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Relations between the boiling points of perfluoro-ethers, perfluoroalkanes and normal alkanes

A. A. Woolf
Faculty of Applied Sciences, Bristol Polytechnic, Bristol BS16 1QY (UK)

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Abstract

The boiling points of linear and cyclic mono- and poly-perfluoro-ethers containing n carbon and m oxygen atoms can be estimated as being equal to the boiling point of perfluoroalkanes of chain length $(n+m)$ less $m(22-m)$, independent of whether the ether is branched or cyclized. Deviations from a smooth increase in boiling point with molecular mass can occur when ethers close in molecular mass have different structures.

The non-available boiling points of the higher perfluoroalkanes have been estimated from the relationship $T_F=0.247T_H \times M_F/M_H$ where T_F and T_H are the respective absolute boiling points of a fluoroalkane and the corresponding normal alkane with masses of M_F and M_H. The limiting boiling point for the fluorocarbon series derived from this relationship is 899 K.

Introduction

The favourable chemical and thermal stabilities of perfluoroethers have generated a diverse set of applications. Recent synthetic work has been aimed at designing ethers with specific volatilities [1]. However, this presupposes an initial estimate of boiling points (b.ps.) covering a wide range of structures. One proposed relationship used a third-order polynomial fit [1] to the relative molecular mass (M) of the compounds.

$$\text{B.p. }(^\circ\text{C}) = -84.8+0.530M-2.83\times10^{-4}M^2+6.61\times10^{-8}M^3 \qquad (1)$$

Although the correlation coefficient of 0.98 so obtained may seem satisfactory, there are too many deviations outside reasonable errors in b.p. values, especially when extended to compounds of lower M values, to trust its general validity. The purpose of this paper is to show that the expectation of a smooth relation between b.p. and M will not hold for ethers of different structure having about the same value of M. A new relationship independent of M is proposed.

Results and discussion

Non-linear expressions are needed to fit b.ps. in homologous series because the rate of increase of b.p. with M gradually decelerates. This can

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be ascribed to a departure from chain linearity and a consequent decrease in average 'end-to-end' length as the chain becomes more flexible and chain interactions no longer increase in a linear fashion. The effect will depend on chain composition, especially for fluorocarbons whose coiling makes them inherently less flexible. Our approach to predicting boiling points has been to avoid the effect of this curvature rather than trying to match it, by comparing each homologous series with a corresponding unsubstituted carbon chain. Differences, or ratios, of b.ps. can then be more linearly related to M values.

Since the b.ps. of perfluoro-ethers are later to be related to those of perfluoroalkanes, which are only available over a limited range, we first relate perfluoroalkanes to n-alkanes. Normal b.ps. for alkanes are known accurately up to $n=18$ and extrapolated values may be obtained via $\ln(T_\infty - T_n) = a - bn^{2/3}$, where a and b are constants or more precisely using two additional constants [2]. The limiting b.p. $T_\infty = 1021$ K keeps extrapolated values within bound unlike higher polynomial extrapolations. In comparing fluorocarbons with hydrocarbons, there is a cross-over above $n=5$ when the b.ps. of the latter exceed those of the former. Hence only values above $n=5$ are used in the comparison. Interpolated fluorocarbon values are given for $n=14$ and 15 and extrapolated ones for $n=17$–20 using the differences encountered between successive hydrocarbons for the fluorocarbons which are shorter by three carbons. This procedure correctly reproduces the known value for $C_{16}F_{34}$. The figures in Table 1 and the constancy in the last column, yields the relationship:

$$T_F = 0.247 T_H \times M_F / M_H \qquad (2)$$

between the b.p. for a fluorocarbon, T_F, and the b.p. for a hydrocarbon, T_H, where M_F and M_H are the respective masses. It is also possible to calculate $T_\infty = 899$ K for fluorocarbons from this constant, since the mass ratio for the infinite chain equals the mass ratio CH_2/CF_2 of 0.2805.

Previous relationships of the form $T_F{}^2 = a + bn$ only fit limited ranges. Aten [3] used $a = 5500$ and $b = 17\,000$ to fit experimental values from $n = 1$–11, whereas Haszeldine and Smith [4] quoted quite different values of $a = 19\,000$ and $b = 15\,400$ to fit $n = 7$–12. Values outside these limits are over-estimated. Thus predicted b.ps. for $C_{30}F_{62}$ are 444.8 °C and 420.4 °C from the above non-linear relations, and 375.7 °C from the linear equation (2); another non-linear equation due to Kinney predicts a b.p. of 412.6 °C [5]. However, if Rouvray and Pandey's treatment of alkanes [6] is followed taking account of the changing curvature of a ln[b.p. (K) − ln(W)] plot, where W is the Wiener index, there is agreement within 3 °C of the values from eqn. (2).

The b.ps. of ethers can also be related to those of hydrocarbons. Aliphatic ethers can be regarded as formed by oxygen insertion into hydrocarbons with an increase in boiling point (Δ) after insertion which is linearly related to the mass ratio (R) before and after insertion by, for example, $\Delta = 174.9 - 171.5R$ ($r = 0.9986$) with methyl ethers [7]. The effect of oxygen insertion on the elevation (Δ) decreases as the chain lengthens. This relation

TABLE 1

Ratios of alkane to perfluoroalkane boiling points and relative molecular masses

Chain length n	B.p. of C_nF_{2n+2} (T_F) (K)	Ratio (1) M_H/M_F	Ratio (2) T_H/T_F	(1)/(2)
1	145.21	0.1821	0.7690	0.2368
2	194.45	0.2179	0.9491	0.2296
3	235.65	0.2345	0.9805	0.2392
4	271.85	0.2442	1.003	0.2345
5	302.45	0.2505	1.022	0.2450
6	330.35	0.2549	1.035	0.2463
7	355.55	0.2582	1.045	0.2470
8	376.55	0.2608	1.059	0.2462
9	398.45	0.2628	1.064	0.2470
10	417.35	0.2644	1.072	0.2467
11	433.95	0.2658	1.081	0.2459
12	451.15	0.2670	1.085	0.2461
13	467.65	0.2679	1.088	0.2463
14	483.15[a]	0.2688	1.090	0.2466
15	497.65[a]	0.2695	1.093	0.2466
16	512.15	0.2702	1.093	0.2471
17	524.85[b]	0.2708	1.096	0.2470
18	537.35[b]	0.2713	1.098	0.2471
19	549.45[b]	0.2718	1.099	0.2472
20	561.05[b]	0.2722	1.100	0.2474
	Mean (1)/(2) from $n=6$–$20=0.2467\pm0.0004$			

[a] Interpolated values.
[b] Extrapolated values.

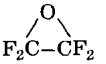
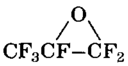
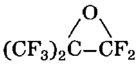
does not apply to perfluoro-ethers for which the effect of oxygen remains almost constant along the series. An alternative approach for estimating b.ps. in the perfluoro series is based on isoelectronic insertions. Inserting CO or NF into fluorocarbons has the same effect as an unit increase in chain length because the inserts are isoelectronic with CF_2. This isoelectronic effect is not fully operative for single-atom insertions presumably because the chain geometry and chain interactions are more affected. Thus replacing CF by N reduces b.ps. by about 10 °C, e.g. C_4F_{10}, -1 and $N(CF_3)_3$, -10 °C; C_9F_{20}, 125 °C and $N(C_3F_7)_2C_2F_5$, 115 °C (fluorocarbon isomers differ from hydrocarbon ones in that b.ps. are close and hence straight chains can be used for comparisons in place of branched ones). Similarly, we find that replacement of CF_2 by oxygen reduces b.ps. by as much as 22 °C. For polyethers, the observed b.ps. indicate a small decrease in this value as each extra oxygen is introduced. The available data (Tables 2 and 3) on perfluoro-ethers can be fitted satisfactorily with the expression:

$$\text{B.p.}[C_nO_m\ \text{ether}]=\text{B.p.}[C_{n+m}F_{2(n+m+1)}]-m(22-m) \qquad (3)$$

The b.ps. of perfluoroacylethers such as $R_fO(CF_2)_2COF$ can be similarly estimated from a carbon count (n). They boil 22 °C below the b.ps. of C_{n+1}

TABLE 2

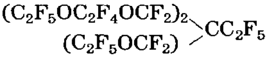
Comparison of the calculated boiling points of cyclic and linear mono- and di-perfluoro-ethers

Ether	*M*	Normal boiling points (°C)		
		Observed	Calc. from polynomial (1)	Calc. from C+O count (3)
FOF	54.0	-145.3	-1	-150
CF_3OF	104.01	-95	-33	-101
	116.02	-64	-27	-60
CF_3OCF_3	154.02	-59	-10	-59.5
	166.03	-28	4	-22
	216.04	4	17	7
1,4-*F*-dioxan	232.04	15.9	24	15
$C_2F_5OC_2F_5$	254.02	1	33	7
$(CF_3OCF_2)_2$	270.04	16.7	39	15
$CF_3OC_4F_9$	304.03	36	52	35
$CF_3OCF_2CF(CF_3)_2$	304.03	36	52	35
$CF_3OC(CF_3)_3$	304.03	38	52	35
2,4-*F*-dimethyl furan	316.16	51	56.4	60
2,5-*F*-dimethyl furan	316.16	54	56.4	60
$C_3F_7OC_3F_7$	354.06	56	70	60
$(CF_3)_2CFOCF(CF_3)_2$	354.06	56	70	60
2,4-*F*-Et, Me-furan	366.06	76	74.5	81
2-*F*-Et-pyran	366.06	80	74.5	81
2-*F*-Pr-furan	366.06	77.3	74.5	81
$[C_2F_5OCF_2]_2$	370.06	62.0	75.9	61
$(CF_3OCF_2CF_2)_2O$	386.06	60	81	65
2,2,6-F-tri-Me-pyran	397.08	107	85	103
$C_3F_7OC_4F_9$	404.06	79[a]	88	81
$C_2F_5C(CF_3)_2CF_2OCF_3$	404.06	90	88	81
2,4-*F*-PrMe-furan	416.06	96.8	92	103
2,2,5,5-*F*-tetra-Me-furan	416.06	99	92	103
2-*F*-Pr-pyran	416.06	95	92	103
2-*F*-Bu-pyran	416.06	116	92	122
$C_4F_9OC_4F_9$	454.06	101.6	104	102
$[(CF_3)_2CFCF_2]_2O$	454.06	98	104	102
$CF_3OC_7F_{15}$	454.06	100	104	102
$C_4F_9OC_5F_{11}$	504.09	120[a]	119	122
$(CF_3)_2CFOC_6F_{13}$	504.09	121	119	122
2-*F*-pentyl-pyran	516.08	137	122	138
$C_4F_9OC_6F_{13}$	554.08	141[a]	133	138
$C_5F_{11}OC_5F_{11}$	554.08	134	133	138
F-neopentoxycyclohexane	566.11	176	137	166
$[(CF_3)_2CFOC_2F_4]_2$	570.1	135	138	136
$CF_3OC_{10}F_{21}$	604.05	154	147	156
$C_6F_{13}OC_6F_{13}$	654.12	181	159	173

[a] Values for these unsymmetrical ethers were obtained as the mean value of the two symmetrical ones.

TABLE 3

Comparison of calculated boiling points of di- to hepta-ethers

Polyether	*M*	Normal boiling points (°C)		
		Observed	Calc. from polynomial (1)	Calc. from C+O count (2)
$[C_2F_5OCF_2]_2$	370.1	62	76	62
$C_2F_5O(CF_2)_3OC_2F_5$	420.1	–	91	83
$[C_2F_5OC_2F_4]_2$	470.1	96	106	102
$[C_2F_5OCF_2]_2C(CF_3)_2$	520.1	108	120	119
$[C_2F_5O]_2(CF_2)_5$	520.1	–	120	119
$C_2F_5OC(CF_2OC_2F_5)_2$	536.1	114	128	118
$CF_3C[CF_2OC_2F_5]_3$	636.1	153	155	150
$C_2F_5C[CF_2OC_2F_5]_3$	686.1	163	167	164
$C(CF_2OC_2F_5)_4$	752.1	169	182	176
$C(CF_2OC_3F_7)_4$	952.5	219	220	222
 $\begin{matrix}(C_2F_5OC_2F_4OCF_2)_2 \\ (C_2F_5OCF_2)\end{matrix}\!\!>CC_2F_5$	918.2	218–220	214	208
$[(C_2F_5OCF_2)_3CCF_2]_2O$	1250	256	265	256

fluorocarbons because of the equivalence of COF and CF_3 groups. The first pair in Table 2 are not strictly ethers but can be regarded as being formed by oxygen replacement of CF_2 groups in the first two fluorocarbons.

The effect of structure is shown by the two inversions for the pairs of ethers with masses at *c.* 400 and 570 in which the higher mass in each pair is coupled with the lower b.p. Also the polynomial expression (1) does not fit values below $M = 300$. Values for the cyclic furans, pyrans and epoxides, or the branched ethers, are predicted equally as well as the linear ethers. In Table 3, values for polyethers up to a hepta-ether are compared (see Table 4 in ref. 1 where the penultimate structure seems incorrect and is probably that of the last entry in Table 5 of the same reference). The average deviation from the polynomial expression is twice as great as that calculated from the carbon plus oxygen count (± 9.3 °C versus ± 4.6 °C).

The boiling points of some recently synthesised perfluoro-ether ketones [8] $\{C_3F_7O[CF_2(CF_3)CF_2O]_xCFCF_3\}_2CO$, estimated by counting the ketone group as equivalent to an extra CF_2, provide a further test for eqn. (3).

x	*n*	*m*	Calc. b.p. (°C)	Lit. values (uncorrected) (°C)
1	17	4	225	216
2	23	6	272	267–271; 259
3	29	8	310	290 (decomp.)

Agreement is satisfactory with the last ketone considering the errors involved in extrapolating b.ps. for both $C_{37}H_{76}$ and $C_{37}F_{76}$ as well as decomposition preventing a true value being reached.

Conclusion

The boiling points of linear, branch and cyclic perfluoro-ethers can be estimated more accurately from the count of n carbons and m oxygens, in the range $n = 0–29$ and $m = 1–7$, than from a polynomial fit with molecular mass. Deviations from eqn. (1) can be real and not due to errors in b.ps.

References

1 A. C. Sievert, W. R. Tong and M. J. Nappa, *J. Fluorine Chem.*, *53* (1991) 397.
2 G. R. Somayajulu, *Int. J. Thermophys.*, *12* (1991) 1039.
3 A. H. W. Aten, *J. Fluorine Chem.*, *8* (1976) 93.
4 R. N. Haszeldine and F. Smith, *J. Chem. Soc.*, (1951) 663.
5 H. H. Anderson, *J. Chem. Eng. Data*, *10* (1965) 156.
6 D. H. Rouvray and R. B. Pandey, *J. Chem. Phys.*, *85* (1986) 2286.
7 A. A. Woolf, *Chem. Ind. (London)*, (1991) 96.
8 L. S. Chen and K. C. Eapen, *J. Fluorine Chem.*, *55* (1991) 92.