SHORT COMMUNICATION

Calculation of Critical Temperatures from the Number of Carbons in Organic Molecules

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The linearity of homolog critical temperatures (T_c,K) with the logarithms of chain length (the latter represented by molecular weight, M, or number of carbons, N_c) was used to develop simple equations correlating T_c,K with M (or with N_c + k) for 40 homologous series. Critical temperatures defined by the equations are presumed to be correct, whereas those in substantial disagreement are considered wrong. The equations can be used to estimate many new critical temperatures by interpolation or by prudent extrapolation.

Because critical temperatures (temperature above which a gas cannot be liquefied) are important, several methods have been proposed for calculating them (1-7). Recent publications estimated critical temperatures from boiling points (5) or by use of a group contribution method (7). A complex expression (Eq. 1) has been suggested (7) for calculating critical temperatures (T_c,K) of organic compounds in homologous series from the number of carbons (N_c).

This paper demonstrates that a simple correlation (Eq., 2) is excellent for estimating homolog critical temperatures from the number of carbons; molecular weights (M) can be used instead of (N_c + k) in Equation 2 (b is intercept and m is slope in Eqs. 1-2):

$$\text{Log } (960 - T_cK) = b + mN_c^{2/3} \quad [1]$$

$$T_cK = b + m \log (N_c + k) \quad [2]$$

TABLE 1

Coefficients for Correlation Equation $T_cK = b + m \log (N_c + k)$[a,b]

Type of compound	Carbon span	Intercept, b	Slope, m	Correlation coefficient, r	Reference
n-Alkanes	6-18	112.95	505.51	4,596[b]	8
2-Me Alkanes	4-9	106.61	502.64	3,769	8
4-Me Alkanes	6-10	106.30	504.72	3,342	2
2,2-Di Me Alkanes	6-9	99.156	499.74	3,712	2
R Cyclopentanes	11-20	175.64	465.96	3,754	2
R Cyclohexanes	7-10	57.366	609.80	3,877	2
Cycloalkanes	6-10	10.764	700.70	2,895	2,8
R Benzenes	6-19	214.11	446.71	3,844	2
p-RC_6H_4R	6-10	226.52	431.41	6,227	8
RC:C	5-16	113.04	502.61	4,534	2
Alkadienes	4-10	136.53	477.86	4,212	8
ROMe	3-6	166.85	446.60	2,855	8
ROR[c]	5-12	135.35	468.76	3,898	2,8
RCOOMe[d]	5-13	150.54	477.30	4,790	8
RCOOEt	6-11	99.032	517.38	3,667	8
RCOOn-Pr	5-7	157.59	464.26	3,240	8
RCOOisoBu	6-8	200.61	401.83	2,890	2
RCOOisoPn	7-9	379.94	230.06	2,630	8
R Formates	3-6	280.36	328.30	2,842	8
R Acetates	5-7	121.52	506.64	5,883	3
MeCOR	4-7	278.85	366.17	2,731	8
RCOR	5-9	282.99	356.55	3,452	8
RCHO	1-5	316.86	300.52	3,083	11
ROH	5-10	292.87	377.67	3,600	2
2-ROH	5-8	221.61	433.43	2,829	8
Branched ROH	4-8	297.34	360.61	3,102	8
m,p-R Phenols	6-8	513.03	213.85	2,750	8
RCOOH	5-10	343.17	353.25	3,172	8
RNH_2	3-6	259.50	392.52	3,367	8,12
R_2NH	4-8	192.48	433.24	3,035	2
R_3N	3-12	187.49	409.52	4,309	2
RCN	4-8	339.35	349.92	3,202	8
RSH	3-10	239.30	424.20	4,700	2
2-RSH	3-10	208.94	441.98	4,577	2
RSR	4-8	233.25	415.75	4,527	2
RSSR	4-12	345.95	328.26	3,829	2

[a] R represents n-alkyl unless otherwise indicated, Me for methyl, Et for ethyl.

[b] Correlation coefficient (r) of 0.9999596 given as 4,596.

[c] n-Propyl and higher n-R ethers.

[d] The T_cK of methyl pentanoate (581 K) was calculated from its boiling point (400.5 K) using equation $T_cK = -232.84 + 40.650 (T_bK)^{1/2}$ (5).

TABLE 2

Coefficients for Correlation Equation $T_cK = b + m \log M$[a]

Type of compound	Carbon span	Intercept, b	Slope, m	Correlation coefficient, r	Reference
ROR[b]	5-12	−441.26	484.07	3,856[c]	8
R Acetates	4-7	−420.95	484.49	2,816	3
RCOOH	4-10	−60.729	350.69	2,865	8
RCl	2-4	−482.99	521.01	3,689	10
$F(CF_2)_nF$	5-10	−699.06	454.44	3,295	8
RSSR	4-12	−86.456	349.32	3,800	2
Me Siloxanes	6-18	−155.74	303.46	3,820	8
Et Siloxanes	12-24	−188.85	368.54	3,844	8

[a] R represents n-alkyl unless otherwise indicated, Me for methyl, and Et for ethyl.

[b] n-Propyl and higher n-R ethers.

[c] Correlation coefficient (r) of 0.999856 given as 3,856.

In Equation 2, k is zero for hydrocarbons; 1 for alcohols, ethers, amines, and nitriles; and 2 for acids, esters, and mono-sulfur compounds.

Equation 2 in modified form is valuable also for correlating homolog critical temperatures with properties and entities that are linear with N_c and M. This is illustrated by the following equations (based on n-alkane data) in which M/d_4^{20}; $(T_bK)^2$; V_c; M/N_D^{20} and ΔH_v (25°C) are substituted for $(N_c + k)$ in Equation 2:

$$T_cK = -744.33 + 594.66 \log(M/d_4^{20}) \quad [3]$$

($N_{c8} - N_{c18}$; r = 0.99982; d_4^{20}, density (4)

$$T_cK = -67.728 + 527.51 \log (T_bK)^2 \quad [4]$$

($N_{c8} - N_{c18}$; r = 0.99953; T_bK, boiling point (8))

$$T_cK = -859.53 + 531.40 \log V_c \quad [5]$$

($N_{c6} - N_{c18}$; r = 0.99984; V_c, critical volume (4))

$$T_cK = -887.94 + 592.81 \log(M/N_D^{20}) \quad [6]$$

($N_{c7} - N_{c18}$; r = 0.99983; N_D^{20}, refractivity (9))

$$T_cK = -280.00 + 524.94 \log \Delta H_v \quad [7]$$

($N_{c6} - N_{c18}$; r = 0.99999; ΔH_v, heat of vaporization (10))

Equation 8 correlates n-alkane critical temperatures with critical pressures (P_c):

$$T_cK = 836.16 - 677.26 \log P_c \quad [8]$$

($N_{c6} - N_{c14}$; r = −0.99944; P_c,MPa)

Equation 2 (or the closely similar Eq. 9) has been applied to 40 homologous series; the various series, carbon spans, and coefficients of Eqs. 2 and 8 are given in Tables 1 and 2.

$$T_cK = b + m \log M \quad [9]$$

As indicated by the correlation coefficients (r), the calculated T_cK values agree well with the literature critical temperatures.

The equations in Tables 1 and 2 have the advantages that much information is provided in little space and new data can be calculated by interpolation and prudent extrapolation. The Table 1 equations were used to calculate, by interpolation, 27 new critical temperatures (T_c,K): n-$C_{17}H_{36}$, 735; 4-methyloctane, 588; n-undecylcyclopentane, 737; cyclononane, 679; four n-alkyl-benzens (C_{12}, 696; C_{14}, 726; C_{16}, 752; C_{18}, 775); Di-n-pentyl ether, 623; n-propyl and higher ethers (C_7, 559; C_9, 604; C_{11}, 641); seven methyl n-alkanoates (C_6, 582; C_7, 606; C_8, 628; C_9, 648; C_{10}, 666; C_{11}, 682; C_{12}, 698); three ethyl n-alkanoates (C_7, 593; C_8, 616; C_9, 638); n-butyl formate, 558; n-hexyl cyanide, 673; di-*n*-propyl ketone, 605; *n*-pentyl amine, 565; and tri-*n*-propyl amine, 597.

An additional 40 new critical temperatures can be calculated by upward extrapolation (by only one carbon) for each of the homologous series shown in Tables 1 and 2. Upward extrapolation by two carbons would give 80 new critical temperatures.

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[Received August 4, 1989; accepted November 20, 1989]
[JS/C 5769]