Several High Molecular Weight Hydrocarbons

W. G. CUTLER,* R. H. McMICKLE,† W. WEBB, AND R. W. SCHIESSLER‡

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

(Received June 16, 1958)

Isothermal compressions were measured for thirteen high-purity liquid hydrocarbons and two binary mixtures of liquid hydrocarbons. These hydrocarbons have a molecular weight range of 170 to 351 and included normal paraffins, cycloparaffins, aromatics, and fused ring compounds. The pressure range for these measurements was from atmospheric to as high as 10 000 bars, being limited to lower values for some compounds to avoid possible solidification of the liquid. The volume changes due to pressure were measured at six temperatures spaced about equally in the range 37.8°C to 135.0°C. The volume changes and pressures were measured by methods similar to those of P. W. Bridgman.

Pressure-volume isotherms can be described adequately by the Tait equation, $v_0 - v = C \log(1 + P/B)$, or for pressures above a certain minimum, whose value depends on the compound, by the Huleston equation

$$\log[v^{2/3}P/(v_0^{1/3} - v^{1/3})] = A + B(v_0^{1/3} - v^{1/3}).$$

For the Tait equation the parameter C can be predicted for hydrocarbon liquids from the relation $C = 0.2058 v_0$.

Compressibility for a given hydrocarbon decreases with increasing

pressure at constant temperature and increases with increasing temperature at constant pressure. The compression, and the compressibility, of liquid hydrocarbons are strongly dependent on molecular structure. Cyclization introduces a rigidity of molecular shape which decreases the compressibility markedly. Furthermore, fused ring cyclization as exemplified by naphthyl and decalyl structures has a considerably greater effect in decreasing compressibility than cyclization to nonfused rings such as cyclopentyl, cyclohexyl, or phenyl, even at equivalent carbon atom in ring percentages.

Isobars and isochores were drawn and studied over the full range of temperature and pressure. The coefficient of thermal expansion, $(1/v_0)(\partial v/\partial T)_P$, for a given hydrocarbon, decreases with increasing pressure at constant temperature. $(\partial^2 v/\partial T^2)_P$ undergoes a sign change at a certain pressure, whose value depends on the compound; $(\partial v/\partial T)_P$ increases with increasing temperature below this pressure and decreases with increasing temperature above this pressure. The pressure coefficient, $(\partial P/\partial T)_v$, is not a function of volume alone but is also dependent on the temperature and pressure. $(\partial E/\partial v)_T$ and $(\partial E/\partial P)_T$ go to zero and then reverse sign for compounds that can be studied to sufficiently high pressures.

INTRODUCTION

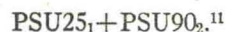
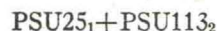
ALTHOUGH the study of liquid compressibility dates back to the English scientist, John Canton, in the eighteenth century only a relatively few experimenters¹⁻⁴ have gathered data on liquid of high molecular weight.

Since 1947 the High Pressure Laboratory and the Hydrocarbon Laboratory at The Pennsylvania State University have cooperated⁵ in the study of the effect of hydrocarbon structure on physical properties. Under the direction of R. W. Schiessler and F. C. Whitmore⁶⁻¹⁰ over 230 high-purity hydrocarbons have

been produced synthetically. These hydrocarbons range in number of carbon atoms from 10 to 50 and present a wide variety of molecular structure. Atmospheric pressure values of the density, viscosity, index of refraction, and melting point of each of these compounds were also available, having been determined by the Hydrocarbon Laboratory as a part of the study of the physical properties. It was logical continuation of the research activity to seek data on the physical behavior of certain of these hydrocarbons under high pressure.

The hydrocarbons selected for the study reported herein are listed in Table I.

Two binary mixtures of pure hydrocarbons were also studied. Each mixture had an average molecular weight and average molecular structure equivalent to one of the other pure compounds available. The mixtures used were as follows (the subscript indicates the number of moles of each constituent in the physical mixture):



The first of the mixtures is equivalent to PSU 111 and the second mixture is equivalent to PSU 19, in

* Present address: Research Laboratories, Whirlpool Corporation, St. Joseph, Michigan.

† Present address: B. F. Goodrich Laboratories, Brecksville, Ohio.

‡ Present address: Socony Mobil Laboratories, Paulsboro, New Jersey.

¹ Bradbury, Mark, and Kleinschmidt, *Trans. Am. Soc. Mech. Engrs.* **73**, 667 (1951).

² *Am. Soc. Mech. Engrs. Research Publication, Pressure-Viscosity Report* (American Society of Mechanical Engineers, New York 1953, Vol. I and II).

³ R. H. McMickle, Ph.D. dissertation, The Pennsylvania State University (1952).

⁴ W. G. Cutler, Ph.D. dissertation, The Pennsylvania State University (1955).

⁵ This work is partly supported by the American Petroleum Institute and known as American Petroleum Institute Research Project 42.

⁶ R. W. Schiessler and F. C. Whitmore, *Ind. Eng. Chem.* **47**, 1660 (1955).

⁷ J. N. Cosby, and L. H. Sutherland, *Proc. Am. Petrol. Inst. Sec. III* **22** 13 (1941).

⁸ Schiessler, Cosby, Clarke, Rowland, Sloatman, and Herr, *Am. Petrol. Inst. Sec. III Proc.* **23** 15 (1942).

⁹ Schiessler, Clarke, Rowland, Sloatman, and Herr, *Prod. Am. Petrol. Inst. Sec. III* **24** 49 (1943).

¹⁰ Schiessler, Herr, Rytina, Weisel, Fischl, McLaughlin, and Kuehner, *Proc. Am. Petrol. Inst. Sec. III* **26** 254 (1946).

¹¹ PSU 90 is 1,5-dicyclohexyl-3(2-ethylhexyl)pentane.