Critical Temperatures of Oil and Fat Chemicals

Sir:

Critical temperatures (above which gases cannot be liquefied) are relatively scarce, particularly for high-boiling compounds, and are sometimes inaccurate. Because of the importance of critical temperatures (1–3), methods based on group contributions or comparison with other properties have been proposed for estimating them (1–4).

In this investigation, simple equations correlating critical temperatures, T_c, K, with homolog chain length (measured by number of carbons, C) were developed because such equations can be used to estimate T_c for many additional homologs (by interpolation or prudent extrapolation) and to identify significantly incorrect T_c, K values. Molar critical temperatures (M/T_c, K, where M is molecular weight) were studied because molar properties (M/P, where P is property) are usually linear with homolog chain length (except for some lower homologs).

The investigation demonstrated (i) critical temperatures can be related (by Eqs. 1 and 2) to the limiting critical temperature ($T_{c\infty}$, K for M_∞ and C_∞); (ii) 1072 K is suitable as $T_{c\infty}$ in Equations 1 and 2; (iii) molar critical temperatures (M/T_c, K) are approximately linear with homolog chain length (Eq. 3); and (iv) a simple equation (Eq. 4) is useful for estimating homolog critical temperatures.

$$T_c, \text{K} = T_{c\infty} + m/(C + k) \quad [1]$$

where $T_{c\infty}$ is the intercept, m is slope, and k is an adjustable parameter.

$$(C + a) / T_c, \text{K} = b + C/T_{c\infty} \quad [2]$$

where a is an adjustable parameter, b is intercept, and the slope is $1/T_{c\infty}$.

$$M/T_c, \text{K} = b + mC \quad [3]$$

where b and m are intercept and slope.

$$T_c, \text{K} = b + mC^{1/2} \quad [4]$$

The adjustable parameter a calculated from Equation 1 ($a = m/T_{c\infty} + k$), can be used to develop Equation 2. Equations 1–4, like other homolog equations, have limited usefulness for estimating properties of some lower homologs.

TABLE 1
Equations [T_c, K = 1072 + $m/(C + k)$] Correlating Critical Temperatures (T_c, K) with Number of Homolog Carbons (C)[a–d]

		Carbons[e]	k	Slope, m	Corr. coeff., r	Ref.
Ethers	ROMe	4–6	10.90	–8,885	–4, 71	6
	ROEt	4–12	13.52	–10,588	–4, 61	5,6
	ROR	4–12	13.51	–10,584	–4, 69	5,6
Esters	RCOOMe	3–13	14.31	–9,846	–3, 54	7
	RCOOEt	4–11	15.7	–10,855	–3, 43	7
	RCOOisoBu	6–8	18.00	–12,201	–3, 29	5
	MeCOOR	4–8	14.89	–10,372	–3, 84	7
Aldehydes	RCHO	2–9	13.04	–9,113	-4, 42	7
Ketones	RCOMe	5–14	13.37	–9,384	–3, 83	9
	RCOR	7–13	13.36	–9,594	–3, 61	9
Alcohols	ROH	5–12	13.79	–9,129	–3, 79	10
	2-ROH	5–10	13.51	–9,495	–3, 79	10
Acids	RCOOH	5–10	15.88	–8,975	–3, 63	6,8
Amines	RNH_2	2–6	12.13	–8,705	–4, 85	6
	R_2NH	4–8	13.11	–9,815	–3, 24	6
	R_3N	6–12	17.83	–12,799	1.00	6
Nitriles	RCN	4–8	13.82	–8,686	–4, 54	6
Chlorides	RCl	2–4	10.94	–7,921	–3, 89	4

[a]R is n-alkyl having one or more carbons.
[b]A few clearly inaccurate data were omitted in forming the equations.
[c]k is adjustable parameter.
[d]Correlation coefficient, r, of –0.999971 given as –4, 71.
[e]In addition to the limiting critical temperature, 1072 K.

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TABLE 2
Equations (T_c, K = $b + m\,C^{1/2}$) Correlating Critical Temperatures (T_c, K) with $C^{1/2}$ (*C* is homolog Carbon)[a–c]

	Carbons	Intercept, *b*	Slope, *m*	Corr. coeff., *r*
ROMe	3–6	174.2	151.6	3, 75
ROR	6–12	227.2	124.2	3, 81
RCOOMe	6–13	329.7	105.9	3, 84
RCOOEt	4–11	303.5	109.4	3, 25
MeCOOR	4–8	291.3	115.9	3, 79
RCHO	2–9	29	12	4, 72
RCOMe	4–11	302.0	116.7	3, 75
RCOR	3–13	320.9	107.3	3, 69
ROH	3–12	351.4	106.2	3, 86
2-ROH	4–10	303.5	115.4	3, 77
RCOOH	4–10	446.9	87.95	3, 77
RNH_2	2–6	269.7	131.4	4, 57
R_2NH	4–8	238.8	130.2	3, 62
RCN	4–8	369.6	107.7	3, 72

[a]Data from references in Table 1.
[b]*R* is *n*-alkyl having one or more carbons.
[c]Correlation coefficient, *r*, of 0.99975 given as 3, 75.

The use of Equation 1 with T_c, K data of many homologous series indicated $T_{c\infty}$ is about 1072 K. Homolog carbons, C, were plotted against $1/(T_c - 1072)$ to get Equation 5, which was rearranged to Equation 1 for 18 homologous series (Table 1).

$$C = b + m/(T_c - 1072) \qquad [5]$$

The correlation coefficients, *r*, obtained with Equations 1–4 indicated good agreement between calculated and literature values. The expressions $(C + a)/T_c$, K (Eq. 2) and M/T_c, K (Equation 3), which are linear with homolog chain length, should also be linear with property functions (e.g., molar volumes) that are chain-length linear.

The equations in Table 1 are presumably more suitable for upward extrapolations than those in Table 2. The Table 2 equations are simple and particularly useful with intermediate and some lower homologs. The M/T_c correlations (Eq. 3) lack special advantages and are not reported.

REFERENCES

1. Marschner, R.F., and J.B. Beverly, The Simple Relation Between Critical Temperature and Boiling Point, *J. Chem. Educ. 33*:604–607 (1956).
2. Yaws, C.L., *Thermodynamic and Physical Property Data*, Gulf Publishing Co., Houston, 1992, pp. 62–71.
3. Somayajulu, G.R., Estimation Procedures for Critical Constants, *J. Chem. Eng. Data 34*:106–120 (1989).
4. Riddick, J.A., W.B. Bunger, and T.K. Sakano, *Organic Solvents*, John Wiley & Sons, New York, 1986, pp. 192–239, 281–417.
5. Reid, R.C., J.M. Prausnitz, and B.E. Poling, *Properties of Gases and Liquids*, 4th edn., McGraw-Hill Book Co., New York, 1987, pp. 692–723.
6. Stephenson, R.M., and S. Malanowski, *Handbook of Thermodynamics of Organic Compounds*, Elsevier, New York, 1987, pp. 545–548.
7. Kudchadker, A.R., D. Ambrose, and C. Tsonopoulos, Oxygen Compounds Other Than Alkanols and Cycloalkanols, *J. Chem. Eng. Data, 46*:457–461 (2001).
8. Lide, D.R. (ed.), *Handbook of Chemistry and Physics*, 78th edn., CRC Press, Boca Raton, FL, 1997–1998,***6***-57–**6**-61.
9. Pulliam, M.K., M.T. Gude, and A.S. Teja, Critical Temperatures and Densities of *n*-Alkanones, *J. Chem. Eng. Data 40*:455–458 (1995).
10. Gude, M., and A.S. Teja, Vapor–Liquid Critical Properties of Elements and Compounds. 4, Aliphatic Alkanols, *Ibid. 40*:1025–1036 (1995).

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