Equations Correlating Properties of *n*-Fatty Acids and Derivatives with Chain Length

Sir:

Oil and fat constituents and derivatives, e.g., *n*-fatty acids, *n*-fatty acid halides, *n*-ROH, *n*-RCOOR, *n*-RCl, *n*-RBr, and *n*-RCN are homologs, and hence expressions (such as Eqs. 1–3) that correlate homolog properties with chain length are useful (1,2). Equations 1–3 can be used to estimate properties, predict new properties by interpolation or prudent extrapolation, identify inaccurate (nonfitting) data, and indicate (with adequate accurate data) limiting properties P_∞ for C_∞ and M_∞ (P, property; C, carbon; and M, molecular weight) (1,2).

Equations 1–3 have the additional advantages of being user-friendly and interrelated (1); Equations 1 and 2 have the same adjustable parameter, *k*, and the adjustable parameter *a* in Equation 3 can be calculated from the Equation 1 parameters: $a = m/b + k$ (1). The adjustable parameter, *k*, can be calculated easily (as shown below) by Equation 4. The property functions in Equations 2 and 3 are linear with chain length, and hence are linear also with other property functions (e.g., molar volumes) that are chain-length-linear:

$$P = b + m/(C + k) \quad [1]$$

$$P(C + k) = b + mC \quad [2]$$

$$(C + a)/P = b + mC \quad [3]$$

where *b* is intercept, *m* is slope, and *k* and *a* are adjustable parameters.

$$k = (-x_1y_1 + x_2y_2 + x_3y_3 - x_4y_4)/(y_1 - y_2 - y_3 + y_4) \quad [4]$$

where $x_2 - x_1 = x_4 - x_3$

The *k* values for Equations 1 and 2 were estimated from four data pairs (*xy*) by Equation 4 (*y* is P and *x* is C, M, or temperature) as illustrated in Table 1. The sums of the products (Σxy) were divided by the sums of the boiling points (Σy) to get the adjustable parameter, *k*.

When the boiling points (3,4) of the C_6, C_9, C_{12}, and C_{15} *n*-fatty acids were used with Equation 4, a *k* value of 47.7 was obtained. The boiling points for the C_5, C_8, C_{13}, and C_{16} acids gave a *k* value of 42.47 (Table 1). The use of 47.7 as the *k* value gave Equations 5 and 6.

The adjustable parameter, *a*, calculated from the Equation 5 parameters (–50,060/1137.5 + 47.7 = 3.69), was used with the C_6, C_9, C_{11} and C_{15} *n*-fatty acid boiling points t_b, to get Equations 7 and 8. The use of molecular weights, instead of carbons, with Equation 4 gave the *k* value of 637 and Equation 9.

TABLE 1
***n*-Fatty Acid Normal Boiling Points, t_b (°C): Calculation of Adjustable Parameter *k* in Equations 1 and 2**

	C	t_b	Ct_b
Group A[a]	6	+205.3	–1231.8
	9	–254.6	+2291.4
	12	–299	+3588
	15	+339.1	–5086.5
Group B[b]	5	+186.2	–931
	8	–239	+1912
	13	–312.4	+4061.2
	16	+351.5	–5624

[a]Σt_b = –9.20; ΣCt_b = –438.9; –438.9/–9.20 = 47.7. C, carbon.
[b]Σt_b = –13.7 ΣCt_b = –581.8 –581.8/–13.7 = 42.47.

$$t_b, C = 1137.5 - 50{,}060/(C + 47.7) \quad [5]$$
(carbons 6, 9, 12, 15; $r = -0.99999994$)

$$t_b\,(C + 47.7) = 4199.2 + 1137.5\,C \quad [6]$$
(carbons 6, 9, 12, 15; $r = -0.99999998$)

$$(C + 3.69)/t_b = 0.04192 + 0.0008795\,C \quad [7]$$
(carbons 6, 9, 12, 15; $r = 0.9999997$)

$$1/t_b = 0.0008796 + 0.038677/(C + 3.69) \quad [8]$$
(carbons 6, 9, 12, 15; $r = 0.99999996$)

$$t_b, C = 1137.4 - 702{,}009/(M + 637) \quad [9]$$
(carbons 6, 9, 12, 15; $r = 0.99999992$)

The *k* values estimated by Equation 4 were used to develop the Equations 1–12 in Table 2 correlating many *n*-fatty acid properties with number of carbons. Equations 13 and 14 in Table 2 correlate densities and viscosities with temperature, *t* (°C).

The *k* values estimated by Equation 4 were used to develop equations (Table 3) correlating properties of *n*-fatty acid methyl esters, triglycerides, alcohols, and dialkyl ethers with number of carbons. In all instances, correlation coefficients and agreement of estimated with literature values were excellent.

TABLE 2
***n*-Fatty Acids: Equations Correlating Properties (P) with Number of Carbons (C) or Temperature (*t*, °C)[a,b]**

No.	Property	Carbons[d]	*k*[a]	Intercept, *b*	Slope, *m*	Correlation coefficient (*r*)	Reference
1	Melt point, t_m (°C)	6,10,14,18	7.15	147.55	–1,980.1	–5, 75	4
2	Melt point, t_m (°C)	16,20,36,46	2.59	133.93	–1,317.5	–4, 84	4
3	Melt point, t_m (°C)	9,17,21,29	3.93	140.63	–1,657.2	–5, 33	4
4	Boil point, t_b (8 tor)	6,10,14,18	36.11	678.0	–24,564	–5, 46	4
5	Boil point, t_b (760 tor)	6,9,12,15	47.7	1137.5	–50,060	–7, 45	3,4
6	Density, d^{70}	8,10,12,14	3.31	0.81614	0.6102.7	6, 84	5
7	Density, d^{80}	8,12,14,18	–0.787	0.8228	0.27940	6, 37	5
8	Refractivity (n_D^{75})	4,8,12,16	2.56	0.4576	–0.53756	–5, 88	6
9	Surface tension, γ (75°)	8,12,1418	7.75	33.293	–143.62	–2, 79	6
10	Dielectric const., ε (71°)	6,8,16,18	2.74	2.0688	5.1869	3, 83	7
11	Solubility param., δ (25°)	4,6,8,10	2.40	17.453	46.428	4, 46	1
12	CST[e]	8,10,14,16	54.5	643.29	–38,004	–3, 79	8
13	Density, *d* (C_8)	30,40,50,60	1030	0.02256	932.42	5, 87	5
14	Viscosity, η, cP	50,60,70,80	–1.78	–1.9708	425.54	6, 16	5

[a]P = *b* + *m*/(C+*k*), where *b* is intercept, *m* is slope, and *k* is adjustable parameter, for equation numbers 1–12.
[b]P = *b* + *m*/(*t*, C + *k*) for equation numbers 13 and 14 (octanoic acid and lauric acid).
[c]Correlation coefficient (*r*) of –0.9999975 given as –5,75.
[d]Carbons of homologs used in developing equations.
[e]Critical solution temperature in nitromethane.

TABLE 3
Additional Homologous Series: Equations Correlating Properties (P) with Number of Carbons (C)[a]

Property	Homologs	Carbons[c]	*k*[a]	Intercept, *b*	Slope, *m*	Correlation coefficient (*r*)[d]	Reference
Melt point, t_m (°C)	Me esters[b]	9,13,15,19	2.99	129.92	–1,997.8	–5, 87	2
Boil point, t_b (10 tor)	Me esters[b]	7,11,15,19	32.34	743.77	–27,607	–5, 73	2
Density, d^{40}_4	Me esters[b]	7,11,15,19	–1.30	0.84217	0.13139	4, 61	2, 7
Refractivity, n_D^{40}	Me esters[b]	7,11,15,19	2.90	0.46967	–0.72642	–6, 86	2,7
Dielectric const., ε (40°)	Me esters[b]	7,11,15,19	1.02	2.1071	18.277	3, 86	7
Boil point, t_b (0.001 tor)	Triglycerides	15,27,39,51	65	668.09	–49,810	–4, 19	2,4
Boil point, t_b (0.05 tor)	Triglycerides	15,27,39,51	65	756.54	–53,218	–4, 65	2,4
Density, d^{40}	Triglycerides	21,27,39,39	–0.63	0.84429	2.4525	4, 76	9
Refractivity, n_D^{40}	Triglycerides	15,21,27,33	15.31	0.47347	–1.3913	–5, 01	9
Dielectric const., ε (40°)	Triglycerides	15,21,27,33	3.36	1.8582	58.959	5, 86	9
CST[e]	Triglycerides	39,45,51,57	132.4	914.18	–140,978	–4, 19	9
Melt point, T_m (K)	*n*-ROH	6,10,14,18	5.76	435.09	–2,432.4	–4, 19	3
Boil point, T_b (K)	*n*-ROH	6,10,14,18	40.52	1369.4	–43,682	–4, 85	10
Critical temp., t_c (°C)	*n*-ROH	8,12,16,20	15.36	840.68	–10,775	–5, 90	3
Boil point, t_b (°C)	*n*-ROR	4,6,8,10	37.52	1240.4	–50,068	–5, 75	11
Density, d_4^{25}	*n*-ROR	4,6,8,10	2.97	0.8619	–1.0743	–4, 87	11
Refractivity, n_D^{25}	*n*-ROR	4,6,8,10	3.46	0.4849	–1.0995	–5, 62	11

[a]P = *b* + *m*/(C + *k*), where, *b* is intercept, *m* is slope, and *k* is adjustable parameter.
[b]Correlation coefficient, *r* , of 0.999961 given as 4,61.
[c]Carbons of homologs used in developing equation.
[d]Me esters of *n*-fatty acids.
[e]In acetonitrile.

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REFERENCES

1. Fisher, C.H., Evaluating and Predicting *n*-Fatty Acid Properties, *J. Am. Oil Chem. Soc. 65*:1647–1651 (1988).
2. Formo, M.W., Physical Properties of Fats and Fatty Acids, in *Bailey's Industrial Oil and Fat Products*, 4th edn., edited by D. Swern, John Wiley & Sons, New York, 1979, Vol. 1, pp. 177–232.
3. Lide, D.R., *Basic Laboratory and Industrial Chemicals*, CRC Press, Boca Raton, 1993.
4. Singleton, W.S., Properties of the Liquid State, in *Fatty Acids*,

Part 1, 2nd edn., edited by K.S. Markley, Interscience Publishers, Inc., New York, 1960, pp. 499–603.
5. Liew, K.Y., C.E. Seng, and E.K. Lau, Viscosities of Some Long-Chain Fatty Acids and Their Relationship with Chain-length, *J. Am. Oil Chem. Soc. 68*:488–492 (1991).
6. Gros, A.T., and R.O. Feuge, Surface and Interfacial Tensions, Viscosities, and Other Physical Properties of Some *n*-Aliphatic Acids and Their Methyl and Ethyl Esters, *Ibid. 29*:313–317 (1952).
7. Singleton, W.S., Properties of the Liquid State, in *Fatty Acids*, Part 5, edited by K.S. Markley, Interscience Publishers, Inc., New York, 1968, pp. 3419–3454.
8. Francis, A.W., *Critical Solution Temperatures*, American Chemical Society, Washington, DC, 1961, p. 137.
9. Litchfield, C., *Analysis of Triglycerides*, Academic Press, New York, 1972, p. 231.
10. Ambrose, D., and C.H.S. Sprake, Vapor Pressures and Normal Boiling Temperatures of Normal Alcohols, *J. Chem. Thermodyn. 2*:631–645 (1970).
11. Riddick, J.A., W.B. Bunger, and T.A. Sakano, *Organic Solvents*, 4th edn., John Wiley & Sons, New York, 1986, p. 281–293.

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