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Densities and Optical Properties of Organic Compounds in the Liquid State. III. The Densities of Aliphatic Hydrocarbons

BY MAURICE L. HUGGINS

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The molal volume of a liquid normal paraffin at 20° is accurately given by the equation $V_n = 16.50n + 27.20 + (27/n)$, where n is the number of carbon atoms in the chain. The molal volumes of branched and unsaturated hydrocarbons can be computed, somewhat less accurately, by means of more complicated expressions.

Introduction

Although the subject of this paper has been dealt with in two previous papers by the writer,[1,2] a revision of the results reported therein seems advisable, in view of the considerable amount of new data available, before extending them to compounds other than hydrocarbons.

The densities considered are those at 20°. Since the molal volumes V are much more nearly additive than the densities, the relationships deduced are given in terms of the former.

Normal Paraffin Hydrocarbons.—A plot of the molal volumes of the normal paraffins against the number n of carbon atoms shows a fairly close approach to a rectilinear relationship, indicating additivity. Using the very accurate density data now available,[3,4] however, the departures from rectilinearity are much larger than the probable experimental errors.

It has been found that the simple equation

$$V_n = 16.50n + 27.20 + (27/n) \qquad (1)$$

gives excellent agreement (usually better than that between the two best experimental determinations) for $n > 6$ and fair agreement for $n = 6$ and 5 (see Table I).

TABLE I

MOLAL VOLUMES AND DENSITIES OF NORMAL PARAFFINS

	Molal volume			Density		
		Experimental			Experimental	
n	Eq. 1	N.B.S.[3]	Timm.[4]	Eq. 1	N.B.S.[3]	Timm.[4]
5	(115.100)	115.205	115.212	(0.62681)	0.62624	0.62620
6	(130.700)	130.688	130.672	(.65931)	.65937	.65945
7	146.557	146.557	146.533	.68368	.68368	.68379
8	162.575	162.573	162.566	.70259	.70260	.70263
9	178.700	178.696	178.690	.71768	.71770	.71772
10	194.900		194.909	.72999		.72996
11	211.155		211.156	.74022		.74022
12	227.450		227.450	.74886		.74886
13	243.777		243.758	.75624		.75630
14	260.129		260.085	.76262		.76275
15	276.500		276.398	.76820		.76848
16	292.888		292.794	.77310		.77335
17	309.288			.77746		
18	325.700			.78134		

The molal volume can also be expressed as a function of the numbers of CH_2 and CH_3 groups in the molecule by the following equation, equivalent to equation 1

$$V_n = 16.50N_{CH_2} + 30.10N_{CH_3} + \frac{27}{n} \qquad (2)$$

One might guess that the $27/n$ term is related to a dependence of the amount of thermal motion of a CH_2 group on its distance from an end of the molecular chain or a dependence of the degree of coiling of the molecules on their chain length. These factors may, in fact, contribute, but it seems more likely that it is primarily a result of an increased end-group volume whenever two end groups are mutually adjacent. With perfect randomness, the chance that any given molecule end is adjacent to another is approximately inversely proportional to the chain length, *i.e.*, to the number of carbon atoms per molecule.

Branched Paraffin Hydrocarbons.—One might hope that the difference between the molal volume of a branched paraffin hydrocarbon and the normal paraffin hydrocarbon having the same number of carbon atoms could be computed as the sum of contributions from the atomic groups (CH_3, CH_2, CH, C) present. This is very inaccurate, however. By adding to such contributions, other contributions for the types of bonds present greater accuracy can be achieved, as has been shown by Taylor, Pignocco and Rossini.[5]

Combining their results with those given above for the normal paraffins, this equation is obtained

$$\begin{aligned} V = {} & a_{CH_3}N_{CH_3} + a_{CH_2}N_{CH_3} + a_{CH}N_{CH} + a_{C}N_{C} + a_{CH_3-CH_3}N_{CH_3-CH_3} \\ & + a_{CH_3-CH_2}N_{CH_3-CH_2} + a_{CH_3-CH}N_{CH_3-CH} + a_{CH_3-C}N_{CH_3-C} + a_{CH_2-CH_2}N_{CH_2-CH_2} \\ & + a_{CH_2-CH}N_{CH_2-CH} + a_{CH_2-C}N_{CH_2-C} + a_{CH-CH}N_{CH-CH} + a_{CH-C}N_{CH-C} \\ & + a_{C-C}N_{C-C} + (27.0/n) \qquad (3) \end{aligned}$$

On making use of certain relationships between the variables involved, the simpler equation

$$\begin{aligned} V - V_n = {} & b_{CH}N_{CH} + b_{C}N_{C} + b_{CH_3-CH_3}N_{CH_3-CH_3} + b_{CH_2-CH}N_{CH_2-CH} \\ & + b_{CH_2-C}N_{CH_2-C} + b_{CH-CH}N_{CH-CH} + b_{CH-C}N_{CH-C} + b_{C-C}N_{C-C} \qquad (4) \end{aligned}$$

can be deduced. From accurate data on 70 paraffin hydrocarbons having 5 to 9 carbon atoms per molecule, Taylor and co-workers obtained the values of the b constants listed in Table II. With this equation and these constants, they computed an average difference between experimental and calculated densities for 11 branched-chain nonanes of 0.0015.

The relationships between the a's and the b's are given by Taylor and co-workers in their paper and need not be reproduced here. The set of values of b constants is insufficient in itself to determine the magnitudes of the larger number of a con-

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(1) M. L. Huggins, THIS JOURNAL, **63**, 116 (1941).

(2) M. L. Huggins, *ibid.*, **63**, 916 (1941).

(3) "Selected Values of Properties of Hydrocarbons," Circular of the National Bureau of Standards C461, U. S. Government Printing Office (1947).

(4) J. Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., Amsterdam, 1950.

(5) W. J. Taylor J., M. Pignocco and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 413 (1945).

Table II

Constants for Use with Equations 3 and 4

	a	*b*
CH_3	28.30	....
CH_2	16.50	....
CH	6.05	2.91
C	−1.10	5.60
CH_3-CH_3	1.8	?
CH_3-CH_2	1.80	....
CH_3-CH	1.72	....
CH_3-C	0.80	....
CH_2-CH_2	0	....
CH_2-CH	−1.90	−1.82
CH_2-C	−4.74	−3.74
CH-CH	−6.38	−6.22
CH-C	−10.97	−9.89
C-C	−18	?

stants. However, one can arbitrarily assign a value (*e.g.*, $a_{CH_2-CH_2} = 0$) to one of the *a*'s and assume smooth curve relationships for each series of related *a*'s (*e.g.*, $a_{CH_3-CH_2}$, $a_{CH_2-CH_2}$, a_{CH_2-CH}, a_{CH_2-C}). In this way the *a* values listed in Table II and plotted in Fig. 1 have been obtained. Although not needed for the calculations, it is of interest to note the general trends.

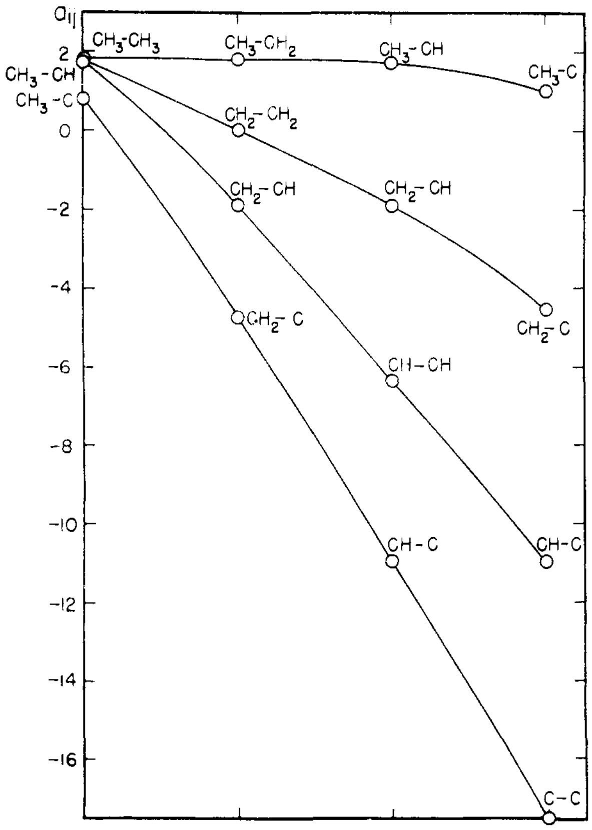

Fig. 1.—Volume constants for various types of single bonds.

Unsaturated Hydrocarbons.—The molal volumes of unsaturated hydrocarbons can most logically be discussed in relation to the molal volumes of the corresponding saturated hydrocarbons having the same carbon skeleton. As would be expected, replacement of a single C-C bond by a double (C=C) bond, with the elimination of two hydrogen atoms, results in a decrease in the molal volume. The magnitude of this decrease is roughly 5 to 10 cc. Even larger decreases are found for triple bonds.

A study[2] of a large number of unsaturated hydrocarbons, 12 years ago, led to the relationship

$V_s - V$ = 6.0 for each terminal double bond
+ 6.5 for each non-terminal double bond
+ 2.0 additional for each double-bond carbon atom attached by single bonds also to two other carbon atoms (5)
+ 2.5 additional for each pair of adjacent or conjugated double bonds
+15.0 for each terminal triple bond
+17.0 for each non-terminal triple bond
+ 1.0 additional for conjugation of a double bond and a triple bond

Another way of expressing this same relationship is

$$V_s - V = 2.75N_{=CH_2} + 3.25N_{=CHR} + 5.25N_{=CR_2} + 6.5N_{\equiv CH} + 8.5N_{\equiv CR} + 9.0N_{=C=} + 2.5N_{=C-C=} + 1.0N_{=C-C\equiv} \quad (6)$$

It will be noted that for the calculation of the molal volumes of monoölefins only three new constants are required. The data available at the time these equations were deduced did not warrant further elaboration. In 1945, Taylor, Pignocco and Rossini,[5] with much better and more abundant data to work with, arrived at the following 5-constant equation, for monoölefins containing 5, 6 or 7 carbon atoms

$$V_s - V = 4.83N_{H_2C=CHR} + 6.72N_{RHC=CHR} + 7.13N_{H_2C=CR_2} + 7.93N_{RHC=CR_2} + 10.22N_{R_2C=CR_2} \quad (7)$$

This equation, like equation 6, is still not very accurate, the standard deviations between calculated and experimental molal volumes averaging more than one milliliter. By taking into account the degree of branching at carbon atoms adjacent to those connected by the double bond, with a total of eight constants, Taylor and co-workers were able to reduce the standard deviation to about 0.7. The equation used was

$$V_s - V = 6.57N_{H_2C=CHR} + 8.66N_{RHC=CHR} + 9.26N_{H_2C=CR_2} + 9.45N_{RHC=CR_2} + 10.74N_{R_2C=CR_2} - 1.05N_2 - 2.39N_3 - 2.75N_4 \quad (8)$$

Here N_2, N_3 and N_4 are the numbers of secondary, tertiary and quaternary carbon atoms adjacent to the two doubly bonded carbon atoms.

Good density data are now available, for *n* values up to 18, for unbranched monoölefins having the double bond at the end of the chain; *i.e.*, having the skeleton formula $C_{n-2}C{=}C$. Figure 2

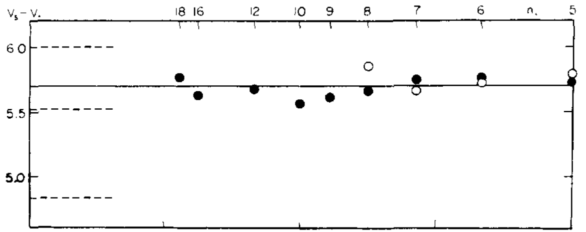

Fig. 2.—Differences between the molal volumes of monoölefins, $C_{n-2}H_{2n-1}CH{=}CH_2$, and those of the corresponding normal paraffins, C_nH_{2n+2}.

shows a plot of the experimental $V_s - V$ values against $1/n$. There is no general trend, hence the effect of the double bond is practically independent of the chain length, at least for n greater than 4. It is probably justifiable to use equations 6, 7 and 8 for all except very small molecular weights.

It is of interest to compare the average value (5.70) of $V_s - V$ for this series of compounds with the values (6.0, 4.83, 5.52) according to equations 6, 7 and 8. The first is inaccurate, owing to imperfections in the experimental data available 10 years ago. The second is even more inaccurate, because it was an average which included compounds of quite different types. The third is much better, though still low, because of the inclusion in the averaging of some branched-chain compounds.

Although some more good data are available on more complex unsaturated compounds than at the time of the writer's previous study, a revision and extension of the relationships then deduced hardly seems warranted.

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[COMMUNICATION NO. 1600 FROM THE RESEARCH LABORATORIES, EASTMAN KODAK COMPANY]

Densities and Optical Properties of Organic Compounds in the Liquid State. IV. The Densities of α-Substituted Normal Alkanes[1]

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The molal volumes of α-substituted normal paraffins, having the general formula, $C_mH_{2m+1}X$, are quite accurately given by the equation, $V = 16.50m + A + B/m$ with A and B characteristic of the substituent X. Values of these constants at 20°, have been deduced for the following substituents: F, Cl, Br, I, OH, SH, CN, NH_2, NO_2, ONO, CO_2H, CHO. The calculated densities appear to be accurate, for $m > 2$, to one or two units in the fourth decimal place in most of these series.

Introduction

The success of a similar relationship for normal paraffins suggests that the molar volumes of α-substituted normal paraffins, $C_mH_{2m+1}X$, might be given by equations of the form

$$V = 16.50m + A + B/(m + b) \qquad (1)$$

with A, B and b characteristic of the substituent X, but independent of the length of the chain, *i.e.*, of m. (The letter m is used here rather than the previously used n, the latter being reserved for the *total* number of carbon atoms in the molecule. In most of the series here considered, m and n are equal.)

This relationship has been tested with data from the literature on 10 series of compounds. Usually, excepting the lowest members of each series, quite good agreement has been found, using b equal to zero throughout. In some instances, non-zero values of b give slightly better agreement, but in view of the inaccuracies of the data now available, it has seemed best to neglect this and list the best A and B values, deduced on the assumption that b is uniformly zero.

A temperature of 20° has been chosen for these comparisons. Use has been made of measurements at other temperatures when reliable extrapolation or interpolation is possible.

Most of the data used are in Timmermans' extensive compilation,[2] but more recent measurements also have been included.

Procedure and Results

The general procedure has been to plot the function $(V - 16.50m)m$ *vs.* m, for each series. The slope and the intercept of the best straight line representing the experimental points are the desired values of A and B, respectively. (Greater weight was given to the points representing the most accurate density determinations, of course.) For greater accuracy, an approximate value of A, which we may designate as $\bar{A}$, was obtained in this way; the function $(V - 16.50m - \bar{A})m$ was then plotted against m. The slope and the intercept of the best straight line then yielded $A - \bar{A}$ and B, respectively. An example of such a plot is shown in Fig. 1.

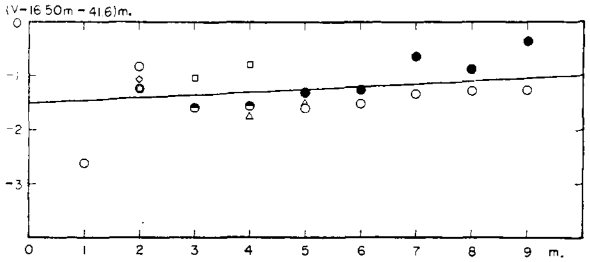

Fig. 1.—Plot to determine constants A and B, for n-alkyl mercaptans: ○, Ellis and Reid[3]; ●, Bingham and Fornwalt[4]; □, Hunter and Partington[5]; ◓, McCullough, *et al.*[6]; △, Walls and Smyth[7].

Points for the lowest one or two members of each series usually departed somewhat from the straight line best representing the others. This departure has been neglected. Densities calculated for these compounds, therefore, usually depart from accurate experimental values more than in the cases of higher members of the series.

As a rule, the experimental densities for the highest members of each series are relatively inaccurate, partly because

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[1] This is a revision of a paper by Maurice L. Huggins and Dorothy L. Davis presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Cleveland, Ohio, on April 3, 1944.

[2] J. Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., Amsterdam, 1950.

[3] L. M. Ellis, Jr., and E. E. Reid, THIS JOURNAL, **54**, 1674 (1932).

[4] E. C. Bingham and H. J. Fornwalt, *J. Rheology*, **1**, 372 (1930).

[5] E. C. E. Hunter and J. R. Partington, *J. Chem. Soc.*, 2062 (1931); 2812 (1932).

[6] J. P. McCullough, D. W. Scott, H. L. Finke, M. E. Gross, K. D. Williamson, R. E. Pennington, G. Waddington, and H. M. Huffman, THIS JOURNAL, **74**, 2801 (1952).

[7] W. S. Walls and C. P. Smyth, *J. Chem. Phys.*, **1**, 337 (1933).