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A boiling point estimation method for alkanes and perfluoroalkanes

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Abstract

The boiling points of non-polar liquids have been found to correlate well with $R_m V^{-1/3}$ where R_m is the molar refractivity and V the molar volume. A method for estimating the boiling points of alkanes and perfluoroalkanes (*F*-alkanes), using estimated values of R_m and V, has been developed. The correlation coefficient was 0.996 for a data set consisting of 19 alkanes and 18 *F*-alkanes.

Introduction

Many methods have been developed for estimating the physical properties of organic compounds [1]. Generally, the goal has been to estimate a specific property, such as boiling point, critical temperature, atmospheric lifetime, etc., using simple mathematical operations, knowing only the chemical structure. While many such methods depend on empirically derived group contributions or molecular connectivity analysis [2], estimation methods which are based on fundamental principles are of special interest from a theoretical standpoint.

A number of methods for estimating boiling points are available [3] and most afford good accuracy. Frequently, however, different equations are required for various classes of compounds. In other methods, empirically derived values for group contributions are not available for all classes of compounds, particularly *F*-alkanes. In connection with other studies, there was a need to estimate the boiling points of alkanes and *F*-alkanes using the *same* equation. Although this may at first appear trivial, it should be recalled that plots of boiling point versus carbon number for *F*-alkanes and alkanes are not parallel, but intersect near the butanes, with the boiling points of *F*-alkanes being higher than the corresponding alkanes of the same carbon number, n, for $n<4$, but with lower boiling points for $n>4$.

For non-polar substances having essentially no permanent dipole moment (such as alkanes and *F*-alkanes), the primary molecular attractive forces are London dispersion forces. The potential energy due to dispersive forces, U_L, is proportional to the polarizability, α, and distance, r, between molecules ($U_L = -3h\nu_0\alpha^2(4r^6)^{-1}$) [4a].

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The approach that was taken in this study assumes that the r^6 term is a function of the molar volume, and that the polarizability term is related to the molar refractivity. The latter is based on the relationship $\alpha = 3R_m(4\pi N)^{-1}$, where R_m is the molar refraction and α is the mean molecular polarizability [4b]. Thus, it should be possible to relate the boiling points of non-polar substances to their molar refractivities and volumes. Estimation methods are available for each and require only slight modification in order to allow their application to cyclic and acyclic *F*-alkanes. This approach is similar (although much simplified) to that of Myers [5] who included shape (spherical, tetrahedral, cylindrical or flat) in his approach, reasoning that shape will affect the closeness of approach (r) between molecules. For the linear alkanes, boiling points were correlated with an expression which required values for R_m, I (ionization potential, representing the frequency term, ν_0, in the expression given above for U_L), V_b (molar volume at the boiling point) as well as the length and cylindrical radius of the molecule.

Estimates of molar refractivities for alkanes and *F*-alkanes have been based on the summation of individual bond refractivities [4b] or on the summation of atomic refractivities [6]. Both methods provide good accuracy, but require different types of adjustment to accommodate structural variations such as multiple bonds or cyclic structures. In the estimation method using bond refractivities, double bonds or single bonds in strained rings are given different values from normal single bonds. When atomic refractivities are used to estimate molar refractivities, multiple bonds are accommodated by assigning higher values to appended groups. For example, an allylic chlorine is assigned a higher atomic refractivity than a non-allylic chlorine.

Experimental

Boiling points for the alkanes used in the correlation were taken from ref. 7. Boiling points for the *F*-alkanes were found in refs. 8–12. An average of the extreme values was used when more than one boiling point for a given compound was reported. The spread in reported boiling points for *F*-alkanes was as large as 6 °C. The midpoint was used in those cases where a boiling point range was reported in order to calculate differences in known and estimated boiling points. The data set includes 19 alkanes and 18 *F*-alkanes, spanning a boiling point range of *c.* 165 °C.

Results and discussion

In order to determine the appropriate *form* of the correlation equation which exists between boiling points and the molar refractivities and volumes for alkanes and *F*-alkanes, a small data set was analyzed statistically without prejudice with respect to Myers' findings. This set consisted of pentane through octane and *F*-pentane through *F*-octane, for which values of R_m

and V were readily available. Using this limited data set, there was an increasingly good correlation from $R_m V^{-1}$ ($r=0.449$) to $R_m V^{-1/2}$ ($r=0.948$) to $R_m V^{-1/3}$ ($r=0.979$).

It is not readily apparent why a good correlation should hold for $R_m V^{-1/3}$. Myers correlated $T_b^{1/2}$ with $R_m I^{1/2} V_b^{-1}$ for spherical molecules (the noble gases and Group IV hydrides; $r=0.9975$), and with the same expression (but plotted separately) for tetrahedral compounds (Group IV halides and tetramethyl compounds; $r=0.9668$). For both spherical and tetrahedral molecules plotted together, $r=0.8724$. For cylindrical compounds (n-alkanes), $T_b^{1/2}$ correlated with $R_m I^{1/2} L^{3/2} V_b^{-3/2}$ ($r=0.9976$), where L is the length of the molecule. For flat molecules (aromatics), $T_b^{1/2}$ correlated with $R_m I^{1/2} A^3 V_b^{-3}$, where A is the area of the molecule ($r=0.798$). Using the same values for R_m, V_b and T_b used by Myers, it was found rather surprisingly that the expression used above for the alkanes and F-alkanes, viz. $R_m V^{-1/3}$, correlated well with T_b, regardless of the shape of the molecule. For example, for the 11 spherical molecules, $r=0.9927$; for the 17 tetrahedral molecules, $r=0.9611$; and for both spherical and tetrahedral compounds, plotted together, $r=0.9773$. For the seven cylindrical compounds, $r=0.9997$. Perhaps most surprising is the far better correlation for the seven flat molecules ($r=0.9758$).

More and Capparelli [13] found that Myers' correlation for cylindrical and flat molecules could be simplified. They correlated $T_b^{1/2}$ with $R_m I^{1/2}$ (using separate lines) for both cylindrical ($r=0.9906$) and flat molecules ($r=0.9834$). Together, the correlation for the flat and cylindrical molecules is 0.9596 (same line). However, for the same group of flat and cylindrical compounds, $r=0.9899$ when T_b is plotted against $R_m V^{-1/3}$ (same line). In fact, for the entire data set of 42 non-polar compounds, spanning a boiling point range of nearly 500 °C, the correlation coefficient using $R_m V^{-1/3}$ is 0.9754. Thus, the simple expression $R_m V^{-1/3}$, which does not distinguish different molecular shapes, nicely correlates the boiling points of a variety of non-polar molecules. A good correlation was also found for this set of 42 compounds using the term $R_m V^{-1/2}$ ($r=0.9703$). To some extent, the shape of a molecule affects its molar volume, which is taken into account through the use of either V or R_m. A more elaborate delineation, however, does not appear to be necessary.

When correlating the boiling points of both linear alkanes and F-alkanes, plots of $T_b^{1/2}$ versus $R_m I^{1/2}$ necessarily must fail to give good straight line plots, since both molar refractivities and ionization potentials* are greater for the F-alkanes than for the corresponding n-alkanes.

Although the correlation of boiling point with $R_m V^{-1/3}$ is very promising, a number of factors will limit the accuracy of the estimation method. First,

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*Although the ionization potentials for relatively few F-alkanes have been measured, there is a clear trend from the following comparisons: CF_4, 15.8–17.8 eV versus 12.7–13.6 for CH_4; C_6F_6, 9.9 eV versus 9.25 for C_6H_6; c-C_5F_{10}, 11.7 eV versus 10.9 for c-C_5H_{10}; c-C_6F_{12}, 13.2 eV versus 9.88 for c-C_6H_{12}; and SiF_4, 15.8 eV versus 12.6 for SiH_4.

bond or atom refractivities are not invariant with structure. Values for estimated group volumes are also variable. For example, the volume for CF_3 and CF_2 groups in *F*-alkanes are given [14] as 57.5 and 23 ml, respectively, while in other molecules the recommended values for the same groups are 46.8 and 20.8 ml. This produces considerable ambiguity regarding what values should be used to estimate the volumes of molecules such as $CF_3CF_2CF_2CH_2CH_2CH_3$. Another, similar set of volumes for fluorinated groups was used by Lawson [15]. Both R_m and, to a greater extent, molar volumes are temperature dependent. The ratio of the molar volume of octane at the boiling point (V_b) to that at room temperature, for example, is *c.* 1.15. Obviously, V_b cannot be used in the estimation of boiling points, and consequently, the recommended group volumes will be in error. The extent of the error will be dependent on the boiling point of the compound in question. Finally, the group volumes and bond refractivities of the methanes and ethanes are substantially different from those used for the higher homologs. Therefore, these four compounds (CH_4, CF_4, C_2H_6, C_2F_6) were excluded from the data set.

Values for bond refractivities and group volumes are given in Tables 1 and 2. Literature [14] group volume values for CF_3 (non-perfluorocarbon),

TABLE 1

Group molar volumes (ml)

Group	Value	Number of entries containing group
F (in CF_3)	22	14
F (in CF_2)	21	10
F (in CF)	18	6
F (attached to ring)	24	7
C (no attached H)	−19.2	7
CH	−1	8
CH_2	16.1	18
CH_3	33.5	14
ring (5 or 6 carbon)	16	7
ring (3 or 4 carbon)	18	7

TABLE 2

Molar bond refractivities (ml)

Bond type	Value	Number of entries
C−C normal single bonds	1.25	32
C−C cyclopropanes and cyclobutanes	1.73	7
C−H	1.69	19
C−F	1.83	18

CF, C, CH, CH_2, CH_3 and ring closure (all types) were used. Changes in group volumes from literature values include only the value for F in a CF_2 group to 21 ml (versus a literature value of 20 ml for each F in non-perfluorocarbons and 23 ml for the CF_2 group in F-alkanes, or 21.1 ml for each F), and the value for F attached to a ring carbon, which was assigned a value of 24 ml (no corresponding literature value).

The values for the bond refractivities for normal C—C bonds and C—H bonds determined by Denbigh [4b] were used to calculate R_m, but the value for the C—F bond was changed from 1.72 to 1.83. This change reflects the choice of reference molecule from CF_4 to F-hexane, using the C—C bond refractivity of 1.25. The value for the C—C bond refractivity in cyclopropanes and cyclobutanes was determined by subtracting the value for the 8 C—H bonds ($20.44-8\times1.69$) from the R_m value for cyclobutane to give the total value for the 4 C—C bonds (1.73 each). This value is consistent with the increase in bond refractivity with increasing p character of the carbon–carbon bond [4b].

For the data set consisting of 18 F-alkanes and 19 alkanes, $R_m V^{-1/2}$ was plotted against the known boiling point ($r=0.934$). However, a better correlation was obtained ($r=0.980$) for a plot of boiling point against $R_m V^{-1/3}$. Some reduction in the errors for cyclic and branched compounds resulted from the use of a correction term $S=S_b S_c$ where S_b has a value of 1.03 for alkanes (only) if the compound has at least one branch point, otherwise its value is 1.00 (including branched F-alkanes). Similarly, S_c has a value of 0.95 for all cyclic F-alkanes and cyclic alkanes having a cyclopentane or cyclohexane ring, otherwise its value is 1.00.

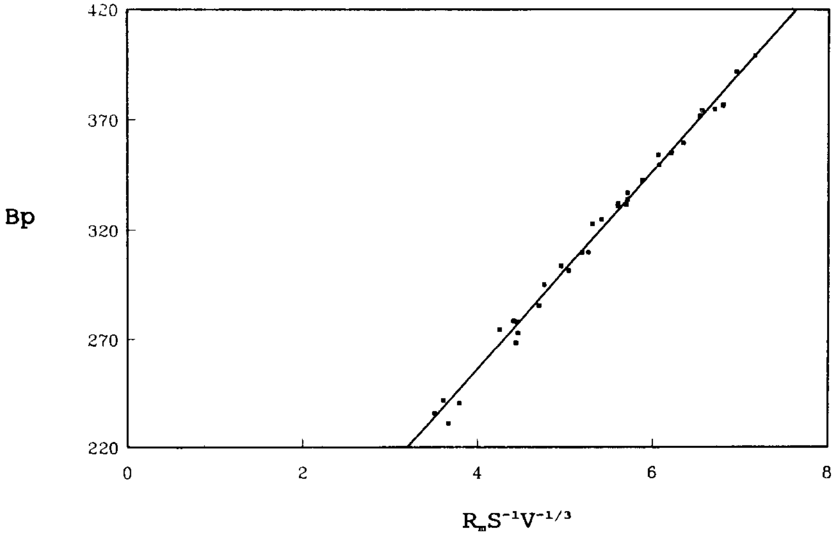

Fig. 1. Plot of known boiling points (K) versus $R_m S^{-1} V^{-1/3}$ for the compounds listed in Table 3.

$$\text{B.p. (K)} = 45.2 R_m S^{-1} V^{-1/3} + 75.5 \tag{1}$$

Thus, a plot of $R_m S^{-1} V^{-1/3}$ versus boiling point (Fig. 1) gave a straight line with $r = 0.996$.

Calculated values using eqn. (1) are listed in Table 3. The average error, on a degree Kelvin basis, was 1.14%.

TABLE 3

Estimated boiling points (K)

Compound	Known b.p.	$R_m S^{-1} V^{-1/3}$	Calc. b.p.	Error (%)
F-propane	235.7	3.51	234.2	0.64
F-butane	274.2	4.25	267.8	2.33
F-pentane	303.0	4.95	299.0	1.32
F-hexane	331.8	5.60	328.4	1.02
F-heptane	354.9	6.21	356.3	0.39
F-octane	376.7	6.80	382.9	1.65
F-cyclopropane	241.7	3.61	238.9	1.16
F-cyclobutane	268.2	4.44	276.4	3.06
F-cyclopentane	294.7	4.76	290.7	1.38
F-cyclohexane	324.6	5.41	319.8	1.48
F-Me-cyclohexane	349.3	6.07	349.9	0.17
F-1,3-di-Me-cyclohexane	374.7	6.71	378.6	1.04
F-2-Me-butane	303.2	4.95	299.0	1.39
F-2,3-di-Me-butane	330.7	5.60	328.4	0.70
F-2-Me-pentane	330.9	5.60	328.4	0.76
F-3-Et-hexane	376.2	6.80	382.9	1.78
F-3-Me-pentane	331.5	5.60	328.4	0.94
F-Me-cyclopropane	278.2	4.41	274.9	1.19
propane	231.1	3.67	241.4	4.46
butane	272.7	4.46	277.1	1.61
pentane	309.3	5.19	310.3	0.32
hexane	342.2	5.88	341.4	0.23
heptane	371.6	6.54	371.0	0.16
octane	398.9	7.16	399.2	0.08
cyclopropane	240.5	3.79	246.7	2.58
cyclobutane	285.2	4.70	287.8	0.91
cyclopentane	322.4	5.31	315.6	2.11
cyclohexane	353.9	6.06	349.2	1.33
Me-cyclohexane	374.1	6.56	371.8	0.61
2-Me-butane	301.0	5.04	303.2	0.73
2,3-di-Me-butane	331.2	5.70	333.3	0.63
2-Me-pentane	333.5	5.71	333.5	0.00
3,3-di-Me-pentane	359.3	6.35	362.7	0.95
3-Et-hexane	391.7	6.95	389.6	0.54
3-Me-pentane	336.5	5.71	333.5	0.89
Me-cyclobutane	309.5	5.26	313.5	1.29
Me-cyclopropane	277.7	4.45	276.5	0.43

Me = methyl; di-Me = dimethyl; Et = ethyl; $R_m S^{-1} V^{-1/3}$ are estimated values using Tables 1 and 2. Per cent error was calculated as 100 × the absolute error divided by the known boiling point.

Sample calculation: methylcyclohexane

1. Estimate R_m: 7 C–C bonds = $7 \times 1.25 = 8.75$
14 C–H bonds = $14 \times 1.69 = 23.66$
Total = 32.41 (expl. 32.65)

2. Estimate V: CH_3 = 33.5
CH = -1
$5 \times CH_2$ = 80.5
ring = 16
Total = 129 (expl. 127.6)
$V^{1/3}$ = 5.053

3. Estimate b.p.: $R_m S^{-1} V^{-1/3}$ = 32.41/(0.95)(1.03)(5.053)
= 6.56
B.p. = $(45.2)(6.56) + 75.5$
= 371.8 (expl. 374.1)
Error = $100\,(|371.8 - 374.1|)/374.1$
= 0.61%

Conclusions

The procedure detailed here allows the boiling points of saturated alkanes and *F*-alkanes (linear, branched or cyclic) to be estimated using a single equation. The term $R_m V^{-1/3}$ can also be used to correlate the boiling points of other non-polar compounds without a knowledge of their ionization potentials. Most notable among these are the noble gases ($r = 0.991$), for which ionization potentials range from 10.75 eV for radon to 24.58 eV for helium.

It is generally found, whether boiling points are correlated with $R_m V^{-1/3}$, $R_m I^{1/2}$ or the other parameters developed by Myers, that the correlation is better when the compounds are grouped into their different types. Nevertheless, good correlations have been obtained using the term $R_m V^{-1/3}$ for data sets comprised of molecules with substantially different shapes, as well as for data sets comprised of different classes of compounds (e.g. alkanes and *F*-alkanes or n-alkanes and aromatics). Consequently, a linear function of $R_m V^{-1/3}$ may be used to represent dispersion forces in liquids.

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