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.

Acknowledgment.—Mrs. Dorothy Davis and Mrs. Ruth Welch ably assisted in much of the earlier work leading to the preparation of this paper.

ROCHESTER, N. Y.

[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]

BY MAURICE L. HUGGINS

RECEIVED SEPTEMBER 3, 1953

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.

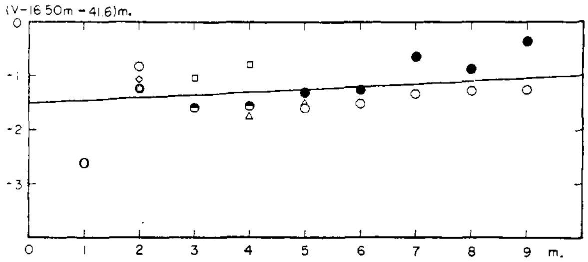

Fig. 1.—Plot to determine constants A and B, for n-alkyl mercaptans: ○, Ellis and Reid[3]; ●, Bingham and Fornwalt[4]; □, Hunter and Partington[5]; ◒, McCullough, *et al.*[6]; △, Walls and Smyth[7].

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).

of difficulties of purification. Some of the "experimental" values for such compounds have, moreover, been obtained by extrapolation from data at higher temperatures. Nevertheless, there seems to be a tendency for the molal volumes of the higher molecular weight compounds to be lower (and the densities higher) than would be expected by extrapolation of the relation deduced from the lower members of the series. This may be associated with the change from truly fluid liquids to glassy "supercooled liquids." The loss of rigidity of the molecules and atomic groups accompanying this change would be expected to produce a molal volume decrease. Changes in the type of molecular packing in the liquid, such as recently discussed by Moore, Gibbs and Eyring,[8] may also be involved. One should, therefore, not expect densities computed from eq. 1, using the constants of Table I, to agree closely with experimental densities for solid (glassy or crystalline) members of the series.

The constants A and B obtained for the various series are listed in Table I.

TABLE I

CONSTANTS FOR USE WITH EQUATION 1

X	A	B	X	A	B
H	27.20	27	SH	41.65	−1.5
CH_3	43.9	22	CN	38.8	−2.8
F	29.4	10.6	NH_2	33.4	−2
Cl	38.2	1.0	NO_2	41.7	−6
Br	41.7	−0.5	ONO	50.1	+3
I	48.9	−3.5	CO_2H	43.3	−2.5
OH	26.1	−2.0	CHO	41.2	−3.2

The corresponding equations are represented by the straight lines of Fig. 2, in which $V - 16.50m$ is plotted against $1/m$, and (for some of the series) by the curves of Fig. 3, in which the density is plotted against m. Some of the more accurate experimental points are included in Fig. 2.

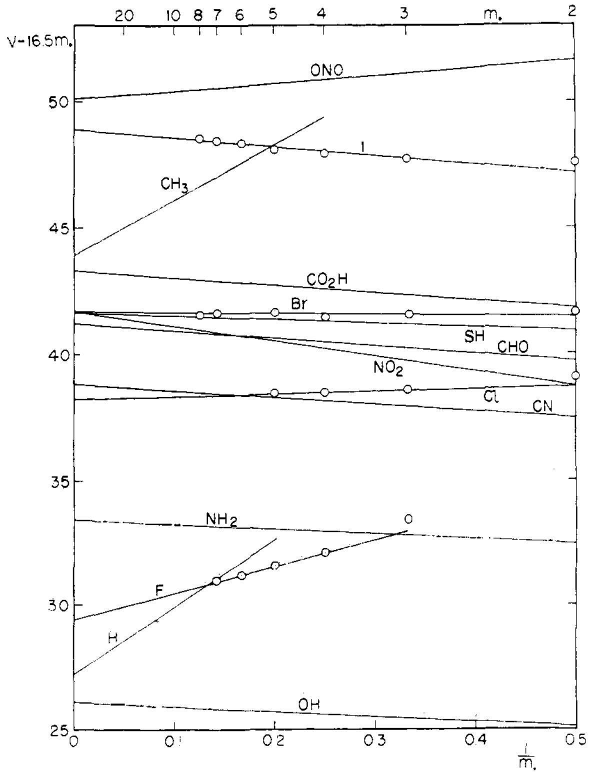

Fig. 2.—Dependence of molal volume on $1/m$ for various series.

For comparison of the constants for the α-derivatives with those for the parent hydrocarbons, the corresponding values for the latter are included in Table I. These are listed both considering X as H, with m equal to the number of carbon atoms n, and considering X as CH_3, with m equal to the number of carbon atoms minus one.

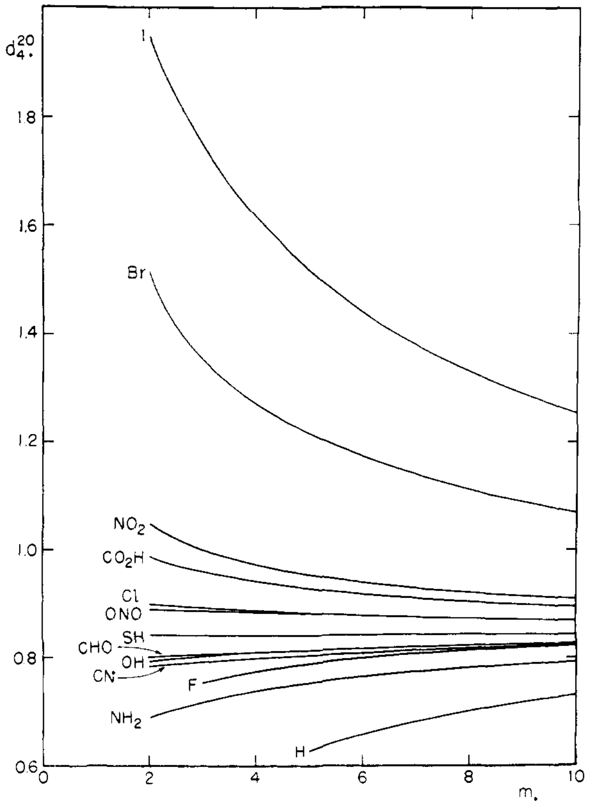

Fig. 3.—Dependence of density on m for various series.

Table II lists the calculated densities for compounds of the series considered, with m from 2 to 10, with (below) the best experimental values from the literature.[2] Except for the ethyl derivatives ($m = 2$) and some of the fatty acids, the agreement is, on the whole, very good—usually within one or two units in the fourth decimal place. This is considerably better than the usual agreement between different experimental values published for the same compound.

Discussion

The values of the constants A are similar to what would have been expected on the basis of previous knowledge. The values of B, on the other hand, are a little surprising, especially the very large positive values found for the normal paraffins (whether H or CH_3 is taken as X) and the moderately large positive value for the fluorine derivatives. As noted in the preceding paper of this series, this constant can be related to the difference between the space requirement of an end group when it is adjacent to another end group and that when it is not so located, and to its probability of

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(8) R. J. Moore, P. Gibbs and H. Eyring, THIS JOURNAL, 57, 172 (1953).

TABLE II

DENSITIES OF n-$C_mH_{2m+1}X$ COMPOUNDS

m	H	F	Cl	Br	I	OH	SH	CN	NH_2	NO_2	ONO	CHO	CO_2H
2			0.8998	1.4637	1.9460	0.7929	0.8408	0.7824	0.6894	1.0470	0.8873	0.8000	0.9871
			.8958	1.4606	1.9358	.7894	.8400	.7818				.8001	.9933
3		0.7532	.8922	1.3512	1.7483	.8020	.8402	.7910	.7188	.9988	.8856	.8044	.9580
			.8923	1.3514	1.7489	.8036		.7909					.9579
4		.7763	.8863	1.2738	1.6139	.8092	.8407	.7986	.7395	.9710	.8825	.8095	.9400
		.7761	.8863	1.2757	1.6154	.8096		.7992				.8095	.9392
5	0.6268	.7905	.8817	1.2172	1.5153	.8147	.8414	.8047	.7547	.9524	.8795	.8139	.9270
	.6262	.7905	.8816	1.2173	1.5165	.8148		.8053				.8139	.9270
6	.6593	.8002	.8781	1.1740	1.4396	.8189	.8422	.8096	.7662	.9390	.8768	.8175	.9175
	.6594	.8002			1.4392	.8189		.8096				.8175	.9181
7	.6837	.8072	.8752	1.1399	1.3795	.8223	.8428	.8136	.7753	.9287	.8745	.8206	.9102
	.6837	.8071		1.1399	1.3790	.8224		.8136					.9088
8	.7026	.8125	.8729	1.1123	1.3306	.8250	.8434	.8169	.7826	.9206	.8726	.8231	.9043
	.7026			1.1129	1.3299	.8256		.8169					.9055
9	.7177	.8166	.8709	1.0895	1.2900	.8272	.8438	.8196	.7886	.9141	.8709	.8253	.8994
	.7177							.8197					
10	.7300	.8200	.8693	1.0703	1.2558	.8291	.8443	.8220	.7936	.9087	.8694	.8271	.8954
	.7300							.8218					

being so placed. Both ends of the molecule must be taken into account, of course. A large positive value of B may be due either to a considerable increase in the volume contribution of the end groups when they are together or to a small or moderate increase, with a considerably greater probability that end groups are together than that they are not. Probably the normal paraffin molecules (and perhaps also those of their α-fluorine derivatives) pack together with parallel chain axes more readily and to a greater extent than do the other types of molecules, this arrangement favoring voluminous end-to-end contacts.

The small negative values of B for most of the series may indicate smaller contributions per pair of ends (H and X) when the ends of different molecules are together (either H...X or the average of H...H and X...X) than when they are isolated from each other. On the other hand, these negative values may be attributed to a possible greater efficiency of packing for very small molecules than for larger ones or to some kinetic effect. The data at hand do not appear to justify any more definite interpretation.

It will be noted that eq. 1 has been used for the fatty acids and the alcohols, in spite of the known hydrogen bond association to double molecules in the former series and to higher aggregates in the latter. This association may be responsible for the departures of the experimental densities from strict regularity in the fatty acid series and the lower alcohols. In any event, the association must be taken into account in any attempt to account for the magnitudes of the A and B constants for these compounds.

ROCHESTER, N. Y.

[COMMUNICATION NO. 1603 FROM THE RESEARCH LABORATORIES, EASTMAN KODAK COMPANY]

Densities and Optical Properties of Organic Compounds in the Liquid State. V. The Densities of Esters from Fatty Acids and Normal Alcohols

BY MAURICE L. HUGGINS

RECEIVED SEPTEMBER 3, 1953

Two alternative, nearly equivalent, equations are deduced, from which one can calculate, within an accuracy of about 0.0001, the densities of most of the "straight-chain" esters. Similar, less general, equations are given for the methyl esters and the formates, acetates and butyrates. Reasons for the forms of these equations and for the minor irregularities observed are briefly discussed.

Introduction

In previous papers[1-3] equations of the form

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

have been shown to give accurately (except for very small values of m) the dependence of the molal volume V on the term number m, for normal paraffins and a variety of series of their derivatives, having the general formula, $C_mH_{2m-1}X$.

A considerable amount of accurate density data is now available[4] for esters of the general formula, $C_{m-1}H_{2m-1}CO{\cdot}OC_pH_{2p+1}$. The success of eq. 1 suggests that a similar form of equation

$$V = 16.50n + A + B/(n - b) \qquad (2)$$

with $n = m + p$, and A, B and b empirical constants, be tested for the various series of esters (m constant or p constant). This has now been done.

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

(2) M. L. Huggins, *ibid.*, **76**, 843 (1954).

(3) M. L. Huggins, *ibid.*, **76**, 845 (1954).

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