Evaluation and Prediction of n-fatty Acid Critical Properties

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To develop new and useful methods for evaluating and predicting the critical properties of n-fatty acid, least-squares equations were developed that correlate, with good agreement, the n-fatty acid critical properties (a) with chain length; (b) with other n-fatty acid properties, e.g., melting points, boiling points, densities, and refractivities; and (c) with the corresponding n-alkane critical properties. Critical properties defined by the equations are presumed to be correct, whereas those in substantial disagreement are considered wrong.

Critical temperature has been defined (1-3) as the temperature above which a gas cannot be liquefied. The minimum pressure required for liquefaction at this temperature is the critical pressure. The critical volume is the volume occupied by one mole of the substance at its critical temperature and pressure.

Although critical properties are important, the availability of these properties is severely limited (4). This is due in part to the difficulty of determining critical properties, particularly for compounds that decompose at temperatures near or below the critical temperature (4,5). It has been claimed (2) that critical temperatures higher than about 750K cannot be determined accurately.

The scarcity of critical properties can be illustrated by pointing out that published (2) n-fatty acid critical temperatures (T_c,K) and pressures (P_c) are limited to the acids having two to ten carbons (N_c2 - N_c10). The published (1,3,4) critical densities (d_c) and critical volumes (V_c) are limited to the N_c2 - N_c5 acids. Because of the paucity of critical properties, group contribution methods are frequently used to estimate such properties (3,4).

The principal objectives of the present investigation were to develop and use improved methods, based primarily on homology and limiting properties (6,7) (properties of an infinite chain length, amorphous homolog), for evaluating published n-fatty acids critical properties and predicting such properties for the acids having as many as eighteen carbon atoms. Other objectives were to apply to the n-fatty acid properties several previously-proposed correlations (8-15) among critical properties and chain length and boiling points (T_b,K); and to develop useful correlations between n-fatty acid critical properties and other n-fatty acid properties, e.g., melting points (T_m,K), densities (d_4^{75}), and refractivities $N_D^{75} = n_D^{75} - 1$).

DATA AND METHODS

Several publications (1,3,4) give critical temperatures for the n-fatty acids having two to five carbons. Stephenson (2) provides critical temperatures (T_c,K) and critical pressures, P_c(MPa), for the N_c2 - N_c10 acids (Table 1). The valeric acid T_c value of 651K (Table 1) is considerably higher than the butyric acid value and the Stephenson valeric acid value (2) of 643K. For the above reasons and the availability of T_c data over a longer chain length interval (N_c2 - N_c10), the data of Stephenson (2) were selected. Critical volumes (V_c, cm^3mol^{-1}) from Dean (3), which have approximately the same increments between adjacent homologs, were selected of Riddick's data (Table 1).

Evaluation of the n-fatty acids critical properties was based primarily on the extent to which the properties had the characteristics normally found in members of homologous series:

(1) With increasing chain length (measured by the number of carbons, N_c, or molecular weight, M) the properties increase or decrease in a regular fashion;
(2) The properties are correlatable, by least-squares equations, with (a) chain length; (b) other n-fatty acid properties, e.g., boiling points, melting points, and densities; and (c) the corresponding properties of the n-alkanes; and

TABLE 1

n-Fatty Acid Critical Properties

N_c	T_c,K[a]	D_t[b]	T_c,K[c]	D_t[b]	V_c[d] cm^3mol^{-1}	V_c[e] cm^3mol^{-1}	D_v[e,f]	P_c[d] MPa	P_c[c] MPa
1	580.0								
2	592.7	12.7	592.7		171.3	171.3		5.79	5.79
3	612.0	19.3	604.0	11.3	235.0	230.0	58.7	5.37	4.53
4	628.0	16.0	624.0	20.0	290.0	292.0	62.0	5.3	4.03
5	651.0	23.0	643.0	19.0	290.0	340.0	48.0	4.67	3.58
6			662.0	19.0					3.20
7			679.0	17.0					2.90
8			695.0	16.0					2.64
9			711.0	16.0					2.40
10			726.0	15.0					2.23

[a]Ref. 4.
[b]Differences between T_c for adjacent homologs.
[c]Ref. 2.
[d]Ref. 1.
[e]Ref. 3.
[f]Differences between V_c for adjacent homologs.

(3) The properties are compatible with the limiting properties.

The proposed (8) limiting critical temperature of 961K appeared low in the present work. The limiting critical pressure of approximately zero (8) and the methylene increment of 59.622 (16) (slope in Eq. 1) have been proposed; and these were found useful. The limiting critical density (d_{coo}), calculated from the slope in Eq. 1 and the methylene unit formula weight (14.027), is 14.027/59.622 or 0.2353: $M/d_c = b + 59.622\ N_c$ [1]

The Ambrose expression (Eq. 2) can be arranged to Eq. 3, which suggests the limiting critical temperature (T_{coo}) is the same as the hypothetical limiting boiling point (T_{boo}, claimed to be 1190K by Huddle) (17): the $T_{coo} - T_{boo}$ ratio is one, and $T_{coo} - T_{boo}$ is zero $T_b/(T_c - T_b) = b + m\ N_c$ [2] and $T_c/T_b = 1 + 1/(b + m\ N_c)$ [3].

Critical temperatures of the n-fatty acids were expected to be compatible with several correlations observed with other homologous series, e.g., the T_b/T_c ratios are approximately 0.7 (1). Some of the additional claimed correlations are represented by Eqs. 4-7 (b, intercept and m, slope):

$(T_c,K)^3 = b + m\ N_c$ (Ref. 11) [4]

$T_b/T_c = b + m\ T_b$ (Ref. 12) [5]

$M/T_c = b + m\ N_c$ (Ref. 13) [6]

$N_c(T_c - T_b) = b + m\ N_c$ (Ref. 15) [7]

Many equations of the present work (e.g., Eqs. 1,2,4,6,7) are based on the linearity of property functions with chain length, represented by N_c. Advantage was taken of the fact that such property functions are linear also with each other.

RESULTS AND DISCUSSION

Critical temperatures. Several least-squares expressions (Eqs. 9,11,13) related indirectly to the hypothetical limiting critical temperature (T_{coo}) were found suitable for correlating T_c (or combinations of T_c and T_b) with chain length. Equation 8, based on the assumption D_t (difference between T_c of adjacent homologs) is zero when N_c is infinite, was developed by plotting N_c against $1/D_t$ to get Eq. 8 which was rearranged to Eq. 9:

$N_c = -12.394 + 334.59/D_t$ [8]

$D_t = 334.59/(N_c + 12.39)$ [9]

On the assumption T_c/T_b is equal to unity when N_c is infinite, N_c was plotted against the reciprocal of $(T_c/T_b - 1)$ to get Eq. 10, which was rearranged to Eq. 11:

$N_c = -22.858 + 11.090/(T_c/T_b - 1)$ [10]

($N_c5 - N_c10$; r = 0.997084

$T_c/T_b = 1 + 11.090/(N_c + 22.858)$ [11]

The n-fatty acid $T_c - T_b$ values are 183.6 for the $N_c5 - N_c10$ n-fatty acids. The $T_c - T_b$ values decrease with increasing chain length for the $N_c10 - N_c18$ acids. On the assumption $T_c - T_b$ is zero for N_{coo}, N_c was plotted against $1/(T_c - T_b)$ to get Eq. 12, which was rearranged to Eq. 13:

$N_c = -176.91 + 34434/(T_c - T_b)$ [12]

$N_c10 - N_c18$; r = 0.972113)

$T_c = T_b + 34434/(N_c + 176.9)$ [13]

Equations 9, 11, 13, which relate n-fatty acid critical temperatures indirectly to the hypothetical (and unknown) limiting critical temperature, provide calculated values (Table 2) that agree with the literature (2) $N_c3 - N_c10$ critical temperatures; the calculated values agree well also with each other for the $N_c12 - N_c18$ acids.

Ambrose (14) found that $T_b/(T_c - T_b)$ is linear with chain length for several homologous series. The same was found to hold true for the n fatty acid critical temperatures (Eq. 14): $T_b/(T_c - T_b) = Q = 2.0649 + 0.08986N_c$ [14] ($N_c5 - N_c10$; r = 0.997094).

The molecular quotients (M/T_c) of the n-alkanes are linear over limited chain lengths (13). As indicated by Eqs. 15 and 16, the same is true for the n fatty acids:

$M/T_c,K = 0.079500 + 0.01596N_c$ [15]

($N_c5 - N_c9$; r = 0.99982)

$M/T_c,K = 0.10504 + 0.013353N_c$ [16]

($N_c10 - N_c18$; r = 0.999768)

The following least-squares expressions (Eqs. 17-19) correlate the n-fatty acid T_c,K values (Eq. 9, Table 2) with carbon numbers ($N_c3 - N_c18$):

$T_c,K = 1388.0 - 29782/(N_c + 34.99)$ [17]

r = -0.999995

$(N_c + 13.4)/T_c = 0.024984 + 0.00072433N_c$ [18]

r = 0.999996

$(T_c/100)^3 = 151.86 + 22.985\ N_c$ [19]

r = 0.999965

TABLE 2

n-Fatty Acids: Literature And Calculated Critical Temperatures (T_c,K)

	T_b[a]	T_c[a]	D_t[a,b]	D_t[b] Eq. 9	Eq. 9	Eq. 11	Eq. 13	Eq. 17
3	414.3	604	11.3					604.0
4	436.9	624	20.0	20.41	624.4			624.2
5	459.3	643	19.0	19.24	643.2	642.1		643.3
6	478.4	662	19.0	18.19	661.2	662.2		661.4
7	495.4	679	17.0	17.26	679.3	679.4		678.7
8	512.0	695	16.0	16.41	695.4	696.0		695.2
9	527.7	711	16.0	15.64	710.6	711.4	712.9	711.0
10	541.9	726	15.0	14.94	725.9	724.8	726.1	726.0
12	572.1			13.72	754.0	754.1	754.4	754.2
14	599.4			12.68	779.9	779.7	779.8	780.1
16	624.7			11.79	803.9	803.0	803.2	803.9
18	649.2			11.01	826.3	825.4	825.9	826.0

[a]From Ref. 2.

[b]T_c differences between adjacent homologs.

TABLE 3

n-Fatty Acid And n-Alkane Properties[a]

	n-Fatty Acids[a]						n-Alkanes[b]		
	T_m,K	d_4^{75}	N_D^{75}	surface tension, γ_{20}	P_r,25C	S_p^c,25C	T_c,K	P_c,MPa	V_c^d
3	252.5		0.3604	26.70	169.3	26.1	369.8	4.250	203
4	268.0	0.9043	0.3758	26.74	209.3	24.7	425.1	3.784	255
5	239.5	0.8892	0.3863	27.47	249.3	23.8	469.7	3.364	311
6	269.7	0.8796	0.3944	28.05	289.3	23.0	507.7	3.011	370
7	266.1	0.8719	0.4013	28.69	329.3	22.4	540.3	2.756	428
8	289.7	0.8662	0.4069	29.20	369.3	21.9	568.9	2.493	492
9	285.7	0.8619	0.4111	29.57	409.3	21.5	594.6	2.288	
10	304.8	0.8583	0.4149			21.2	617.7	2.104	
12	317.4	0.8516	0.4208				658.2	1.824	
14	327.6	0.8481	0.4251				693.0	1.620	
16	336.1	0.8446	0.4288				722.0		
18	342.8	0.8431	0.4318				748.0		

[a]Sources of n-fatty acid properties: melting points, T_m,K (1,6,18); densities, d_4^{75} (6,19); refractivites, $N_D^{20} = n_D^{20} - 1$ (6,19); surface tensions, γ_{20} (1,6); parachors, P_r,25C (4,6); and solubility parameters, S_p,25C (6,20).
[b]Source: (2).
[c]S_p, 25C, $(J/cm^3)^{1/2}$.
[d]V_c, cm^3mol^{-1}.

The correlations represented by Eqs. 9, 11, 13-19 suggest the Stephenson's (2) critical temperatures and the T_c values predicted by Eq. 9 (Table 2) are at least approximately correct. These correlations suggest also the following literature (4) n-fatty acid critical temperatures (K) are incorrect: C_4 = 628; C_5 = 651; and C_{18} = 798.8.

Critical and boiling temperatures. The n-fatty acid critical temperatures can be calculated from the n-fatty acid normal boiling points (T_bK) (Eqs. 20-21). As indicated by the correlation coefficients (r), the calculated critical temperatures agree with the literature values (2):

$$T_c(T_b + 9991) = 1738720 + 10874\, T_b \qquad [20]$$
(N_c4 - 18; 0.999908)

$$T_c = 3200.5 - 6{,}284{,}060/(T_b + 1997) \qquad [21]$$
(N_c5 - 18; 0.999961)

Critical temperatures and other properties. The following expressions (Eqs. 22-27) correlate n-fatty acid critical temperatures with other n-fatty acid properties (Table 3): melting points, T_m,K (1,18); densities, N_4^{75} (6,19); refractivities, N_D^{20} (6,19); surface tensions, γ_{20} (1,6); parachors, P_r (4,6); and solubility parameters, S_p (6,20). As indicated by the correlation coefficients (r), the agreement between the calculated and the literature properties is good:

$$1000/T_c\text{,K} = 1.8927 - 5.9504(T_m\text{,K}/1000)^2 \qquad [22]$$
(N_c5 - N_c19 (odd carbons); r = -0.999968

$$T_c\text{,K} = 267.31 + 0.72532\, T_b\text{,K}/d_4^{75} \qquad [23]$$
(N_c5 - N_c18; r = 0.999964

$$(T_c/100)^3 = 66.104 + 0.75898\, M/N_D^{75} \qquad [24]$$
(N_c3 - N_c18; r = 0.99932)

$$(T_c/100)^3/\gamma_{20} = 6.6432 + 0.61053\, N_c \qquad [25]$$
(N_c4 - N_c9; r = 0.999776)

$$(T_c/100)^3 = 123.53 + 0.57462\, P_r \qquad [26]$$
(N_c3 - N_c18; r = 0.999965)

$$(T_c/100)^3/S_p = 4.3301 + 1.3749\, N_c \qquad [27]$$
(N_c3 - N_c10; r = 0.999975)

Critical pressure. Equations 28-30 correlate n-fatty acid critical pressures (P_c, MPa) with the number of carbons, N_c. Adjustable parameters were selected to give the best fit except for Eq. 29, whose adjustable parameter (3.765) was selected to give an intercept of approximately zero (possibly the hypothetical limiting critical pressure):

$$P_c = -0.78905 + 48.131/(N_c + 6.03) \qquad [28]$$
(N_c3 - N_c10; r = 0.999872)

$$P_c = 0.00003 + 31.033/(N_c + 3.765) \qquad [29]$$
(N_c3 - N_c10; r = 0.999093)

$$1/P_c = 0.11150 + 0.033637\, N_c \qquad [30]$$
(N_c4 - N_c10; r = 0.999697)

Equations 31-33 correlate n-fatty acid critical pressures (P_cMPa) with other n-fatty acid properties (critical temperature, T_c,K; boiling points, T_b,K; and molar volumes (M/d_4^{20}):

$$T_c^{1/2} = 29.579 - 7.6169 \log P_c \qquad [31]$$
(N_c3 - N_c10; r = -0.999910)

$$1/P_c = 0.021544 + 0.0026746(T_b/100)^3 \qquad [32]$$
(N_c4 - N_c10; r = -0.999517)

$$1/P_c = 0.059614 + 0.0020286\, M/d_4^{20} \qquad [33]$$
(N_c4 - N_c9; r = 0.999554)

Critical volumes. The expression (Eq. 34) based on Dean's data (3) for the N_c2 - N_c4 n-fatty acids has a slope (60.350) similar to Somayajulu's (16) methylene increment (59.622). Equation 35 was adjusted to have the slope of 59.622. The limiting critical density suggested by Eq. 35 is 14.027/59.622 = 0.23527.

Equation 36 was divided by Eq. 35 to get Eq. 37, which is useful for calculating critical densities:

$$V_c = 50.050 + 60.350\, N_c \qquad [34]$$
(N_c2 - N_c4; r = 0.999875)

$$V_c = 52.234 + 59.622\, N_c \qquad [35]$$

$$M = 32.00 + 14.027\, N_c \qquad [36]$$

$d_c(N_c + 0.876) = 0.53671 + 0.23527\ N_c$ [37]

Equations 38-40 correlate critical volumes with other properties of the n-fatty acids (T_bK; T_cK; and P_c,MPa):

$V_c = -106.19 + 4.7331\ (T_b/100)^3$ [38]
($N_c3 - N_c10$; r = 0.999920)

$(T_c/100)^3 = 129.96 + 0.38955\ V_c$ [39]
$N_c3 - N_c10$; r = 0.999961)

$1/P_c = 0.081245 + 0.00056568\ V_c$ [40]
($N_c4 - N_c10$; r = 0.999733)

Comparison of n-fatty acid and n-alkane critical properties. Equations 41-43 define the relations between the fatty acid critical properties and the critical properties of the n-alkanes having the same number of carbons:

T_c (RCOOH) = $465.45 + 0.00060393\ T_c^2$(RH) [41]
$N_c5 - N_c18$; r = 0.999842)

V_c (RCOOH) = $33.717 + 1.0150\ V_c$(RH) [42]
($N_c4 - N_c10$; r = 0.999862)

In developing Eq. 43, which correlates n-fatty acid critical pressures with the n-alkane critical pressures, the $N_c3 - N_c10$ plus N_{coo} data were used (P_{coo} = zero):

P_c (RCOOH) = $-0.055780 + 1.0793\ P_c$ (RH) [43]
($N_c3 - N_c10$ and N_{coo}; r = 0.999935)

REFERENCES

1. Riddick, J. A., W. B. Bunger, and T. K. Sakano, *Organic Solvents*, 4th edn., John Wiley & Sons, Inc., New York, 1986.
2. Stephenson, R. M., and S. Malanowski, *Handbook of the Thermodynamics of Organic Compounds*, Elsevier Science Publishing Co., Inc., New York, 1987.
3. Dean, J. A., *Handbook of Organic Chemistry*, McGraw-Hill Book Co., Inc., New York, 1987.
4. Reid, R. C., J. M. Prausnitz, and B. E. Poling, *Properties of Gases And Liquids*, 4th edn., McGraw-Hill Book Co., New York, 1987.
5. Mogollon, E., W. B. Kay, and A. S. Teja, *Ind. Eng. Chem Fundam. 21*:173 (1982).
6. Fisher, C. H., *J. Am. Oil Chem. Soc., 65*:1647 (1988).
7. Fisher, C. H., and B. P. Huddle, Jr., *Chem. Eng.*, Feb. 8, 1982, p. 99.
8. Kudchadker, A. P., G. H. Alani, and B. J. Zwolinski, *Chem. Reviews, 68*:659 (1968).
9. Kobe, K. A., and R. E. Lynn, Jr., *Chem. Reviews, 52*:134 (1953).
10. Spencer, C. F., and T. E. Daubert, *AICHE Journal 19*:482 (1973).
11. Grunberg, L., and A. H. Nissan, *Trans. Faraday Soc. London 44*:1013 (1944).
12. Varshni, V. P., and S. N. Srivastava, *J. Chem. Phys., 22*:349 (1954).
13. Fisher, C. H., *Chem. Eng.*, Jan. 11, 1982, p. 107.
14. Ambrose, D., B. E. Broderick, and R. Townsend, *J. Appl. Chem. Biotechnol, 24*:359 (1974).
15. Mitra, S. S., *J. Chem. Phys., 22*:56 (1954).
16. Somayajulu, G. R., *Thermodynamics Research Center (Texas) Bulletin*, Sept. 1984 - March 1985.
17. Huddle, B. P., Jr., private communication.
18. Markley, K. S., Editor, *Fatty Acids, Part 4*, John Wiley and Sons, Inc., New York, 1967.
19. Gros, A. T., and R. O. Feuge, *J. Am. Oil Chem. Soc., 29*:313 (1952).
20. Fujii, Y., and M. Tanaka, *Bull. Chem. Soc. Japan, 54*:3696 (1981).

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