

# Correlation and Prediction of Vapor Pressures of Homologs

## Use of Structure Parameters and Gas Chromatography Data

ARTHUR ROSE and VERLE N. SCHRODT<sup>1</sup>

The Pennsylvania State University, University Park, Pa.

An equation is given for predicting vapor-pressure temperature relations for a homologous series when data are available for three or more members of the series, or a related series. The method, which also serves to correlate and evaluate data for the members of such series, has been applied to various series of fatty esters, fatty acids, alcohols, hydrocarbons, and chloroalkanes. The same prediction and correlation relation holds true when retention volumes from gas chromatography are substituted for the numerical parameter values.

### THE EQUATION

$$\log N_p = G - \frac{H}{t + k} \quad (1)$$

may be used with a modification of the molecular structure factors of Poizat (7), or with gas chromatography retention volumes, to predict the equilibrium temperature  $t$  corresponding to a particular vapor pressure,  $p$ , for a compound for which no experimental data at all are available, if equilibrium temperatures are known or can be predicted for the particular vapor pressures for three or more homologs of the compound for which data are desired.

A study made of the vapor pressure-temperature data for an homologous series of compounds showed that for each pressure,  $p$ , there can be found a single set of values of  $G$ ,  $H$ , and  $K$  applicable to all members of the series. Every compound has a characteristic structure parameter,  $N_p$ , depending on the number and kind of groups in its molecule computed by appropriate combination of the modified Poizat structure factors, as summarized in a subsequent section of this article.

Retention volumes of gas chromatography can be used instead of  $N_p$  parameters, with certain restrictions. The method also serves to correlate vapor pressure-temperature data for the members of a series.

Equation 1 is of the same form as the conventional Antoine equation, but the two equations should not be confused even though they both may be used with vapor pressure-temperature correlations and predictions. The common Antoine equation relates temperature and equilibrium vapor pressure in terms of three constants (usually designated  $A$ ,  $B$ ,  $C$ ) that are characteristic of one particular compound. Equation 1 relates the temperature at which vapor pressure has a particular value to a function of the carbon number in an homologous series of organic compounds, in terms of three constants (here designated  $G$ ,  $H$ , and  $K$ ) that are characteristic of an entire homologous series and the particular vapor pressure for which temperatures are given.

### CORRELATION

The procedure may be illustrated by summarizing the first two applications that were made of the relation. The first application was to correlate the vapor pressure data that were available (9, 11) for seven normal straight-chain fatty acid methyl esters having carbon numbers 6, 10, 12, 14, 16, 18, and 22. The  $N_p$  structure parameters for these are listed in Table I along with the temperatures at which these compounds have a vapor pressure of 10 mm Hg.

The least squares computer method of Rose and others (8) was used on these data to calculate a best set of values of  $G$ ,  $H$ , and  $K$ . The degree of correlation of this set of data is also indicated in Table I by comparing the experimental values of  $t$  for the several compounds with the value of  $t$  calculated by Equation 1, using the "best" values of  $G$ ,  $H$ , and  $K$ .

### PREDICTION

Equation 1, by using the values of  $G$ ,  $H$ , and  $K$ , can predict temperatures corresponding to a vapor pressure of 10 mm. of Hg for other members of the same homologous series of fatty acid esters. This can be done by substituting into Equation 1 the values of  $G$ ,  $H$ , and  $K$  already obtained and the appropriate values of  $N_p$  for the homologs for which temperature-pressure data are desired. This was done for the 12 esters in Table II. No experimental data exist in the literature for most of these compounds, but the agreement between experimental data and the predicted values is probably similar to that shown in Table I.

### APPLICATION FOR A RANGE OF PRESSURES

The method used for methyl esters at 10 mm. of Hg was repeated for 24 other integral values of the pressure from 1 to 200 mm. of Hg so that complete sets of vapor pressure-temperature values were computed for the methyl esters of Table I and II. The data for each compound were then fitted to the conventional Antoine equation, and the resulting complete set of conventional Antoine equation constants for the fatty acid methyl esters from C6 to C24

<sup>1</sup> Present address, Monsanto Chemical Co., St. Louis 66, Mo.

Table I. Structure Parameters and Boiling Points of Fatty Acid Methyl Esters at 10 Mm. (9, 11)

Methyl Ester	Calcd. Structure Parameter $N_p$	Temp., ° C.	
		Exptl.	Predicted <sup>a</sup>
Caproate	13.4	41.7	41.8
Caprate	17.4	106.1	106.7
Laurate	19.4	134.6	134.5
Myristate	21.4	160.9	159.9
Palmitate	23.4	183.3	183.3
Stearate	25.4	205.4	205.1
Behenate	29.4	243.9	244.6

<sup>a</sup> Based on Equation 4 with  $G = 7.44192$ ,  $H = 22417.67$ ,  $K = 3508.23$ .

Table II. Structure Parameters and Predicted Temperatures for Fatty Acid Methyl Esters at 10 Mm.

Methyl Ester	Calcd. $N_p$	Predicted Temp., ° C.
Heptanoate	14.4	59.5
Caprylate	15.4	76.1
Nonanoate	16.4	91.8
Hendecanoate	18.4	120.9
Tridecanoate	20.4	147.4
Pentadecanoate	22.4	171.8
Heptadecanoate	24.4	194.4
Nonadecanoate	26.4	215.4
Arachidate	27.4	225.5
Heneicosanoate	28.4	235.2
Tricosanoate	30.4	253.7
Lignocerate	31.4	262.6

Table III. Antoine Equation Constants from Experimental and Predicted Vapor Pressure Data for Methyl Esters of Normal Saturated Fatty Acids

Carbon No.	Methyl Ester		Antoine Constants			Pressure Range, Mm. Hg
			A	B	C	
6	Caproate	<i>x</i>	7.83000	1935.93	241.771	10-200
7	Heptanoate	<i>p</i>	7.45148	1768.74	214.777	10-200
8	Caprylate	<i>x</i>	7.25830	1711.90	197.660	10-200
9	Nonanoate	<i>p</i>	7.02181	1622.62	177.730	10-200
10	Caprate	<i>x</i>	7.55167	2038.05	204.938	10-200
11	Hendecanoate	<i>p</i>	7.19033	1830.53	174.851	1.0-200
12	Laurate	<i>x</i>	7.14872	1851.00	166.415	1.0-200
13	Tridecanoate	<i>p</i>	6.91197	1740.55	146.878	1.0-200
14	Myristate	<i>x</i>	6.85551	1744.95	137.943	1.0-200
15	Pentadecanoate	<i>p</i>	6.80568	1754.03	130.057	1.0-175
16	Palmitate	<i>x</i>	6.37002	1528.00	101.209	1.0-175
17	Heptadecanoate	<i>p</i>	6.30962	1537.53	94.9218	1.0-75
18	Stearate	<i>x</i>	5.90665	1352.70	70.2761	1.0-75
19	Nonadecanoate	<i>p</i>	5.67993	1258.58	53.2910	1.0-40
20	Arachidate	<i>p</i>	5.55289	1220.16	42.3277	1.0-40
21	Heneicosanoate	<i>p</i>	5.00903	983.482	9.93311	1.0-20
22	Behenate	<i>x</i>	4.82924	921.793	-4.07148	1.0-20
23	Tricosanoate	<i>p</i>	5.61974	1309.59	30.0640	1.0-10
24	Lignocerate	<i>p</i>	5.50366	1272.62	20.3138	1.0-10

Note: *x* = from experimental data; *p* = predicted values; no experimental data for this compound.

Table IV. Constants for Equation 1 for Various Kinds of Compounds

Compound	Carbon No.	$G$	$H$	$K$	Pressure, Mm. Hg	Root Mean Square Deviation, ° C.
Hydrocarbons	5 to 16	22.37989	317,868.8	14,811.63	500	0.065
Acids	4 to 20	4.92045	6,304.28	1,508.28	50	0.89
Alcohols	3 to 20	4.39283	6,085.41	1,834.21	50	0.65
1-Chloroalkanes	3 to 40	-8.38363	66,701.5	-7,175.26	50	0.93

is given in Table III. The usefulness of the technique is illustrated by this table because the Antoine constants for the odd carbon methyl esters and also the C20 and C24 esters were derived entirely without experimental vapor pressure-temperature data on these compounds.

#### OTHER APPLICATIONS

The method has also been applied to homologous series of hydrocarbons, acids, alcohols, and 1-chloroalkanes.

Data from the literature for typical compounds of these classes at pressures of 500, 50, 50, and 50 mm. of Hg respectively, were fitted to Equation 1; the corresponding constants for Equation 1 are listed in Table IV. The data were taken from the tables of the API (1) and the MCA (6) research projects.

The root-mean-square deviations for the predicted temperatures from the experimental values also appear in

Table IV. A prediction was also made using the 1-chloroalkane temperatures and structure parameters from five homologs only. The resulting predicted temperatures for all 38 compounds had a root-mean-square deviation of 1.2° C.

The equation, although developed for an homologous series, may also be used to predict branched chain isomer boiling temperatures as will be discussed in a later section.

No other simple method known to the authors has either the accuracy or the range of this new prediction and correlation scheme.

#### PROCEDURE

The general method involves use of Equation 1 and four successive steps. The first and second steps are the assembly of three or more sets of the basic data and the determination of the structure parameters. The third step is the

Table V. Poizat Molecular Structure Factors

Straight Chain Compd., Mol. Sub-group	Factor
—CH <sub>3</sub>	+3.0
—CH <sub>2</sub> —	+1.0
—CH—	-1.3
—C—	-3.7
=CH <sub>2</sub>	+2.84
=CH—	+0.98
=C—	-0.92
≡CH—	+3.05
≡C—	+1.10
—CH <sub>2</sub> Cl	+5.35
—CH <sub>2</sub> OH	+9.85
—CO—	+4.85
—CO <sub>2</sub> H	+4.7
—CO <sub>2</sub> —	+3.0

(Values to be added to the structure parameter for esters)

Methyl	+0.40
Ethyl	+0.10
Formates	+2.60
Acetates	+0.30
Propionates	+0.14

Branched Chain Isomers: Subtract 0.40 if there are one or more groups larger than a methyl group on the carbon next to the functional group. Also subtract 0.4 if more than one methyl group is attached to this carbon.

computation of the constants  $G$ ,  $H$ , and  $K$  for equation 1 using the values from steps 1 and 2. Step 4 is the final operation and is the data prediction step.

**Step 1. ASSEMBLE EXPERIMENTAL DATA.** At least three data points must be available. These are the boiling temperatures at constant pressure for compounds of the series of interest. These points should encompass the range over which predictions are desired since the procedure is designed for interpolation rather than extrapolation. For example, if one were interested in predicting boiling temperatures at 10 mm. of Hg for the C10 through C20 normal aldehydes it would first be necessary to get the boiling temperatures at this pressure for three members of the series. Ideally these might be the C10, C15, and C20 compounds.

Three values is a minimum number and if more data are available they should be used. As with any empirical prediction scheme the accuracy of the prediction improves as more experimental data are used in its development.

**Step 2. SPECIFY THE STRUCTURE PARAMETERS.** The structure parameters for each of the compounds selected in step 1 must be obtained. These are determined by using the factors and rules listed in Table V. The factors are from Poizat (7) who used a group contribution type of approach to the study of vapor pressures. He based his work on the expression.

$$t = (\log N_p - G')/H' \quad (2)$$

which is much less precise and has a more limited range than Equation 1 but served quite well for the factor determination. The structure factors were taken directly from his work with a minor simplification permitted by use of Equation 1 instead of Equation 2. This simplification was to abandon entirely his numerous adjusting factors for branched chain structure and to incorporate a single new

factor applicable if more than one methyl or larger group is attached to the carbon atom next to a functional group.

The calculation of the structure parameters will be illustrated for methyl laurate. The molecular structure CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>CO<sub>2</sub>CH<sub>3</sub> contains 2 CH<sub>3</sub> groups, 10 CH<sub>2</sub> groups, and 1 CO<sub>2</sub> group and in addition is a primary methyl ester. From Table V we find that the various contributions are +3.0, +1.0, and +3.0, respectively.

Combining these and including the methyl ester contribution of 0.4 we have 2(3.0) + 10(1.0) + 1(3.0) + 0.4 = 19.4. This then is the structure parameter for methyl laurate.

At the conclusion of this step 2 we have a table which includes the names of the compounds (three or more), their boiling temperatures at a specified pressure, and their structure factors.

**Step 3. DETERMINE THE CONSTANTS FOR EQUATION 1.** In this phase of work the constants  $G$ ,  $H$ , and  $K$  of Equation 1 are calculated using the numerical values from steps 1 and 2. In this work the equation was fitted to the data by the method of least squares and all calculations were done on an IBM 650 computer using a standard procedure (8). The computer output consisted of values of  $G$ ,  $h$ , and  $K$  for Equation 1 and a root-mean-square deviation which indicates the agreement between the temperatures listed from step 1 and those calculated using Equation 1.

To illustrate: the data listed in the middle two columns of Table I for the normal saturated fatty acid esters are the result of steps 1 and 2. The temperatures are for a pressure of 10 mm. of Hg, and the structure parameters were calculated using the factors in Table V.

These structure parameters and temperatures were fed into the computer which carried out the calculations to give the constants for Equation 1. These are  $G = 7.44192$ ;  $H = 22,417.67$ ,  $K = 3508.23$ . Thus Equation 1 becomes

$$\log_{10} N_p = 7.44192 - \frac{22417.67}{3508.23 + t} \quad (3)$$

This equation represents analytically the variation of the boiling temperature with structure parameter (dependent upon carbon number), at 10 mm. of Hg for these normal esters.

Because the constants for the equation can also be determined by a semigraphical procedure developed by Lu (5), a computer is not a necessity. However, the time required to obtain the constants for one pressure is only of the order of 2 minutes with an IBM 650 computer. In addition, the fit will probably be better than for the graphical method. If an appreciable amount of work is to be done, the use of a computer is recommended.

**Step 4. DATA CORRELATION AND PREDICTION.** The final step is to produce temperature values for cases where they are not known at all, or where known values need to be confirmed or evaluated. For correlation purposes we have the results of step 3 which in this work consisted of the constants and the root-mean-square temperature deviation that automatically indicates the quality of fit. Thus the RMS for temperatures computed using Equation 3 and the experimental data listed in Table I for the fatty acid methyl esters was 0.54°C. For prediction usage Equation 1 is written

$$t = \frac{H}{G - \log N_p} - K \quad (4)$$

The structure parameter for the compound is calculated, plugged into the equation with its appropriate values of  $G$ ,  $H$ , and  $K$ , and the boiling temperature is calculated.

Table II lists predicted temperatures obtained in this way for a number of fatty acid esters.

Table VI. Predictions Using Relative Retention Volumes of Gas Chromatography

Compound	Carbon No.	Relative Retention Volume	Temp., ° C.	
			Exptl.	Calcd.
Polydiethylene Glycol Succinate Substrate Pressure, 1.95 mm. Hg				
Methyl Ester				
Hendecanoate	11	0.42	90.4	89.9
Laurate	12	0.57	103.5	104.1
Tridecanoate	13	0.73	116.0	115.1
Myristate	14	1.00	127.8	128.4
Pentadecanoate	15	1.31	139.1	139.2
Palmitate	16	1.77	150.1	150.8
Heptadecanoate	17	2.29	160.5	160.2
Stearate	18	3.09	170.6	170.7
Nonadecanoate	19	4.02	180.2	179.6
Arachidate	20	5.50	189.5	189.6
Heneicosanoate	21	7.30	198.5	198.4
Behenate	22	9.83	207.1	207.1
Tridecanoate	23	13.71	215.7	216.5
Lignocerate	24	17.51	223.8	223.1
$\Delta\text{RMS} = 0.53^\circ\text{C. } G = -5.12591 \ H = 2488.08 \ K = -613.778$				
Paraffin Substrate, Atmospheric Pressure				
Amine				
Methyl	1	0.61	-6.5	-6.1
Ethyl	2	1.00	16.6	15.6
Propyl	3	2.20	48.7	48.3
Butyl	4	4.70	77.8	77.6
Amyl	5	10.5	104.0	106.6
Hexyl	6	22.6	132.7	132.4
Heptyl	7	49.5	158.3	157.3
$\Delta\text{RMS} = 1.14^\circ\text{C. } G = -9.28229 \ H = 8516.99 \ K = 933.169$				
Carbitol Substrate, Atmospheric Pressure				
Acid				
Acetic	2	0.26	117.9	117.0
Butyric	4	1.00	163.3	165.0
Caproic	6	3.58	205.7	205.2
Caprylic	8	12.0	239.9	239.3
Capric	10	40.5	270.0	270.3
Lauric	12	138.5	298.7	298.7
$\Delta\text{RMS} = 0.88^\circ\text{C. } G = -9.19959 \ H = 6511.31 \ K = -872.8$				
Stearic Acid Substrate, Atmospheric Pressure				
Hydrocarbon				
Propane	3	0.082	-42.1	-46.2
Butane	4	0.298	-0.5	+4.5
Isobutane	4	0.190	-11.7	-10.0
Isopentane	5	0.738	+27.9	+27.2
Pentane	5	1.00	+36.1	+33.4
Cyclopentane	5	2.65	+49.3	+49.8
$\Delta\text{RMS} = 2.95^\circ\text{C. } G = -2.77130 \ H = 342.222 \ K = -156.895$				

### CHROMATOGRAPHIC RETENTION VOLUMES AS PARAMETERS

The most obvious place to modify the method is in the calculation of the structure parameter. Various authors have proposed different kinds of isomeric variation and group contribution schemes, at best long and complex, that could be considered for the problem (3, 10).

An entirely new approach to the problem was made by obtaining the parameter by experiment instead of by computation. With certain restrictions, the retention volumes of gas chromatography can be used as structure parameters. The relative retention volume of a compound in gas chromatography is a measure of its volatility, and this is the basis for the relation to vapor pressure.

Table VII. Predictions Using Relative Retention Volumes of Gas Chromatography

Compound	Carbon No.	Relative Retention Volume	$t(\text{Atm. Press.}), ^\circ\text{C.}$	
			Exptl.	Calcd.
Benzylidiphenyl Substrate				
Methyl Esters				
Formate	1	0.117	31.5	33.5
Acetate	2	0.261	56.9	56.7
Propionate	3	0.530	79.7	78.7
Butyrate	4	1.00	102.7	99.8
Valerate	5	2.13	128.4	126.9
Caproate	6	4.37	151.2	154.9
$\Delta\text{RMS} = 2.21^\circ\text{C. } G = 8.17285 \ H = 5291.21 \ K = 547.611$				
Paraffin Wax Substrate				
Methyl Esters				
Formate	1	0.090	31.5	32.2
Acetate	2	0.228	56.9	57.2
Propionate	3	0.495	79.7	79.6
Butyrate	4	1.00	102.7	101.2
Valerate	5	2.15	128.4	126.3
Caproate	6	4.70	151.2	153.8
$\Delta\text{RMS} = 1.51^\circ\text{C. } G = 10.00517 \ H = 7303.38 \ K = 628.714$				
Dioctyl Phthalate Substrate				
Methyl Esters				
Formate	1	0.124	31.5	31.1
Acetate	2	0.256	56.9	56.7
Propionate	3	0.510	79.7	80.5
Butyrate	4	1.00	102.7	103.1
Valerate	5	2.12	128.4	127.9
Caproate	6	4.36	151.2	151.1
$\Delta\text{RMS} = 0.68^\circ\text{C. } G = -26.69577 \ H = 54704.97 \ K = -2152.35$				

Table VIII. Predicted and Experimental Boiling Temperatures of Alcohol Branched-Chain Isomers (50 Mm. Hg)

Compound	Calcd. Structure Parameter	Temp., ° C.		Diff.
		Exptl.	Calcd.	
2-Methyl-1-propanol	14.55	48.2	49.8	+1.6
2-Methyl-1-butanol	15.55	65.8	66.8	+1.0
3-Methyl-1-butanol	15.55	67.3	66.8	-0.5
2,2-Dimethyl-1-propanol	14.55	51.0	49.8	-1.2
2-Methyl-1-pentanol	16.55	79.7	83.0	+3.2
3-Methyl-1-pentanol	16.55	84.0	83.0	-1.0
4-Methyl-1-pentanol	16.55	84.1	83.0	-1.1
2-Ethyl-1-butanol	16.35	77.3	79.9	+2.6
2,2-Dimethyl-1-butanol	15.75	69.1	70.1	+1.0
2,3-Dimethyl-1-butanol	16.25	81.0	78.2	-2.8
3,3-Dimethyl-1-butanol	16.15	76.0	76.6	+0.6

Comparison of experimental temperatures with predicted temperatures based on gas chromatography retention volumes for methyl esters, acids, amines, and hydrocarbons are listed in Table VI. The structure parameters determined by chromatography are adequate for the reproduction of the vapor pressure data for these compounds.

In gas chromatography the pure compound volatilities are almost always modified by the stationary phase. In an homologous series such modification is likely to be closely similar for the several members of the series. However, since there is no assurance of this, it may be necessary to try more than one substrate to find a satisfactory one. The data in Table VII for the lower fatty acid methyl esters illustrate this situation. The root-mean-square deviation of the calculated from the experimental tempera-

Table IX. Predicted and Experimental Boiling Temperatures of Methyl Ester Branched Chain Isomers

Compound	Calcd. Structure Parameter	Temp., ° C.		Press., Mm. Hg
		Exptl.	Calcd.	
20-Methylheicosanoate	29.1	202.5	204.6	1.95
18-Methylnonadecanoate	27.1	185	186.8	1.95
16-Methylheptadecanoate	25.1	166.5	167.7	1.95
14-Methylpentadecanoate	23.1	146.5	147.0	1.95
12-Methyltridecanoate	21.1	124.5	124.4	1.95
10-Methylhendecanoate	19.1	100.5	99.5	1.95
8-Methylnonanoate	17.1	75	71.9	1.95
4,8,12-Trimethyloctadecanoate	27.5	194	204	3.75
4-Methyloctadecanoate	26.1	194	190	3.75
2,3,4-Trimethylhexadecanoate	25.5	180	184	3.75
4-Ethyl-4-butylnonanoate	21.7	130-2	143	3.75
2-Ethyl-2-butylnonanoate	21.3	130	139	3.75
2-Ethylheptanoate	15.3	110	109	50

tures varied from 2.21 to -0.5 to 0.68 for the benzyldiphenyl, paraffin wax, and dioctyl phthalate substrates, respectively. The importance of reducing the root-mean-square error becomes even more obvious when the equations developed for the normal series data are used to predict boiling temperatures for branched chain isomers. The greater the deviation the less confidence one may place in the predicted values.

#### PREDICTION OF DATA ON ISOMERS

Both the structure and retention volume parameters have been used to predict data on branched-chain isomers. The calculated structure parameters were used for the prediction of values for a series of alcohol and methyl ester compounds and for one acid. The experimental boiling point of 2-ethylheptanoic acid at 50 mm. of Hg is 163.9° C. The boiling point predicted using Equation 1 and the constants from Table IV was 162.0° C. This acid has a structure parameter of 14.0.

Data for alcohols are listed in Table VIII. The experimental data selected from the tables of the API and the predicted temperatures for these 11 isomers have an average deviation of 1.5° C. Structure parameters are listed in the table and were used in Equation 1 with the constants from Table IV to calculate the temperatures. Some values for methyl ester branched-chain isomers are given in Table IX. The temperatures were predicted using Equation 1, the calculated structure parameters shown, and the constants for methyl esters. Agreement for the first seven compounds and the last compound is relatively good (average deviation of 1.2° C.), but for compounds with multiple branching the discrepancy is larger. The predicted temperatures are probably more accurate for these compounds than the reported experimental temperatures are. For instance, the reported temperatures (2) for 4,8,12-trimethyloctadecanoate and 4-methyloctadecanoate are both 194° C., yet one has 21 carbons to the other's 19. The predicted temperatures are 204 and 190° C., respectively. The temperatures for the normal straight chain C21 and C19 compounds are 212 and 193° C., respectively. This casts doubt on the 194° C. temperature for the C19 branched isomer. The predicted 190° C. temperature is a more realistic value since branching results in a decrease in the boiling temperature. The 194° C. value for the C21 triply branched isomer is completely out of line since the mere introduction of three branches would not be likely to decrease the boiling point of such a long chain compound by 18° C. The value of 204° C. is much more realistic when compared with the value of 212° C. for the straight chain C21 methyl ester. This

Table X. Predicted and Experimental Boiling Temperatures of Methyl Ester Branched Chain Isomers

Compound	(1.95 Mm. Hg)		
	Relative Retention Volume	Temp., ° C.	
16-Methylheptadecanoate	2.78	166.5	167.1
14-Methylheptadecanoate	1.56	146.5	146.0
12-Methylheptadecanoate	0.88	124.5	123.1

Table XI. Predicted and Experimental Boiling Temperatures of Odd Carbon Acids and Isomers at Atmospheric Pressure

Compound	Relative Retention Volume	Temp., ° C.	
		Exptl.	Calcd.
Propionic	0.54	140.8	143.8
Isobutyric	0.81	154.7	157.9
Isovaleric	1.48	176.5	177.9
Valeric	1.91	185.5	186.0
4-Methylvaleric	2.94	199.5	199.3
Heptanoic	6.55	223.0	222.7
Nonanoic	22.0	255.6	255.1
Hendecanoic	72.8	284.2	284.2

same kind of analysis can be applied to the other compounds where large discrepancies occur.

The gas chromatography retention volume structure parameters have also been used to predict isomer boiling temperatures. The constants in Table VI were used with Equation 1 to calculate temperatures in Table X for methyl ester isomers, and the agreement is good.

The data in Table XI are for eight odd-carbon and branched-chain acids and were predicted using Equation 1 and the constants from Table VI. Once again the agreement is good.

This method provides a practical tool for accelerating laboratory programs that determine vapor pressure data and for checking existing data.

The retention volumes reported in this work were taken from Journal of Chromatography (4); other data came from the compilation of Doss (2).

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