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An Analysis of the P-V-T Data for Several High Molecular Weight Hydrocarbons*

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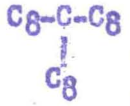
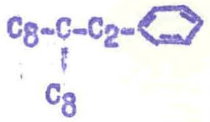
The work reported in this paper was performed at the Pennsylvania State University and was jointly supported by the University and the American Petroleum Institute. Volume-pressure data to 10 kilobars were determined for a series of structurally related, high molecular weight hydrocarbons synthetically produced by API Research Project 42 at Penn State. The volume changes due to pressure were measured at six temperatures about equally spaced in the range 37.8° C - 135° C. The structures of the compounds used for this study were as follows: (Slide #1)

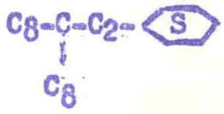
PSU 528 $n\text{-}C_{12}$

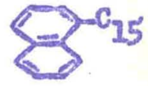
532 $n\text{-}C_{15}$

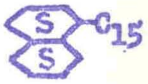
537 $n\text{-}C_{18}$

25

$C_8-\underset{\underset{C_8}{|}}{C}-C_8$

87


88


174


175


The PSU number is assigned for identification purposes and C_n refers to an unbranched, saturated chain of n carbon atoms with the substituent hydrogens. Details of experimental technique for measurement of the volume changes of these liquids have been previously reported.

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The pressure-volume isotherms can be described mathematically by two equations. Of chief interest is the Tait equation (Slide #2):

$$v_0 - v = C \log (1 + P/B)$$

where v_0 is the specific volume at atmospheric pressure, v is the specific volume at pressure P, and C and B are constants. C/v_0 is a constant independent of temperature. The average value of C/v_0 from this study and others conducted by API #42 (covering 103 isotherms for 20 compounds) is 0.2058. The standard deviation is 0.0045. The B is temperature dependent and can be expressed as a quadratic about 79.4° C. For example, for PSU 87: (Slide #3)

$$v_0 - v = C \log (1 + P/B)$$

$$C = 0.2058\ v_0$$

$$B = B_{79.4} + a(t - 79.4) + b\ (t - 79.4)^2$$

$$B = 1048 - 5.916\ (t - 79.4) + 0.0121\ (t - 79.4)^2$$

A comparison between observed values of the specific volume change and the specific volume change computed from the Tait equation was made. The average per cent of difference, without regard to sign, was 0.45%, which is less than the experimental uncertainty in the data. The largest differences are at low pressures, this being particularly true for the normal paraffins.

An intermolecular force law proposed by Hudleston can be put in the following form: (Slide #4)

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

where v_0 is the specific volume at atmospheric pressure, v is the specific volume at pressure P, and A and B are constants. To check the Hudleston equation with the data obtained in this study, $\log \left[v^{2/3}\ P/(v_0{}^{1/3} - v^{1/3})\right]$ was plotted against $(v_0{}^{1/3} - v^{1/3})$. If the Hudleston equation is valid the locus of the points plotted should be a straight line having slope B and intercept A. For the compounds checked straight lines did result except for some deviations at pressures of 700 bars or lower. These deviations are to be expected because the mathematical form of the Hudleston equation is such that it would not be expected to hold as atmospheric pressure is approached.

For a given compound the plots of the Hudleston equation at a series of temperatures proved to be a family of approximately parallel lines, indicating that B is constant for a given compound. The intercept, A, approximates a linearly decreasing function of the temperature. Using the relations discovered for A and B it was possible to write a general Hudleston equation for each compound. For example: (Slide #5)

PSU 87

$$\log \left[v^{2/3}P/(v_o^{1/3} - v^{1/3})\right] = A + B\,(v_o^{1/3} - v^{1/3})$$

$$\log \left[v^{2/3}P/(v_o^{1/3} - v^{1/3})\right] = 4.615 - 0.00250\,(t - 60) + 6.209\,(v_o^{1/3} - v^{1/3}).$$

An examination of the compressibilities of the hydrocarbons studied led to a number of general conclusions. For a given compound and temperature the compressibility decreases with increasing pressure, the rate of decrease becoming smaller at higher pressures, as the following example shows: (Slide #6)

PSU 88, 135° C

P(bars)	k $(\text{bar})^{-1}$
atmos.	12.2×10^{-5}
670	6.36
1340	4.22
3350	2.14
6700	1.18
10050	0.81

$$k = \text{compressibility} = -1/v_o\,(\partial v/\partial P)_T$$

Pronounced structural dependence is apparent in the values of the compressibility. The effect of structure, however, tends to disappear as the pressure increases as shown in the following example: (Slide #7)

Compressibility $(\text{bar})^{-1}$
135° C

P(bars)	PSU 174	PSU 87	PSU 528
atmos.	9.16×10^{-5}	11.8×10^{-5}	18.3×10^{-5}
3350	2.02	2.14	2.28
6700	(1.14)	1.18	1.21

The value in parentheses was computed from the Tait equation for the 135° C isotherm for PSU 88, as 6700 bars was above the maximum pressure to which PSU 174 could be taken.

The isobars, with specific volume as a function of temperature, were plotted for each compound at 335 bar intervals. The isobars for each hydrocarbon had the same general form and were almost linear. Representative isobars are shown in the next slide. (Slide #8)

Slopes of the isobars were determined from large scale graphical plots by the use of a tangentometer. These slopes revealed a change in sign of $(\partial^2 v/\partial T^2)_p$ at elevated pressures. This effect is observed by noting that at lower pressures the magnitude of the slope of the isobar, $(\partial v/\partial T)_p$, increases with increasing temperature but above a certain pressure, the value of $(\partial v/\partial T)_p$ decreases with increasing temperature.

Representative values of the pressure range in which the sign reversal of $(\partial^2 v/\partial T^2)_p$ has been observed in the present study are as follows: (Slide #9)

PSU 174	1000 - 1340 bars
87	1000 - 1340
528	2340 - 2680
532	1680 - 2020

Isochores (curves of constant specific volume) were drawn over the entire range of temperature and pressure at intervals of 0.01 cc/gram. Representative isochores are shown in the next slide (Slide #10). Slopes of the isochores were also read with a tangentometer. It was especially noted that the isochores are not straight lines. The slope of a given isochore, $(\partial P/\partial T)_v$, decreases with increasing pressure and temperature. Since the isochores are not straight lines, one can state that $(\partial P/\partial T)_v$ is not a function of volume alone. The quantity $T(\partial P/\partial T)_v + B$, where B is the Tait equation parameter B, was examined for a number of the hydrocarbons in this study and the results support the idea that $T(\partial P/\partial T)_v + B$ is solely a function of volume.

It can be shown from thermodynamics that: (Slide #11)

$$(\partial E/\partial v)_T = T(\partial P/\partial T)_v - P$$

and

$$(\partial E/\partial P)_T = - T(\partial v/\partial T)_P - P(\partial v/\partial P)_T$$

From these equations one can show that:

$$(\partial E/\partial v)_T = (\partial E/\partial P)_T = 0 \text{ when } P = T(\partial P/\partial T)_v.$$

The pressure for which $P = T(\partial P/\partial T)_v$ has been determined experimentally for some of the hydrocarbons in this study. For example, for PSU 87 this pressure is 8900 bars at 135° C. Since at this pressure $(\partial E/\partial v)_T$ and $(\partial E/\partial P)_T = 0$ it represents a minimum energy for the liquid. It has been proposed (by Bridgman and Hildebrand) that the volume of the liquid at this pressure should correspond to the volume of the liquid at 0°K. For PSU 87: (Slide #12)

Specific volume at P for which $P = T(\partial P/\partial T)_v$	0.99 cc/gram
Specific volume at 0°K (extrapolated from density data)	0.96 cc/gram

Czaputowicz, E.

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