Molal Volumes of Some *n*-Fatty Acids and Their Methyl and Ethyl Esters

K.Y. Liew* and **C.E. Seng**
School of Chemical Sciences, Universiti Sains Malaysia, Minden, 11800 Pulau Pinang, Malaysia

The densities of some pure methyl and ethyl esters of *n*-fatty acids were determined at temperatures between 10° to 80°C. The molal volumes of these esters and the long-chain fatty acids were correlated with temperature and chainlength. The reciprocals of the average methylene contribution at long-chain and the end group contribution to the molal volumes were found to be linear functions of the temperature. With the introduction of a correction term to account for mutual interaction of the end groups, three equations, one for each of the esters and the acids, were developed. These equations were used to calculate the molal values of the acids with carbon numbers up to 30 and up to 20 for the esters at temperatures ranging from 10° to 100°C. Excellent agreements were obtained between the molal volumes calculated by the equations and those obtained from the literature and experimental data.

KEY WORDS: Chainlength, density, methyl and ethyl esters, molal volume, *n*-fatty acids.

The *n*-fatty acids and their esters are important intermediary chemicals. The esters have also been evaluated as alternatives for diesel fuels. The densities for some pure fatty acids (1–10) and the methyl and ethyl esters (1,5,8, 11–19) have been reported at various temperatures. It is generally agreed that the densities of these long-chain compounds are, to a good approximation, linear functions of temperature between 10° to 100°C. Thus, linear equations have been developed relating the density with temperature for individual fatty acids (10) and methyl esters (18). Based upon the limiting property of homologous series, equations relating the molal volume with carbon number at constant temperatures have also been developed for the fatty acids (4,8,9) and their methyl esters (17). As the methylene contribution to the molal volume is approximately constant, the equations took the form:

$$V = a'N + b' \qquad [1]$$

where N is the number of carbon atoms in the chain, and a′ and b′, which are specific to the series, are constants at constant temperature. By assuming that these constants are linearly dependent on temperature near 20°C, equations relating the molal volume to the carbon number and temperature near 20°C have also been developed (8). However, agreements between the calculated and experimental molal volumes are rather poor at 30°C and higher.

We have reported the densities of some mid-chain fatty acids (10) and their methyl esters at regular temperature intervals (18). We have now determined additional density data for the methyl and ethyl esters. Combining these and other literature data, we attempted to correlate these molal volumes with the carbon number and the temperature for each of the series.

*To whom correspondence should be addressed.

EXPERIMENTAL PROCEDURES

Analytical reagent-grade methyl esters of C_{14} and C_{18} and ethyl esters of C_8 to C_{14} fatty acids with better than 99% purity from Sigma Chemical Co. (St. Louis, MO) were redistilled and dried over molecular sieve before use.

A narrow-necked (3 mm i.d.) flask-type pycnometer of approximately 10 mL capacity was used for density determinations. The procedure was the same as reported earlier (10).

RESULTS AND DISCUSSION

The densities of methyl tetradecanoate and octadecanoate and the mid-chain ethyl esters were determined from 20° to 80°C at 5°C intervals. These results are shown in Table 1. The deviations between the present data and the available literature data are better than 0.1% in all cases. These data were further evaluated by correlating them with temperature (°K) with the equation:

$$d = k + \varphi T \qquad [2]$$

Good correlations were obtained. The values of k, φ and the correlation coefficient are shown in Table 2.

TABLE 1

Measured Densities of Methyl and Ethyl Esters of *n*-Fatty Acids

Temp. (°C)	Methyl esters		Ethyl esters			
	Carbon numbers		Carbon numbers			
	14	18	8	10	12	14
15			0.8714	0.8681	0.8651	0.8641
20			0.8668	0.8639	0.8616	0.8607
25			0.8625	—	0.8575	0.8573
30	0.8594		0.8582	0.8555	0.8538	0.8529
35	0.8557		0.8538	0.8515	0.8498	0.8494
40	0.8517	0.8501	0.8494	0.8474	0.8464	0.8458
45	0.8480	0.8464	—	—	—	—
50	0.8444	0.8428	0.8407	0.8397	0.8384	0.8380
55	0.8404	0.8389	—	—	—	—
60	0.8366	0.8353	0.8316	0.8312	0.8302	0.8300
65	0.8330	0.8316	—	—	—	—
70	0.8291	0.8280	0.8231	0.8232	0.8229	0.8230
75	0.8253	0.8244	0.8185	0.8190	0.8186	0.8187
80		0.8206	0.8143	0.8149	0.8148	0.8150

TABLE 2

Methyl and Ethyl Esters of *n*-Fatty Acids: Coefficients of Equations Correlating Densities with Temperatures (T,K)

Esters	Carbon number	Intercept (k)	Slope ($\varphi \times 10^4$)	Correlation coefficients
Methyl	14	1.08899	−7.5733	−0.999971
	18	1.08065	−7.3633	−0.999974
Ethyl	8	1.12448	−8.7855	−0.999986
	10	1.10282	−8.1517	−0.999966
	12	1.08919	−7.7667	−0.999923
	14	1.08358	−7.6028	−0.999885

The molal volumes of the esters and the acids at different temperatures were calculated from the above data and other available literature data. These are shown in Tables 3, 4 and 5. It has been reported that the molal volumes of *n*-fatty acids (8,10) and of the esters (8) are linear functions of temperature within the accuracy of the experimental data. However, it has also been reported that for the methyl esters at 20° and 40°C, the contribution by the methylene increment to the molal volume decreased slightly with increasing chainlength, reaching a constant value at chains longer than dodecanoate (17). This is demonstrated from the molal volumes at 20°C and 40°C for the methyl esters, for which most experimental data are available (Table 6).

We believe that the variation of the methylene increments with chainlength for the ester is due to changes in the mutual attraction of the methyl and the ester end groups, which form the opposite ends of a dipole. At larger separation, as in the longer-chain esters, this attraction is minimal; shortening of the chain by removal of each methylene group resulted in a constant decrease in the molal volume. Equation 1, which can be written in the form (Equation 3):

$$V_n = a'n + b \quad [3]$$

where $n = N - 2$ and $b = b' + 2a'$, is obeyed. At shorter chain, the mutual attraction, which may cause the chainlength to contract, is increasingly felt as the chain shortens, leading to a progressively larger decrease in the molal volume.

An analogous situation can be found in the straight-chain hydrocarbons where the methylene increment increases slightly with increasing chainlength (20). In this case, the similar methyl end groups are expected to be mutually repulsive, resulting in higher molal volume than without interaction. Hence, an increase in the number of the interrupting methylene groups, which will progressively weaken the interaction, shall lead to higher decremental contributions.

We have commented previously (10) that the constants a′ and b′ in Equation 1 refer to the contributions from the methylene increments and the end groups, respectively. The comment shall be revised as in Equation 3 where the value of b, instead of b′, shall correspond to the end group contributions.

If we assume that the contribution of the molal volumes of the end groups for a particular series is constant at b irrespective of the chainlength, we may write:

$$V_n = \sum_i^n a_i + b \quad [4]$$

where a_i's are the i^{th} methylene group contributions. Since the average methylene contribution approaches a constant value, a, at large n, we can write:

$$\sum_i^n a_i = \sum_i^\infty a_i - \sum_{n+1}^\infty a_i = n(a - x_n) \quad [5]$$

where $a = \lim_{m\to\infty} \sum_i^m a_i/m$ and $x_n = \lim_{m\to\infty} \sum_{n+1}^m a_i/m$

Substituting Equation 5 into Equation 4, we obtain

$$V_n = (a - x_n)n + b \quad [6]$$

Since the average contribution from the n methylene groups increases as n decreases, x_n shall be some inverse function of n. Careful examination of the variation of molal volumes of the methyl ester series reveals that, beginning with methyl butanoate where $n = 2$, the molal volumes can be closely approximated by equating $x_n = 1/(n - 1)$. Equation 6 becomes

$$V_n + n/(n - 1) = an + b \quad [7]$$

However, Equation 7 is valid only for $n > 1$. Introduction of the first methylene into methyl ethanoate resulted in an anomalous increase in the molal volume for the resulting methyl propanoate. This is understandable because the disruption of the intramolecular interaction between the methyl and ester end groups may be much more than from the regular disruption in subsequent methylene introductions into the molecule where the end groups have already been separated by methylene.

To test the validity of Equation 7, the left-hand side of the equation was correlated with n by a linear least square fit. Excellent correlations (r better than −0.999999 for the esters and −0.999995 for the acids) were obtained in all cases. The values of a and b are shown in Table 7. When these values were used to calculate the molal volumes of the acids and the esters at various temperatures, the average deviation from the experimental data is less than 0.04%, which is as good as the deviation for the calculated values from experimental data.

According to Equation 7, the value of a corresponds to the average methylene contribution to the molal volume of the acids or the esters when the chain is sufficiently long. Since the molal volume of a molecule is largely determined by the dimension of the constituent groups, the values for the three series are similar at the same temperature. The small variations between them are likely the result of the differences in the intramolecular interaction of the end groups between the series. The a values increase approximately linearly with temperature, with the increase for the fatty acids being slightly higher than for the two esters.

As the end group increases in bulkiness from the carboxylic acid to the methyl and the ethyl esters, the b values are also increased. They also increase approximately linearly with temperature.

For the *n*-fatty acids and their esters, it is known that the density is a linear function of the temperature. Since the molal volume is reciprocally proportional to the density, it is likely that the reciprocals of the constants a and b are separately linear functions of temperature.

For the methyl esters, plots of 1/a and 1/b *vs.* temperature are shown in Figure 1. For any pair of data points, if 1/a was below its straight line plot, 1/b was proportionately above its straight line plot and *vice versa.* In other words, the errors are mutually compensated. Thus we can write:

$$1/a = rT + p \quad [8]$$

$$1/b = sT + q \quad [9]$$

Similarly, we correlated 1/a and 1/b with temperature T(°K) for the ethyl esters and the acids. Good correlations were obtained. The values of r, s, p and q for the acids and

TABLE 3

Comparison of Molal Volumes of *n*-Fatty Acids from Equation 10 and from the Literature

Temp. (°C)	Carbon number, N(= n + 2)																	
	4	5	6	7	8	9	10	11	12	14	16	18	20	22	24	26	28	30
20 C[a]	91.87	108.79	125.38	141.88	158.35	174.60												
L[b]	91.95	108.77	125.28	141.80	158.38	174.82												
25 C	92.34	109.32	125.97	—	159.07	175.57												
L	92.43	109.29	125.85	—	159.08	175.57												
30 C	92.81	109.85	126.56	—	159.77	—												
L	92.96	109.82	126.50	—	159.82	—												
35 C	—	—	—	—	—	—	193.76											
L	—	—	—	—	—	—	194.08											
40 C	—	—	—	—	161.22	—	194.61											
L	—	—	—	—	161.31	—	194.81											
45 C	—	—	—	—	—	—	195.46											
L	—	—	—	—	—	—	195.58											
50 C	94.75	—	—	—	162.70	179.51	196.33	213.12	229.93	—								
L	94.82	—	—	—	162.74	179.56	196.29	213.13	230.09	—								
55 C	—	—	—	—	—	—	197.20	—	230.92	—								
L	—	—	—	—	—	—	197.26	—	231.00	—								
60 C	—	—	—	—	164.20	—	198.08	—	231.93	265.78								
L	—	—	—	—	164.25	—	198.03	—	232.15	265.90								
65 C	—	—	—	—	—	—	198.97	—	232.97	266.92								
L	—	—	—	—	—	—	198.90	—	233.10	266.89								
70 C	—	—	—	—	165.73	—	199.86	—	233.98	268.07								
L	—	—	—	—	165.75	—	199.85	—	234.02	268.24								
75 C	97.29	—	132.17	—	166.51	—	200.77	—	235.01	269.24	303.45	337.67						
L	97.43	—	132.06	—	166.50	—	200.68	—	235.22	269.28	303.61	337.43						
80 C	—	—	132.83	150.07	167.29	184.49	201.69	—	236.06	270.41	304.76	339.11						
L	—	—	132.74	150.16	167.40	184.65	201.93	—	236.23	270.61	304.77	339.08						
100 C													379.85	414.72	449.59	484.47	519.33	554.20
L													379.30	414.30	449.19	483.90	518.57	553.49

[a]C: calculated from Equation 10. [b]L: calculated from literature data (9,10).

TABLE 4

Comparison of Molal Volumes from Equation 10 and Literature Data for Methyl Esters

Temp. (°C)	Carbon number, N(= n + 2)																
	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
10 L[a]			145.59a	162.22a	178.64a		211.56a		244.59a								
C[b]			145.68	162.19	178.66		211.58		244.46								
15 L			146.44a	163.05a	179.51		212.59a		245.47a								
C			146.47	163.03	179.55		212.56		245.54								
20 L	113.70b	130.50b	147.17a	163.87a	180.43a	197.03b	213.54a	230.02b	246.59a	263.06b	279.53b	295.97b					
C	113.55	130.57	147.27	163.87	180.45	197.00	213.56	230.09	246.64	263.17	279.71	296.24					
25 L			148.02a	164.74a	181.36a		214.58a		247.83a								
C			148.08	164.73	181.36		214.56		247.74								
30 L			148.90a	165.61a	182.30a		215.59a		248.92a								
C			148.89	165.60	182.27		215.58		248.86								
35 L			149.71a	166.53a	183.19a		216.65a		250.11a		283.29d						
C			149.72	166.48	183.20		216.61		249.99		283.36						
40 L	116.55b	133.53b	150.48a	167.37a	184.15a	200.92b	217.68a	234.42b	251.19b	267.91b	284.61d	301.26b	317.98b	334.69b	351.25d	367.97b	384.71b
C	116.44	133.67	150.56	167.37	184.14	200.90	217.66	234.39	251.14	267.87	284.61	301.35	318.07	334.81	351.53	368.27	385.00
45 L			151.38a	168.32a	185.08a		218.73a		252.35a		285.85d				352.68d		
C			151.41	168.27	185.10		218.71		252.30		285.87				353.00		
50 L			152.25a	169.15a	186.03a		219.82a		253.61a		287.07d				354.19d		
C			152.28	169.18	186.06		219.78		253.47		287.14				354.47		
55 L			153.13a	170.04a	187.02a		220.91		254.78a		288.44d				355.83d		
C			153.15	170.11	187.04		220.86		254.65		288.43				355.97		
60 L			153.85a	170.97a	188.00a		221.99a		255.94a		289.74d				357.37d		
C			154.03	171.04	188.03		221.95		255.84		289.73				357.48		
65 L			154.80a	172.05a	188.97a		223.05a		257.17a		291.01d				358.96d		
C			154.93	171.99	189.03		223.06		257.05		291.04				359.00		
70 L			155.71a	172.94a	190.01a		224.21a		258.41a		292.37d				360.42d		
C			155.84	172.96	190.04		224.18		258.28		292.37				360.54		
75 L	122.18c		156.59a	173.92a	191.01a		225.29a		259.61a		293.74d		327.94c		362.09d		
C	121.91		156.76	173.93	191.07		225.31		259.52		293.72		327.91		362.10		
80 L			157.52a	174.93a	192.10a		226.47a		260.89a		295.25d				363.77d		
C			157.69	174.92	192.11		226.46		260.77		295.08				363.67		

[a]L = calculated from a: Ref. 18; b: Ref. 17; c: Ref. 5; d: this work. [b]C = calculated from Equation 10.

TABLE 5

Comparison of Molal Volumes from Equation 10 and Experimental and Literature Data for Ethyl Esters

Temp. (°C)	Carbon number, N(= n+2)							
	4	6	8	10	12	14	16	18
15 E[a]	131.34a		197.69	230.76	263.99	296.76		
C[b]	131.20		197.84	230.82	263.77	296.71		
20 E			198.74	231.88	265.06	297.03		
C			198.82	231.90	264.93	297.99		
25 E	132.92a		199.73		266.33	299.12		
C	132.77		199.81		266.15	299.29		
30 E			200.73	234.16	267.48	300.66		
C			200.82	234.10	267.36	300.60		
35 E		168.30b	201.73	235.15	268.62	301.86	335.12b	368.26b
C		168.37	201.83	235.22	268.58	301.93	335.26	368.60
40 E			202.81	236.40	269.82	303.18		
C			202.86	236.35	269.81	303.26		
50 E		171.16b	204.94	238.54	272.32	305.95	339.52b	373.05b
C		171.18	204.95	238.65	272.32	305.98	339.64	373.29
60 E			207.15	241.30	275.09	308.95		
C			207.09	241.00	274.88	308.76		
65 E		174.09b	208.08b	242.08b	276.12b	310.08b	344.08b	377.92b
C		174.08	208.18	242.20	276.19	310.17	344.14	378.11
70 E			209.29	243.35	277.53	311.58		
C			209.28	243.41	277.51	311.59		
75 E			210.47	244.60	278.99	313.22		
C			210.26	244.63	278.84	313.03		
80 E		177.15b	211.49	245.80	280.20	314.52	348.72b	382.97b
C		177.10	211.52	245.87	280.18	314.49	348.78	383.08
95 E		180.31b	214.88b	249.59b	284.23b	318.87b	353.53b	388.15b
C		180.24	214.99	249.67	284.32	318.94	353.58	388.21

[a]E: calculated from a: Ref. 19; b: Ref. 13. [b]C: calculated from Equation 10.

TABLE 6

Difference in Molal Volume, $V_n - V_{n-1}$, Between Adjacent Methyl Esters at 20° and 40°C

n	20°C	40°C
3	16.80	16.98
4	16.67	16.95
5	16.70	16.91
6	16.56	16.78
7	16.60	16.77
8	16.51	16.76
9	16.48	16.74
10	16.57	16.77
11	16.47	16.72
12	16.47	16.70
13	16.44	16.65
14	—	16.72
15	—	16.71
16	—	16.56
17	—	16.72
18	—	16.74

TABLE 7

Coefficients of the Equation V + n/(n − 1) = an + b at Different Temperatures

Temperature (T − 273.15) K	*n*-Fatty acids		Methyl esters		Ethyl esters	
	a	b	a	b	a	b
10	—	—	16.453	81.136	—	—
15	—	—	16.469	81.921	16.463	100.297
20	16.416	61.035	16.504	82.600	16.520	100.862
25	16.475	61.396	16.598	82.971	16.544	101.796
30	16.524	61.819	16.632	83.702	16.638	102.155
35		—	16.673	84.384	16.648	103.098
40	—	—	16.709	85.092	16.709	103.811
45	—	—	16.756	85.781	—	—
50	16.788	63.216	16.812	86.400	16.807	105.291
55	—	—	16.876	86.987	—	—
60	16.936	63.798	16.937	87.555	16.942	106.784
65	16.985	64.227	16.987	88.284	16.971	107.496
70	17.064	64.524	17.044	88.958	17.035	108.262
75	17.098	65.144	17.087	89.769	17.114	108.929
80	17.167	65.595	17.161	90.320	17.135	109.915
95	—	—	—	—	17.304	112.328
100	17.405	67.197	—	—	—	—

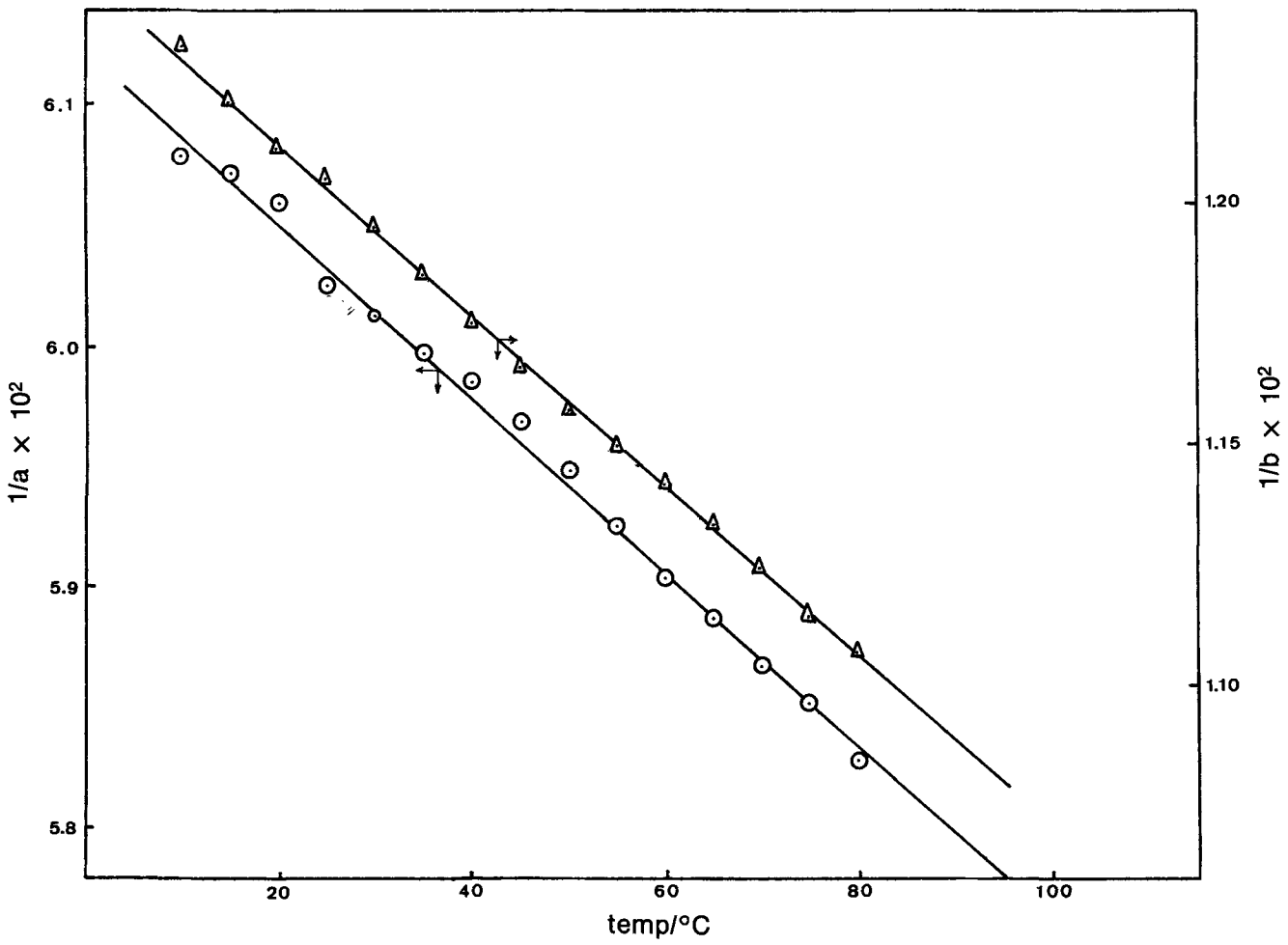

FIG. 1. Plots of 1/a and 1/b against temperature for methyl esters.

TABLE 8

Coefficients for the Equations $1/a = rT(K) + p$ and $1/b = sT(K) + q$

	Gradient	Intercept	Correlation coefficient
n-Fatty acids	$r = -4.4225 \times 10^{-5}$	$p = 0.07387$	−0.9988
	$s = -1.8558 \times 10^{-5}$	$q = 0.02182$	−0.9988
Methyl esters	$r = -3.6368 \times 10^{-5}$	$p = 0.07118$	−0.9977
	$s = -1.7764 \times 10^{-5}$	$q = 0.01733$	−0.9994
Ethyl esters	$r = -3.7282 \times 10^{-5}$	$p = 0.07150$	−0.9985
	$s = -1.3373 \times 10^{-5}$	$q = 0.01382$	−0.9997

the esters, together with their correlation coefficients, are shown in Table 8.

Combining Equations 7, 8 and 9, we obtained:

$$V_n = n/(rT + p) + 1/(sT + q) - n/(n - 1) \quad [10]$$

Substituting the values of the constants from Table 8, the molal volumes for the acids with carbon number from 4 to 30, and for the esters with carbon numbers from 4 to 20, at temperatures up to 100°C can be calculated. These calculated values were compared with the experimental and literature values in Table 3-5. Absolute errors for the three equations are less than 0.1% (except for some butanoate esters, the C_4 acid at 3 temperatures and the C_{20} and C_{28} acids at 100°C, where the deviations are less than 0.16%). The average absolute deviation for the acids is <0.06% and for both the methyl and the ethyl esters they are <0.04%. Although density determinations can be carried out easily, accurate data can only be obtained with high-purity materials, which are difficult to obtain. Accurate density can, however, be easily calculated from Equation 8 at the temperature range studied. These equations are especially useful for the odd-numbered esters for which pure samples are more difficult to obtain.

ACKNOWLEDGMENT

This work was supported in part by USM R&D Grant No. 123/3206/2501.

REFERENCES

1. *Bailey's Industrial Oil and Fat Products*, Vol. 1, 4th edn., edited by D. Swern, John Wiley & Sons, New York, NY, 1979, p. 189.
2. Riddick, J.A., and W.B. Bunger, *Organic Solvents*, 3rd edn., John Wiley & Sons, New York, NY, 1970, pp. 252-264.
3. Singleton, W.S., *Fatty Acids*, Part 1, edited by K.S. Markley, Interscience Publishers, New York, NY, pp. 535-536.
4. Dorison, A., M.R. McCorkle and A.W. Ralston, *J. Am. Chem. Soc. 64*:2739 (1942).
5. Gros, A.T., and R.O. Feuge, *J. Am. Oil. Chem. Soc. 29*:313 (1952).
6. Berchiesi, G., M.A. Berchiesi and D. Leonesi, *J. Thermal Anal. 9*:455 (1976).
7. Lutskii, A.E., *Chem. Abstr. 44*:9205f (1950).
8. Hammond, E.G., and W.O. Lundberg, *J. Am. Oil Chem. Soc. 31*:427 (1954).
9. Fisher, C.H., *Ibid. 65*:1647 (1988).
10. Liew, K.Y., C.E. Seng and E.K. Lau, *Ibid. 68*:488 (1991).
11. Bonhorst, C.W., P.M. Althouse and H.O. Triebold, *Ind. Chem. Eng. 40*:2379 (1948).
12. Nevin, C.S., P.M. Althouse and H.O. Triebold, *Ibid. 28*:325 (1951).
13. Shigley, J.W., C.W. Bonhorst, C.C. Liang, P.M. Althouse and H.O. Triebold, *J. Am. Oil Chem. Soc. 32*:213 (1955).
14. Vogel, A.I., *J. Chem. Soc.*:133 (1946).
15. Vogel, A.I., *Ibid.*:607 (1948).
16. Vogel, A.I., *Ibid.*:634 (1948).
17. Gouw, T.H., and J.C. Vlugter, *J. Am. Oil Chem. Soc. 41*:142 (1964).
18. Liew, K.Y., C.E. Seng and L.L. Oh, *Ibid. 69*:155 (1992).
19. Riddick, J.A., and W.B. Bunger, *Organic Solvents*, 3rd edn., Wiley-Interscience, New York, NY, 1970, p. 296.
20. Bretsznajder, S., *Prediction of Transport and Other Physical Properties of Fluids* (English translation), Pergamon Press, Oxford, England, 1971, p. 33.

[Received January 10, 1992; accepted March 26, 1992]