Viscosities of Some Long-Chain Fatty Acids and Their Relationship with Chainlength

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

The densities and viscosities of octanoic, decanoic, dodecanoic and tetradecanoic acids were determined at temperatures ranging from 20 to 80°C. When the fluidities were plotted against the molal volumes of the acids, curves were obtained. The intrinsic volumes were determined by extrapolation to zero fluidity and compared with previously reported values. Based upon Hildebrand's equation for non-associated liquids, semi-empirical equations relating the fluidity with the carbon number were obtained. The equations predict the fluidities of fatty acids with carbon number ranging from 4 to 18 at 4 temperatures from 20°C to 75°C with reasonable agreement with the experimental values.

KEY WORDS: Chainlength, density, fatty acids, fluidity, molal volume, viscosity.

Empirical equations with adjustable parameters have been developed for evaluating and predicting the physical properties of n-fatty acids and their esters with different carbon numbers in the chain (1-5). The regular variation in the physical properties is attributed to the methylene increments in a homologous series. Viscosity is one of the physical properties of the fatty acids and their derivatives that have been examined by various workers (3-9), and were found to be exponential functions of the absolute temperature. Further, the logarithms of the viscosities of saturated fatty acids were found to be approximately linearly related to the molecular weights. However, the linear relationship is not valid over the whole range (7).

Berchiesi and co-workers (8,9) measured the viscosities of a series of n-fatty acids at a limited range of temperatures. When they plotted the fluidity, the inverse of the viscosity, against the molal volume according to the Batschinski's equation (10), they obtained an approximate linear relationship, although it had been noted previously that the linear relationship is only applicable to non-associated liquids (11).

Hildebrand (11-13) showed that for a simple liquid, the fluidity (ϕ) depends upon the relative expansion of the liquid, $(V\text{-}V_o)/V_o$, where V is the molal volume and V_o is the intrinsic volume, which is the volume of the liquid at which its molecules are so crowded as to inhibit self-diffussion and viscous flow. The relationship can be written as:

$$\phi = B(V - V_o)/V_o \qquad [1]$$

where the constant B is a measure of the extent at which the external momentum that produces viscous flow is absorbed by the molecules of the liquid. This relationship is not applicable for associated liquids such as those in which hydrogen bonding exists. For such liquids, linear relationship between fluidity and molal volume is not observed over a range of temperature and pressure (10).

For liquids in a homologous series, such as the fatty acids, the molal volume is a linear function of the chainlength at a particular temperature (1). Similarly, we shall expect the intrinsic volume, V_o, to be a function of the chainlength. For straight-chain alkanes, the B values have been shown to be a function of the carbon number in the chain with the magnitude decreasing linearly as the chainlength is increased (12). If the basic assumption of Equation [1] is sound, the viscosities of the liquids in a homologous series, such as the fatty acid series, may be predicted if the magnitude of B can be estimated taking into account the intermolecular interaction. The present investigation aims to determine accurate densities and viscosities of some pure fatty acids at various temperatures and to attempt to correlate these with the carbon number by using a modified form of Equation [1].

EXPERIMENTAL PROCEDURES

Analytical reagent-grade saturated fatty acids with better than 99% purity from Sigma Chemical Co. were redistilled and dried over activated 4A molecular sieve before use.

A narrow-necked (3 mm i.d.) flask-type pycnometer of approximately 10 mL capacity was used for density determination. The filled pycnometer was equilibrated for at least 30 min at a temperature controlled to better than 0.05°C. The masses were corrected and the reproducibility was better than 4×10^{-5} g cm^{-3}.

The viscosity was determined in an Ubbelohde viscometer, which was mounted on a brass frame held in a vertical position in the thermostatted bath. The viscometer was calibrated with double distilled water and triply distilled ethanol.

RESULTS AND DISCUSSION

The densities and viscosities of octanoic, decanoic, dodecanoic and tetradecanoic acids were determined at temperatures ranging from 20 to 80°C. These values are shown in Table 1. The differences between the present density data and available literature data (4,5) are less than 0.1% in nearly all cases. The differences between the viscosities at 75°C of the present work agreed with literature data (5) at better than 1%.

The accuracy of the density data was also evaluated by correlating them with temperatures °C with the equation:

$$d = k + l\,T \qquad [2]$$

Good correlations were obtained. The values of k and l, together with the correlation coefficients, are shown in Table 2.

The viscosity data were also evaluated with the equation:

$$\log \eta = m + n\,T \qquad [3]$$

*To whom correspondence should be addressed.

TABLE 1

Viscosities and Densities of n-Fatty Acids at Different Temperatures

Octanoic acid									
Temp. (°C)	20	25	30	40	50	60	70	75	
ϱ(g cm^{-3})	0.9105	0.9065	0.9022	0.8940	0.8859	0.8780	0.8701	0.8661	
η(cp)	5.738	5.249	4.587	3.670	2.986	2.421	2.021	1.852	
Decanoic acid									
Temp. (°C)	35	40	45	50	55	60	65	70	75
ϱ(g cm^{-3})	0.8876	0.8843	0.8808	0.8771	0.8733	0.8699	0.8661	0.8620	0.8586
η(cp)	6.680	5.861	5.151	4.576	4.080	3.666	3.240	2.885	2.573
Dodecanoic acid									
Temp. (°C)	46	48	50	55	60	65	70	75	80
ϱ(g cm^{-3})	0.8732	0.8721	0.8707	0.8672	0.8629	0.8594	0.8560	0.8517	0.8483
η(cp)	7.536	7.170	6.855	6.030	5.336	4.773	4.269	3.849	3.469
Tetradecanoic acid									
Temp. (°C)	56	58	60	65	70	75	80		
ϱ(g cm^{-3})	0.8617	0.8604	0.8589	0.8557	0.8514	0.8481	0.8440		
η(cp)	8.158	7.756	7.452	6.526	5.785	5.054	4.431		

TABLE 2

n-Fatty Acids: Coefficients of Equations[a] Correlating Densities with Temperatures (T, °C)

Carbon number (n)	Intercept (k)	Slope, $\times 10^4$	Correlation coefficient
8	0.92650	−8.0728	−0.999950
10	0.91355	−7.3180	−0.999961
12	0.90771	−7.4295	−0.999637
14	0.90314	−7.3654	−0.999347

[a] $d = k + l\,T$.

TABLE 3

n-Fatty Acids: Coefficients of Equation[a] Correlating Viscosities (η) with Temperatures (T, °C)

Carbon number	Intercept (m)	Slope (n)	Correlation coefficient
8	0.93566	−0.0090485	−0.999026
10	1.1781	−0.010266	−0.999714
12	1.3323	−0.009981	−0.999362
14	1.5320	−0.011042	−0.999742

[a] $\text{Log}\ \eta = m + n\,T$.

TABLE 4

Parameters in the Equation V = an + b for the Molal Volumes of n-Fatty Acids at Various Temperatures

Temp. (°C)	a	b	Correlation coefficient
75	17.14	29.37	0.999996
70	17.08	29.09	0.999999
65	17.00	28.96	0.999994
60	16.95	28.63	0.999998
20[a]	16.66	25.07	0.999954

[a] Calculated with data from Reference 5, p. 541.

Approximate straight lines were obtained for the four acids. The values of m and n, together with the correlation coefficients, are shown in Table 3.

The molal volume of a liquid at a particular temperature, obtained by dividing the molecular weight by its density, is a linear function of the carbon number expressed by the relationship:

$$V = an + b \qquad [4]$$

where a is the contribution from the methylene increments and b refers to the contribution from the end group. These a and b values for the acids are tabulated in Table 4.

The intrinsic volume, V_o, is the molal volume of the liquid at zero fluidity. For liquids that obey Equation [1], these are determined from the intercept of the linear plots of fluidity *vs.* molal volume. For the n-fatty acids, the fluidity plots deviate from linearity, as shown in Figure 1, in contrast to the result of Berchiesi and co-workers (8), but in agreement with the observations of Batschinski (10) and Hildebrand (11) for associated liquids. However, the curvature decreases as the chainlength increases. The intrinsic volumes were obtained by extrapolation of the curves to zero fluidity and are shown in Table 5.

Fluidity decreases with decreases in $V - V_o$ values. For associated liquids, such as the n-fatty acids studied in this work and n-butanoic acid (4), as well as for cogwheel molecules with long arms (12), fluidity decreases less quickly when $V - V_o$ is smaller than when it is large, resulting in fluidity plots that curve towards the left as the fluidity approaches zero. For the acids, the extrapolated intrinsic volumes are thus the upper limits of the "true" intrinsic volumes. For the simple liquid, the intrinsic volume is identified with the molal volume of the solid substance if the molecules retain rotational freedom in the solid state. The molal volumes of the solid fatty acids are lower than the V_o values obtained, because the molecules cannot rotate freely in the solid state.

By assuming that the fatty acid molecules formed rigid dimers through hydrogen bonding in either the *cis,cis* or the *trans,trans* configuration, freely rotating, forming a

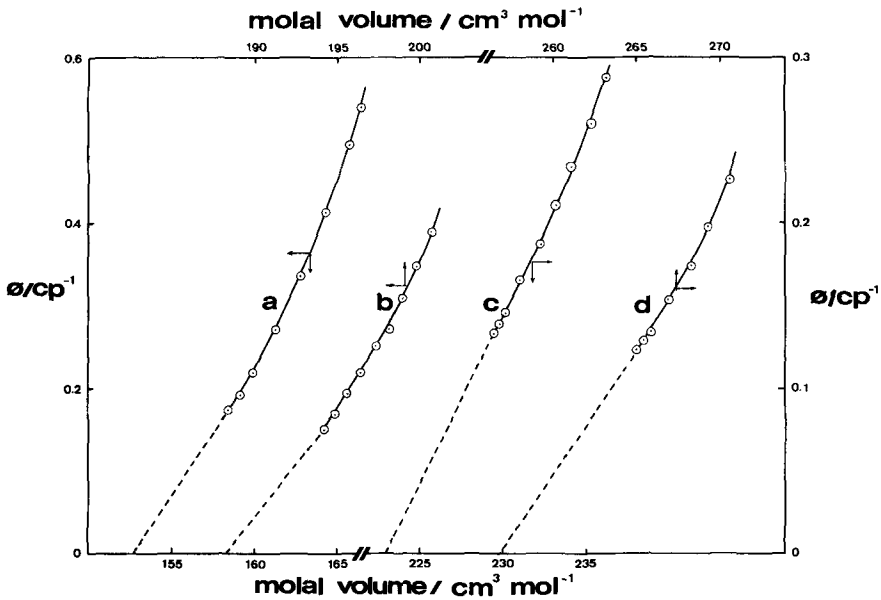

FIG. 1. Plots of the fluidities against the molal volume of octanoic (a), decanoic (b), dodecanoic (c) and tetradecanoic (d) acids.

TABLE 5

Intrinsic Volumes, V_o/cm³, of n-Fatty Acids

Carbon number	This work	V_o = 12.41 + 17.54n	V_b[a]	V^a_{cyl}
4	—	82.57	—	—
6	—	117.65	—	—
8	152.7	152.73	—	—
9	—	170.27	170.3	169.9
10	187.8	187.81	189.4	188.7
11	—	205.35	204.1	204.7
12	223.0	222.89	224.0	225.6
13	—	240.43	240.1	244.1
14	257.9	257.97	257.4	262.5
15	—	275.51	273.8	281.0
16	—	293.05	292.2	299.4
17	—	310.59	309.4	317.9
18	—	328.13	325.2	336.3

[a]From references 8 and 9, as explained in text.

cylinder along the long axis and closely packed, Berchiesi *et al.* (8) calculated the intrinsic volumes of the n-fatty acids (Table 5). They obtained V_{cyl} values that are comparable but slightly larger than their experimental values, V_b, obtained from the intercepts of the linear ϕ *vs.* V plots, by less than 3% for the higher fatty acids. The slightly higher calculated values may be because hydrogen bonding is not rigid in the dimers or the dimers may not be rotating freely along the long axis at zero fluidity.

The V_o values for the acids can be expressed in terms of the following equations:

$$V_o = 12.41 + 17.54\ n \qquad [5]$$

(Correlation coefficients, r = 0.999998)

The B value in Equation [1] is obtained from the gradient of the fluidity *vs.* molal volume plot for simple liquids. For the n-fatty acids, the fluidity plots are nonlinear. The B values are calculated from Equation [1] for each of the fatty acids at each temperature separately. These calculated B values are listed in Table 6. It is noted that the calculated values depend strongly on the molal volumes and the intrinsic volumes. For example, an inaccuracy of 0.5% in V_o or V for octanoic acid at 75°C will magnify into a 6% error in the value of B. It is also dependent upon temperature.

For the straight-chain alkanes with carbon number greater than 3, the value of B decreases linearly with an increase in the carbon number (12). The B values determined for the fatty acids are nearly linear with the decrease in carbon number, n, of the acids at fixed temperature, expressed as:

$$B = B' - c\ n \qquad [6]$$

TABLE 6

Values of B and Parameters B′ and c in the Equation B = B′ − cn

Carbon number:	B (cp^{-1})[a] 8	10	12	14	B′	c	Correlation coefficient
75°C	5.96	5.68	4.76	4.48	8.12	0.27	0.9715
70°C	5.79	5.40	4.74	4.31	7.87	0.26	0.9953
60°C	5.46	5.01	4.57	4.33	6.95	0.19	0.8999

Carbon number:	4	5	6	7	8	B′	c	Correlation coefficient
20°C[b]	5.77	5.24	4.93	5.20	4.63	7.00	0.32	0.9733

[a]B values calculated from Equation [1].

[b]Values of V and η from ref. 5, p. 541 and p. 562, respectively. Values for V_0 calculated from Equation [5].

TABLE 7

Comparison of Calculated and Experimental Fluidities (cp^{-1})

	75°C		70°C		60°C		20°C	
Carbon number:	Expt.	Calc.[a]	Expt.	Calc.[a]	Expt.	Calc.[a]	Lit.[c]	Calc.
3							0.910	0.931
4	1.374[b]	1.319	—	1.228	—	1.039	0.650	0.633
5							0.434	0.446
6	0.782[b]	0.811	—	0.747	—	0.626	0.310	0.319
7							0.231	0.229
8	0.538	0.541	0.495	0.493	0.413	0.409	0.174	0.163
9							0.124	0.115
10	0.391	0.377	0.347	0.339	0.273	0.277	—	—
12	0.260	0.269	0.234	0.238	0.187	0.192		
14	0.198	0.193	0.173	0.168	0.136	0.132		
16	0.141[b]	0.139	0.128[c]	0.118	—	0.090		
18	0.110[b]	0.098	0.101[c]	0.082	—	0.060		

[a]Calculated from Equation [7] with the parameters a and b from Table 5, and B′ and c from Table 6.

[b]Data from ref. 5, p. 565.

[c]Data from ref. 5, p. 562.

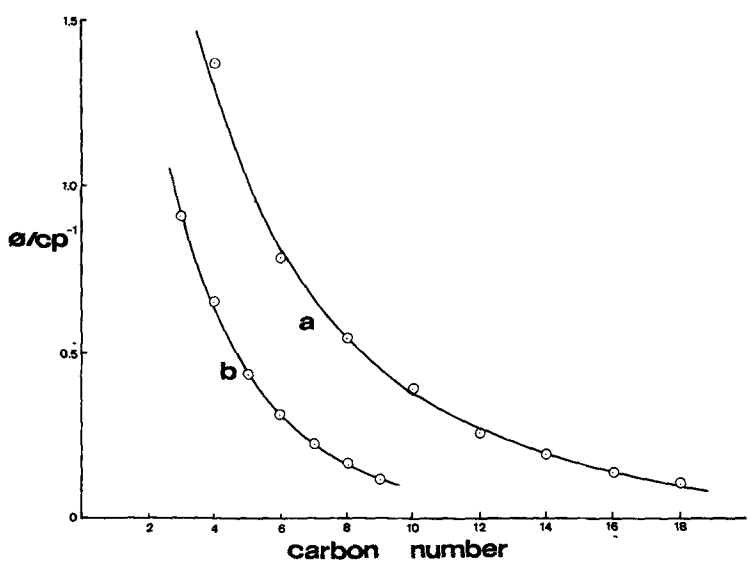

FIG. 2. Plot of the fluidities of the fatty acids against the carbon numbers at 75°C (a) and 20°C (b). The points are the experimental values and the lines are drawn from the calculated values.

where B′ and c are constants. The least square parameters B′ and c are listed in Table 6. These parameters were used to calculate the B values for the acids whose viscosities, together with their densities, have not been determined at the three temperatures.

Substituting Equations [5] and [6] into Equation [1], we obtained, for the fluidity of the liquids in a homologous series at a particular temperature:

$$\phi = (B' - cn)\left(\frac{an + b}{12.41 + 17.54n} - 1\right) \qquad [7]$$

Using the numerical values of a and b from Table 4 and B′ and c from Table 6, the ϕ values were calculated and compared with the experimental values in Table 7. Similarly, using literature data (5), the values of B were estimated and the predicted fluidities at 20°C were calculated for the short-chain acids from carbon number 3 to 9. When the calculated fluidities of the even-numbered fatty acids from butanoic to octadecanoic acid at 75°C and of the short-chain fatty acids at 20°C were plotted against carbon number, as shown in Figure 2, smooth curves were obtained. The experimentally measured fluidity values distribute along the curves randomly but closely.

The predicted fluidities and the known experimental values agree reasonably well at all temperatures for the acids examined, except for the C_{18} acid at higher temperature and the C_9 acid at 20°C. These discrepancies are attributed to the inadequacy of the linear equations for predicting the intrinsic volumes since it is obtained from the extrapolated values of the non-linear curves of four mid-chain fatty acids. As noted earlier, a small error in the intrinsic volume caused a large error in the B values, and hence the estimated values for fluidity. Viscosity determination with accuracy better than 1% is rarely achieved (14) either because of experimental difficulties or because of the standard viscosity values used. Considering the random nature of the discrepancies between the predicted fluidities and the measured values, the semi-empirical equation formulated is a reasonable representation of the fluidities of n-fatty acids from propanoic acid to octadecanoic acid at temperatures ranging from 20°C to 75°C.

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