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.

Procedure and Results

Molal volumes were computed from the best experimental densities and the molecular weights. For each series, graphs were then made of $V - 16.50n$ against $1/(n - b)$ and/or of $(V - 16.50n - \bar{A})(n - b)$ *vs.* $(n - b)$, where $\bar{A}$ is an approximate value of A (Figs. 1 and 2). Different values of b were tried until the one giving the best rectilinear relationship was obtained, neglecting the points for the lowest values of p in the m-constant series and those for the lowest values of m in the p-constant series.

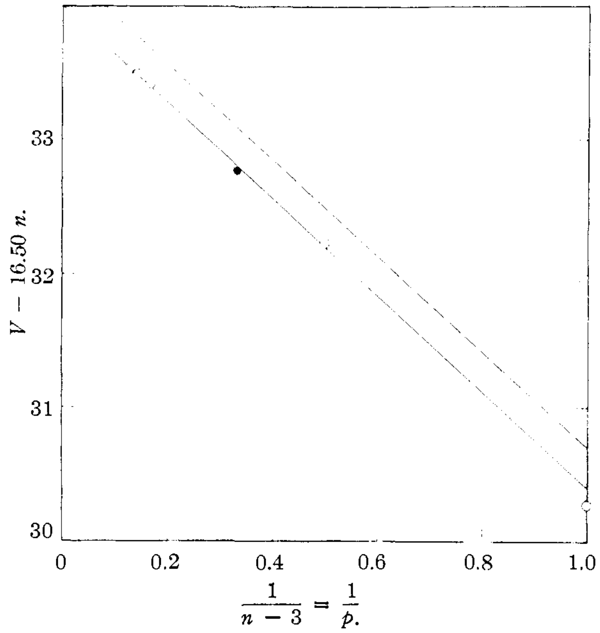

Fig. 1.—Illustrating procedure for obtaining constants A' and B', using data for propionates. The full line is for $A' = 34.00$ and $B' = -3.6$. The dashed line is for $A' = 34.3$ and $B' = -3.6$. The open circles represent the most accurate data; the dot is for data which are presumably less accurate.

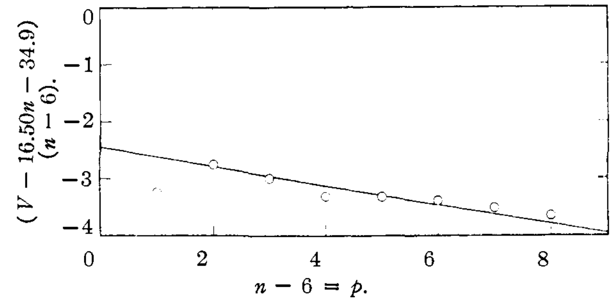

Fig. 2.—Illustrating an alternative procedure for deducing the constants A' and B', using data for caproates. The line corresponds to $A' = 34.73$ and $B' = -2.45$.

It was found that the best b-values were always approximately equal to m in the p-constant series (*e.g.*, the methyl esters) and to p in the m-constant series (*e.g.*, the acetates). Quite accurate agreement is obtained, in fact, by assuming this approximate relation to be an exact one, eq. 2 being replaced by

$$V = 16.50n + A' + (B'/p) \tag{4}$$

for the m-constant series and by

$$V = 16.50n + A'' + (B''/m) \tag{5}$$

for the p-constant series.

These two equations cannot both be *exactly* correct. Using the empirical values of A', B', A'' and B'', however, the two sets of calculated values of the molal volume agree quite closely (usually within two in the second decimal place) with each other and with the experimental results.

Figures 3–6 show how the constants A', A'', B' and B'' vary with m and p. The only significant departure from smooth relationships is the very low value of A' for the propionates (Fig. 3). From the trend of the other A' values, one would expect a magnitude of at least 34.3. The corresponding smooth-curve value of B' for the propionates is between −3.5 and −3.6 (Fig. 5). The dashed line in Fig. 1, drawn for the constants 34.3 and −3.6, is obviously not in good agreement with the experimental points.

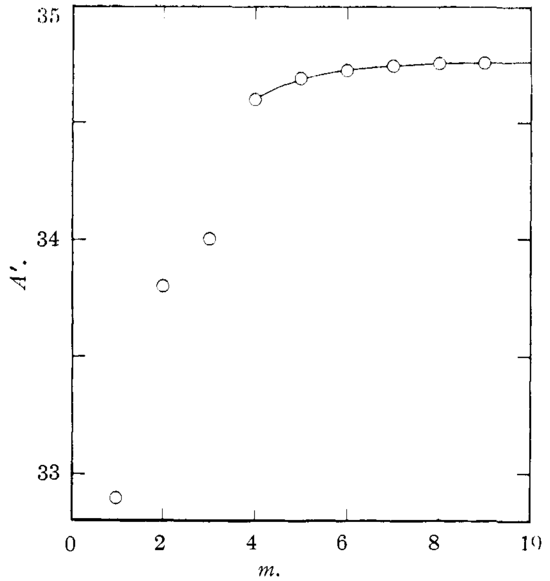

Fig. 3.—Variation of A' with m, the number of carbon atoms in the acidic radical. The curve represents eq. 6.

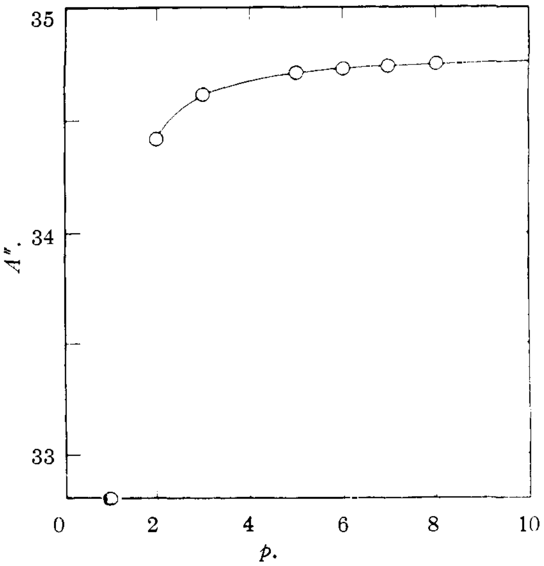

Fig. 4.—Dependence of A'' on p, the number of carbon atoms in the alcohol residue. The curve represents eq. 8.

Neglecting the formates, acetates and propionates ($m = 1$, 2 and 3), the empirical A' and B' values agree well with the simple equations

$$A' = 34.80 - 0.24/(m - 2.8) \qquad (6)$$

and

$$B' = -23/(m + 3.5) \qquad (7)$$

Likewise, excepting only the methyl esters ($p = 1$), the A'' and B'' values agree well with the relations

$$A'' = 34.80 - 0.38/(p - 1.0) \qquad (8)$$

and

$$B'' = -19/(p + 1.58) \qquad (9)$$

For $m > 3$ and $p > 1$, one can thus write the two alternative equations

$$V = 16.50n + 34.80 - \frac{0.24}{m - 2.8} - \frac{23}{(m + 3.5)p} \qquad (10)$$

$$V = 16.50n + 34.80 - \frac{0.38}{p - 1.0} - \frac{19}{m(p + 1.58)} \qquad (11)$$

For the formates, acetates and propionates, respectively, the following equations apply, when $p > 1$

$$V = 16.50n + 32.90 - (4.4/p) \qquad (12)$$

$$V = 16.50n + 33.80 - (4.0/p) \qquad (13)$$

$$V = 16.50n + 34.00 - (3.6/p) \qquad (14)$$

For the methyl esters with $m > 4$

$$V = 16.50n + 32.80 - (6.7/m) \qquad (15)$$

For methyl formate, acetate and propionate, fair concordance is obtained with the equation

$$V = 16.50n + 30.90 - (2/m) \qquad (16)$$

The degree of agreement between the calculated densities and the best experimental values[4] from highly purified compounds is shown in Table I. Not counting the figures enclosed in parentheses, the concordance is very good, the differences averaging less than one unit in the fourth decimal place, whether one uses the upper calculated values, from eq. 10, 13 and 14, or the lower ones, from eq. 11 and 15. Many of the experimental values may be in error by this amount, especially since most of them were obtained by interpolation or extrapolation from data at other temperatures.

The agreement with eqs. 12, for the formates, and 16, for the lower methyl esters, is only fair. There seems to be an alternation effect in the formates.

The experimental value listed for propyl caprylate is enclosed in parentheses, because it differs from the computed densities by 0.0018. This is much greater than any other difference found, except for the formates and the lower methyl derivatives.

Discussion

Although the simple form of equation for the molal volume, which was found applicable to the paraffins and for various end-substituted derivatives, has been found inapplicable to the esters, the somewhat more complicated relationships deduced hold very well. These involve the numbers of carbon atoms on each side of the –CO·O– group or, equivalently, the distances, measured along the molecule, between this group and the ends of the chain. Following the line of interpretation suggested in the third and fourth papers of this series, we may assume that the magnitude of $V - 16.50n$ is determined largely by the probabilities that two chain ends, two $-CO_2-$ groups, and a chain end and a $-CO_2-$ group are in close proximity, together with the magnitudes of the volume changes associated with each of these proximities. A more detailed interpretation will not be attempted at this time.

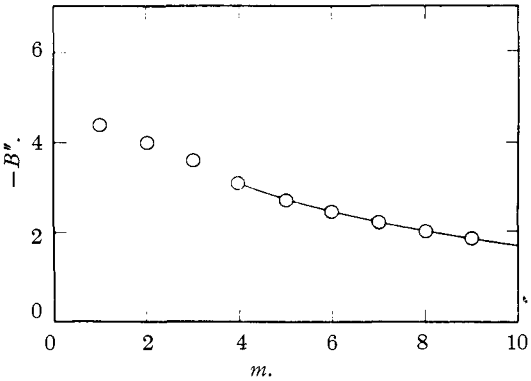

Fig. 5.—Variation of B' with m. The curve represents eq. 7.

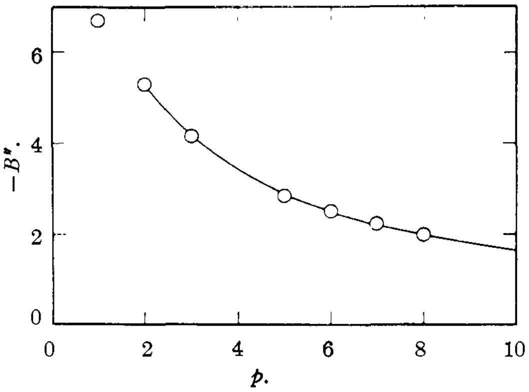

Fig. 6.—Variation of B'' with p. The curve represents eq. 9.

It seems improbable that the experimental data are sufficiently inaccurate to account for the irregularity of the A' value deduced for the propionates. There seem to be but three alternatives: (1) The preferred packing of the propionate molecules in the liquid differs in some unknown way from the preferred molecular packing of the other esters. (2) The preferred manner of packing in the formates, acetates and propionates differs from that in the other esters. (3) An alternation effect is being exhibited, closer packing being possible when the end carbon atom (of the acid residue) is on the same side of the zigzag axis as the C=O (in the extended molecule), than when it is on the opposite side. If this is the correct explanation, the experimental A' value for the valerates would be expected to be less than that deduced from the smooth curve through the values for the acetates, butyrates, caproates, etc. The experimental data would permit a decrease of 0.01 or perhaps 0.02, but not more; hence the alternation effect, if present, rapidly fades out as the length of the chain of the acid residue increases.

The alternation effect in the formate series is

TABLE I

COMPARISON OF CALCULATED AND OBSERVED DENSITIES, d^{20}_4

The figures in the first row are calculated from eqs. 10, 12, 13 and 14. Those in the second row are from eq. 11, 15 and 16. The third-row values are observed densities from ref. 4, usually interpolated from data at other temperatures.

	m	Methyl $p \rightarrow 1$	Ethyl 2	Propyl 3	Butyl 4	Amyl 5	Hexyl 6	Heptyl 7	Octyl 8
Formate	1		(0.9237)	(0.9043)	(0.8935)	(0.8866)	(0.8816)	(0.8779)	(0.8749)
		(0.9701)							
		.9742	.9225	.9057			.8813	.8784	.8744
Acetate	2		.9009	.8883	.8813	.8766	.8733	.8707	.8687
		(.9330)							
		.9335	.9007	.8883	.8817		.8733	.8707	
Propionate	3		.8904	.8813	.8761	.8725	.8699	.8679	.8662
		(.9155)							
		.9152	.8902				.8698	.8679	.8663
Butyrate	4		.8795	.8732	.8696	.8671	.8652	.8638	.8626
		.8988	.8794	.8733	.8697	.8671	.8652	.8637	.8625
		.8987	.8792				.8652	.8637	.8629
Valerate	5		.8746	.8698	.8670	.8650	.8635	.8623	.8613
		.8904	.8745	.8699	.8671	.8651	.8635	.8623	.8613
Caproate	6		.8713	.8674	.8651	.8635	.8622	.8612	.8604
		.8845	.8712	.8674	.8652	.8635	.8623	.8613	.8604
		.8847	.8712	.8675	.8653	.8635	.8622	.8612	.8603
Enanthate	7		.8687	.8656	.8637	.8623	.8612	.8604	.8596
		.8802	.8686	.8656	.8637	.8623	.8613	.8604	.8597
		.8801	.8686	.8656	.8638	.8623	.8611	.8604	.8596
Caprylate	8		.8667	.8641	.8625	.8613	.8604	.8596	.8590
		.8768	.8667	.8641	.8625	.8613	.8604	.8597	.8590
			.8665	(.8659)	.8627	.8613	.8603	.8596	.8592
Pelargonate	9		.8651	.8629	.8615	.8605	.8597	.8590	.8585
		.8742	.8651	.8629	.8615	.8605	.8597	.8590	.8585
			.8651						
Caproate	10		.8637	.8618	.8606	.8598	.8591	.8585	.8580
		.8720	.8638	.8619	.8607	.8598	.8591	.8585	.8580

such that the high density values are for the compounds in which the end carbon atom is on the same side of the zigzag axis as the C=O, in the extended zigzag chain.

It would be interesting to look for corresponding regularities and irregularities in amides, ethers, secondary amines, etc., but the data in the literature which could be used for this purpose are very meager.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

The Microwave Spectrum, Structure, and Dipole Moment of Thionyl Fluoride[1]

BY RAYMOND C. FERGUSON

RECEIVED OCTOBER 12, 1953

The microwave spectrum of thionyl fluoride, SOF_2, from 16,900 to 36,000 mc. has been recorded, and approximately thirty pure rotational transitions identified. The reciprocal moments of inertia fitting the $S^{32}O^{16}F^{19}_2$ spectrum are a = 8614.75 mc., b = 8356.98 mc., c = 4952.96 mc.; and those for the $S^{32}O^{18}F^{19}_2$ spectrum are a = 8582.33 mc., b = 7843.37 mc., c = 4777.90 mc. The structural parameters fitting these moments are: $r_{SO} = 1.412 \pm 0.001$ Å., $r_{SF} = 1.585 \pm 0.001$ Å., $\angle FSF = 92°49' \pm 5'$, $\angle OSF = 106°49' \pm 5'$. Stark effect measurements give a dipole moment of 1.618 ± 0.010 debye units along an axis 38°50' ± 30' from the SO bond and 80°23' ± 30' from the SF bond.

The closely related compounds thionyl fluoride, SOF_2, and sulfuryl fluoride, SO_2F_2, are ideal for the study of the effect of strongly electronegative substituents on the adjacent sulfur–oxygen bond. The analysis of the microwave spectrum of sulfuryl fluoride gave structural parameters which definitely disagreed with the electron diffraction results,[2] the most noteworthy feature of the microwave structure being an unusually short S–O bond distance. The present work was undertaken to determine whether a shortening of the S–O bond would be observed in thionyl fluoride. This compound has also been studied by the electron diffraction method, but the results have not been reported in full.[3]

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(1) This work was supported by the Navy Department through the ONR under Task Order V of Contract N5ori-76.

(2) R. M. Fristrom, *J. Chem. Phys.*, **20**, 1 (1952).

(3) D. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, p. 307.