n-Fatty Acids: Comparison of Published Densities and Molar Volumes

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ABSTRACT: Because some published *n*-fatty acid densities and molar volumes disagree significantly with others, an attempt was made, based primarily on the principle of homology, to distinguish between reasonably accurate and inaccurate data. Literature densities compatible with each other and with requirements of homology (including limiting densities) were identified. These densities, considered to be at least reasonably accurate, were used as standards and compared with other published densities. Most published *n*-fatty acid densities, judged by these criteria, appear to be reasonably accurate.
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KEY WORDS: Densities, densities comparison, density equations, density temperature dependence, homology, limiting densities, molar volumes, *n*-fatty acids.

Densities (d) and molar volumes ($V = M/d$, where M is molecular weight) have long been favorite subjects of investigation. More than 150 years ago, Herman Kopp investigated molar volumes at boiling points of various chemicals and gave the following values for the *n*-fatty acids: C_2, 63.7; C_3, 85.4; C_4, 107.1; and C_5, 130.7 (1,2). Since then, densities and molar volumes of numerous compounds (including the C_1–C_{30} *n*-fatty acids) have been published (3–27). Important twentieth century investigations that provide experimental densities of the *n*-fatty acids include those by Garner and Ryder in 1925 (27); Hunten and Maass in 1929 (18); Dorinson *et al.* in 1942 (8); Gros *et al.* in 1952 (7); Costello and Bowden in 1958 (19); Berchiesi *et al.* in 1976 (20); Bernardo-Gil *et al.* in 1990 (24); Noureddini *et al.* in 1992 (22); and Liew and Seng in 1992 (23).

Useful reviews of research on densities and molar volumes include those published by Partington in 1952 (28); Hammond and Lundberg in 1954 (29); Singleton in 1960 (5); and Halvorsen *et al.* in 1993 (30). Various methods for estimating densities and molar volumes have been described by Hammond and Lundberg (29); Partington (28); Halvorsen *et al.* (30); Huggins (31); Rossini (32); Van Krevelen and Hoftyzer (33); Lyman *et al.* (34); Kurtz and Sankin (35); Reid (36); and Girolami (37).

The great attention given to molar volumes is justified because of their value as such (22,38) and as essential components of various additive functions, e.g., molar refractions (3,26), molar dielectric polarizations, molar attraction functions, molar parachors, and solubility parameters (3,26,33).

In addition, molar volumes are useful in developing various correlations. At a given temperature, molar volumes are linear with homolog chainlength (except for a few lower homologs). Molar volumes easily can be correlated with other properties and property functions that also are linear with homolog chainlength (39).

Because there is wide disagreement among the published molar volumes and densities of both the C_2–C_9 acids (Table 1) and the higher acids (Table 2), a method is needed to distinguish between the reasonably accurate and the inaccurate data. The present paper attempts to meet this need by noting which densities are compatible with each other and also with requirements of homology. More specifically, densities (d) at a given temperature may be expected to correlate (except for those of a few lower homologs) with chainlength (x) by Equations 1 and 2 (11,40):

$$d = d_\infty + m/(x + k) \quad [1]$$

$$(x + a)/d = b + x/d_\infty \quad [2]$$

In Equations 1 and 2, d_∞ is the limiting density of an amorphous, infinite-length homolog, m is slope, b is intercept, k and a are adjustable parameters, and x is either the number of carbons, C, or molecular weight, M.

Because the adjustable parameters, k and a, are relatively unimportant for the higher homologs, molar volumes ($V = M/d$) of the higher homologs are linear with chainlength, at least over wide and useful carbon spans.

The *n*-fatty acid densities and reciprocal molar volumes ($1/V$) are linear with temperature (t,°C) by Equation 3:

$$d = b + m\, t,°\text{C}) \quad [3]$$

The d vs. t equations may be expected, at least for the higher *n*-fatty acids, to converge at a common point. It is suggested that this common point for the *n*-fatty acid densities is 0.721 at 250°C. [The hypothetical convergence point of $d = 1.29$ at −737°C has been proposed (41) for the *n*-alkane densities.]

TABLE 1
***n*-Fatty Acids: Densities (*d*) at 20 and 50°C[a]**

	Carbons (C)						
	3	4	5	6	7	8	9
20°C							
Reference 3	0.9935	0.9582	0.9390	0.9272		0.9106	0.9052
Equation A[b]	.9940	.9589	.9390	.9261	.9172	.9106	.9055
Equation B[c]		.9573	.9397	.9273	.9180	.9108	.9050
Reference 14	.9942	.9583	.9394	.9276	.9181	.9105	.9052
Reference 23		.9591	.9389	.9265	.9176	.9108	.9063
Equation C[d]	.9935	.9588	.9391	.9265	.9176	.9111	.9061
Reference 19	.9942	.9572	.9374	.9243	.9181	.9090	.9052
Reference 24	.9922	.9635	.9382	.9216	.9176	.9106	
Reference 10	.9942	.9583	.9394	.9276	.9181	.9105	.9052
50°C							
Table 3	0.9615	0.9292	0.9123	0.9013	0.8927	0.8864	0.8814
Equation D[e]	.9618	.9301	.9121	.9005	.8924	.8864	.8818
Reference 23		.9299				.8864	.8815
Equation E[f]		.9291	.9130	.9016	.8932	.8868	.8816
Reference 19	.9605	.9281	.9109	.8991		.8848	
Reference 24	.9639	.9393	9146	.8990	.8962	.8890	

[a]*n*-Alkanoic acids liquid at room temperature (C_3–C_9). [b]Equation A: $C/d^{20} = 0.44239 + 1.1535\ C$; Reference 3. [c]Equation B: $d^{20} = 0.854 + 0.50472/(C + 0.888)$; Reference 3. [d]Equation C: $C/d^{20} = 0.43690 + 1.1522\ C$; Reference 23. [e]Equation D: $C/d^{50} = -0.42448 + 1.1812\ C$. [f]Equation E: $d^{50} = 0.837 + 0.43281/(C + 0.698)$ (C_4–C_{12}); Reference 23.

DATA SOURCES AND EQUATIONS

In the first stage of the present investigation, it was found that the densities (Table 3) of Riddick *et al.* (3), Dreisbach (4), Gros and Feuge (7), Dorinson *et al.* (8), Lide (14,21), and Markley (42) are compatible with each other and with the requirements of homology (11). The *n*-fatty acid densities published by Liew and Seng (23) are similar to those in Table 3; their densities also meet the requirements of homology. In the second stage, the densities published by other investigators (18–20,22,24) were compared with those in Table 3.

Equations correlating Table 3 densities with temperature are given in Table 4. Similar equations can be derived from Liew and Seng's densities (23). Equations (Table 4) for the higher *n*-fatty acids converge at a density of 0.721 at 250°C.

The Noureddini *et al.*'s *d* vs. *t* equations (22), and similar equations developed with the densities listed by other scientists (18–20,24) were used to calculate some of the densities

TABLE 2
***n*-Fatty Acids: Densities at 80, 100, and 120°C**

	Carbons (C)						
	8	9	10	12	14	16	18
80°C							
Table 3	0.8620	0.8577	0.8537	0.8484	0.8447	0.8418	0.8395
Reference 23	.8621	.8577	.8541	.8486	.8446	.8414	.8389
Reference 22		.8594	.8549	.8494	.8453	.8431	.8397
Reference 20		.8580	.8563	.8504	.8459	.8414	.8407
Reference 19	.8605		.8520	.8454	8434	.8414	.8377
Reference 18	.8638		.8561	.8460	.8471	.8455	.8415
100°C							
Table 3	0.8459	0.8418	0.8384	0.8333	0.8300	0.8273	0.8256
Reference 23	.8458	.8419	.8384	.8336	.8301	.8273	.8251
Reference 22		.8442	.8400	.8347	.8318	.8299	.8276
Reference 20		.8423	.8423	.8366	.8313	.8273	.8267
Reference 19	.8442		.8373		.8294	.8278	.8247
Reference 18	.8475		.8406	.8312	.8339	.8324	.8279
120°C							
Reference 23	.8296	.8253	.822	.8186	.8156	.8131	.8112
Reference 22		.8290	.8251	.8201	.8184	.8166	.8154
Reference 2		.8268	.8284	.8229	.8165	.8130	.8125
Reference 19	.8280		.8224	.8168	.8156	.8141	.8117
Reference 18	.8313		.8252	.8165	.8207	.8194	.814

TABLE 3
***n*-Fatty Acid Densities (*d*)[a]**

Carbons (C)	t_m, °C[b]	20[a]	25[a]	30[a]	50[c]	75[d]	80[e]	100[f]	250[f]
		Temperature (°C)							
2	16.6	1.0496	1.0439	1.0382	1.0160[f]	0.9878	0.9878	0.9601[f]	0.7925[f]
3	−20.7	.9935	.9881	.9826	.9615[f]	.9350[f]	.9297	.9084[f]	.7492[f]
4	−5.7	.9582	.9532	.9478	.9292	.9043	.8995	.8800[f]	.7338[f]
5	−34.0	.9390	.9345	.9300	.9123[f]	.8900[f]	.8856	.8678[f]	.7344[f]
6	−3.0	.9272	.9230	.9183	.9013[f]	.8796	.8756	.8582[f]	.7289[f]
7	−7.5	.9181	.9140	.9097[f]	.8928[f]	.8717[f]	.8675	.8506[f]	.7240[f]
8	16.3	.9106	.9066	.9025	.8864	.8662	.8620	.8459[f]	.7246[f]
9	12.3	.9052	.9013	.8973[f]	.8814	.8616[f]	.8577	.8418[f]	.7230[f]
10	31.9			.8931[f]	.8774	.8583	.8537	.8384[f]	.7210[f]
11	28.6			.8892[f]	.8742	.8548[f]	.8597	.8357[f]	.7210[f]
12	43.2				.8709	.8516	.8484	.8333[f]	.7210[f]
14	53.9				.8664[f]	.8481	.8447	.8300[f]	.7210[f]
16	61.8					.8446	.8418	.8273[f]	.7210[f]
18	68.8					.8431	.8395	.8256[f]	.7210[f]

[a]Densities at 20, 25, and 30°C from References 3, 10, 4, and 21. [b]Melting points from Reference 14. [c]C_4 density from Reference 6; C_8–C_{12} densities from References 27 and 42. [d]Densities at 75°C from Reference 7. [e]C_2–C_{10} densities calculated from Dorinson's molar volumes; C_{11}–C_{18} densities calculated from Equation 5. [f]Calculated from Table 4 equations: $d = b + t_m$, °C.

in Tables 1 and 2. [The Costello and Bowden densities (19) have also been reported by Doss (15) and Small (17).]

The equations for the C_{20}–C_{30} *n*-fatty acids (Table 4) are based on $d = 0.721$ at 250°C, the 100°C densities of Bleyberg (43) and the 20 and 80°C densities (some hypothetical) calculated by Equations 4 and 5:

$$d_4^{20} = 0.854 + 0.51166/(C + 1.005) \quad [4]$$

$$M/d^{80} = 30.612 + 17.125\ C \quad [5]$$

The limiting density at 80°C, indicated by Equation 5, is 14.027/17.125 = 0.8191, which is similar to that (0.8193) calculated by Equation 6:

TABLE 4
***n*-Fatty Acids: Equations[a] Correlating Densities (*d*) with Temperature (*t*,°C)[b–d]**

Carbons (C)	Temperature range (°C)	Intercept (*b*)	Slope (*m*)	Correlation coefficient (r)	*d* at 250°C
2	20–80	1.0718	−11.171E-04	$-\underline{4},83$	0.7925
3	20–80	1.0146	−10.618E-04	$-\underline{5},2$	.7492
4	20–80	.97753	−9.7502E-04	$-\underline{4},30$	.7338
5	20–80	.95674	−8.8933E-04	$-\underline{5},8$	.7344
6	20–80	.94438	−8.6178E-04	$-\underline{4},74$	.7289
7	20–80	.93504	−8.4421E-04	$-\underline{5},8$	.7240
8	20–80	.92680	−8.0897E-04	$-\underline{5},6$	.7246
9	20–80	.92106	−7.9229E-04	$-\underline{5},8$	.7230
10	50–250	.91660	−7.8237E-04	$-\underline{5},2$	.7210
11	50–250	.91220	−7.6496E-04	$-\underline{5},4$	.7210
12	50–250	.90813	−7.4862E-04	$-\underline{5},2$	.7210
14	75–250	.90274	−7.2693E-04	$-\underline{5},87$	.7210
16	75–250	.89809	−7.0831E-04	$-\underline{4},86$	.7210
18	75–250	.89535	−6.9741E-04	−1,00	.7210
20	20–250	.89229	−6.8480E-04	$-\underline{5},7$	.7211
22	20–250	.88981	−6.7517E-04	$-\underline{5},5$	.7210
24	20–250	.88786	−6.6760E-04	$-\underline{4},89$	.7210
26	20–250	.88615	−6.6069E-04	$-\underline{5},3$	.7210
28	20–250	.88481	−6.5517E-04	$-\underline{5},4$	.7210
30	20–250	.88349	−6.5017E-04	$-\underline{5},0$	.7210

[a]$d = b + t_m$,°C; the C_2–C_{18} equations based on the densities in Table 3.
[b]The C_{20}–C_{30} equations were developed from 20°C densities calculated by $d_4^{20} = 0.854 - 0.51166/(C + 1.005)$; 80°C densities calculated by $V^{80} = 30.612 + 17.125C$; and *d* at 250°C = 0.721.
[c]The intercepts, *b*, are the estimated densities at 0°C.
[d]Correlation coefficients such as −0.999983 given as $-\underline{4},83$.

$$d_\infty = 0.8655 - 0.0005777\, t, \text{°C} \qquad [6]$$

Equations 5 and 7 can be used, presumably, to calculate the d^{80} values of all the higher *n*-fatty acids.

$$d^{80} = 0.819 + 0.40294/(C + 1.673) \qquad [7]$$

The *n*-fatty acid molar volumes at 100°C (Ref. 23) and −25°C (Ref. 26) are defined by Equations 8 and 9, respectively:

$$V^{100} = 31.148 + 17.435\, C \qquad [8]$$

$[C_{20}–C_{30};\ r = 1.0000;$ (Ref. 23)]

$$V^{-25} = 26.564 + 16.682\, C \qquad [9]$$

$[C_4–C_{18};\ r = 0.999993;$ (Ref. 26)]

Noureddini *et al.* (22) and Costello and Bowden (19) determined *n*-fatty acid densities at the high temperatures of 110 and 300°C. The following equations define their densities at these temperatures:

$$C/d^{110} = -0.38775 + 1.2405\, C \qquad [10]$$

$(C_9–C_{18};\ r = 0.9999985)$

$$C/d^{300} = 0.64815 + 1.4285\, C \qquad [11]$$

$(C_{10}–C_{18};\ r = 0.999997)$

The equations (based on the Table 3 densities) shown in Table 5 were developed by plotting the number of carbons, C, against $1/(d - d_\infty)$ to get $C = -k + m/(d - d_\infty)$ which was rearranged to:

$$d = d_\infty + m/(C + k) \qquad [12]$$

Limiting densities, d_∞, were calculated by Equation 6.

As indicated by the Table 5 expressions, the limiting densities (d_∞, Equation 6) are useful in developing equations that correlate densities with chainlength. As illustrated by Equations 13 and 14, limiting densities are also useful in correlating densities (indirectly) of individual *n*-fatty acids with temperature:

$$C_4\text{: } d = -0.47553 + 1.6787\, d_\infty \qquad [13]$$

(20–80°C; $r = 0.999964$)

$$C_8\text{: } d = -0.27864 + 1.3926\, d_\infty \qquad [14]$$

(20–80°C; 0.999907)

The Table 3 densities were used successfully to develop equations that correlate densities of the *n*-fatty acids (at given temperatures) with chainlength: d vs. oxygen content; and $d^{1/2}$ vs. $[C/(C + 2)]^{1/2}$.

COMPARISON OF DENSITIES

Most literature densities (Tables 1 and 2) agree with the Table 3 densities and other similar densities (23). Before disagreeing densities are categorized as being inaccurate, consideration should be given (i) to the possibility that some of the Table 3 densities are inaccurate and (ii) the densities calculated by extrapolation might be inaccurate.

Densities at 20 and 50°C that disagree significantly with the Table 3 densities are those published by Bernardo-Gil *et al.* (24).

The Hunten and Maass densities (18) at 80, 100, and 120°C (Table 2) disagree with the Table 3 densities. The C_{16} and C_{18} densities at 120°C of Noureddini *et al.* (22) are considerably higher than the corresponding Table 3 densities.

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TABLE 5
***n*-Fatty Acids: Equations[a] Correlating Densities (*d*) with Number of Carbons (C)[b]**

Temperature (°C)	Carbon range	Adjustable parameters	d_∞	Slope (m)	Correlation coefficient (r)
20	5–9	1.005	0.854	0.51166	$\underline{3}$,884
25	5–9	0.996	.851	.50222	$\underline{3}$,858
30	4–8	0.849	.848	.48178	$\underline{4}$,28
50	4–12	0.704	.837	.43212	$\underline{3}$,842
60[c]	8–14	0.928	.831	.42262	$\underline{5}$,6
70[c]	8–14	0.781	.825	.39775	$\underline{4}$,65
75	4–18	0.737	.822	.38574	$\underline{2}$,874
80	10–18	1.673	.819	.40294	$\underline{4}$,31
100[d]	20–30	−2.089	.808	.28285	$\underline{2}$,712

[a]$d = d_\infty + m/(C + k)$. [b]Densities from Table 3, except those for 60, 70, and 100°C. [c]Densities from Reference 23. [d]Densities from References 25 and 43.

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