Viscosities and Densities of the Methyl Esters of Some n-Alkanoic Acids

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The densities and viscosities of the methyl esters of hexanoic, heptanoic, octanoic, decanoic and dodecanoic acids were determined at temperatures ranging from 10 to 80°C at 5°C intervals. The densities of the methyl esters vary linearly with temperature. When fluidities were plotted against molal volumes of the esters, smooth curves were obtained. Intrinsic volumes were determined by extrapolation to zero fluidity. Based upon Hildebrand's equation, the B values, which represent a measure of the molecules resisting transport of momentum, were calculated for each ester and found to be exponentially related to the temperatures. A modified equation relating the fluidity with temperature was formulated. Excellent agreement was obtained between calculated and experimental fluidities.

KEY WORDS: **Density, fluidity, intrinsic volume, methyl esters, viscosity.**

Many empirical relations have been proposed to correlate viscosity with temperature for pure liquids (1). Most of these correlations are based upon the Andrade equation (2), which yields a linear relation between the logarithm of the viscosity and the reciprocal of the temperature. For associated liquids and many other compounds, the Andrade relation fails and a large number of modifications have been proposed (3).

Batschinski (4) found that fluidity, which is the reciprocal of the viscosity, is a linear function of the molar volume for a large number of nonassociated liquids. Later, Hildebrand (5,6) modified the original Batschinski equation to the form (Equation 1)

$$\phi = B\,(V - V_0)/V_0 \qquad [1]$$

where ϕ is the fluidity, V the molal volume, V_0 the intrinsic volume, which is the molal volume at zero fluidity, and B is a constant, which depends upon the capacity of the molecule to absorb momentum. A plot of ϕ against V showed straight lines over a wide range of temperatures for scores of nonassociated liquids. More recently, we used a modified form of equation 1 to account for the viscosities of n-alkanoic acids (7). In the modified equation, the values of B were taken to be a linear function of the carbon number at a particular temperature. The fluidities calculated were found to be in reasonable agreement with the experimental values.

The densities and viscosities of the methyl esters of n-alkanoic acids have been determined at a few temperatures ranging from 20°C to 100°C (8-11). Based upon the viscosities of the various methyl esters at four temperatures, Bonhorst *et al.* (11) found that the viscosity-temperature relationships conformed to the empirical A.S.T.M. equation which is an equation with many adjustable parameters (12,13). Later, Gouw and Vlugter (9) found that the viscosities of a number of esters measured at three temperatures conform to their rather complicated equation with two adjustable parameters and two constants.

We report here the densities and viscosities of five pure methyl esters of n-alkanoic acids at 15 temperatures and our attempt to correlate the viscosity with the temperature by using a modified form of Equation 1.

EXPERIMENTAL PROCEDURES

Analytical reagent-grade methyl esters of C_6 to C_{12} fatty acids with better than 99% purity from Sigma Chemical Co. (St. Louis, MO) were redistilled and dried over molecular sieve before use.

The density and the viscosity were determined with a 10-mL flask-type pycnometer and an Ubbelohde viscometer, respectively. The details were described previously (7).

RESULTS AND DISCUSSION

The densities and viscosities of the methyl esters of hexanoic, heptanoic, octanoic, decanoic and dodecanoic acids were determined from 10 to 80°C at 5°C intervals. These results are shown in Table 1. The differences between the present density data and available literature data (8-11) are less than 0.1% in all cases. The viscosities differences are less than 1%.

The accuracy of the density data was further evaluated by correlating them with temperature (K) by means of Equation 2:

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

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

When the changes in viscosity with temperature were plotted in the form of log η *vs* 1/T, smooth curves were obtained with the exception of methyl hexanoate, which yielded a reasonably good straight line. Thus, for methyl esters of the fatty acids, when enough data points are used, the Andrade relation fails. This also means that the viscosity-temperature relationship of Van Velzen *et al.* (2) with two adjustable parameters cannot be applied. Makhija and Stairs (3) used a three-parameter equation to correlate the viscosity with temperature for associated liquids and obtained good agreement with experimental data. Their equation (Equation 3),

$$\log \eta = m + n/(T - T_0) \qquad [3]$$

where m, n and T_0 are adjustable parameters, was used to evaluate the viscosity data. Using a least-square program, the values of the adjustable parameters for the various methyl esters were obtained and tabulated in Table 3. Good fits were obtained. Although the agreements between the calculated and the experimental values are good, the significance of the parameters is obscure (3). However, the fact that the experimental values can all be fitted well by an equation showed that the determined values are reasonably accurate.

The viscosities of the methyl esters were calculated with

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TABLE 1

Densities and Viscosities of Methyl Esters of n-Alkanoic Acids at Various Temperatures

	C_6		C_7		C_8		C_{10}		C_{12}	
Temp (°C)	d^a	η^b	d	η	d	η	d	η	d	η
10	0.8942	1.0540	0.8890	1.3323	0.8858	1.7422	0.8806	2.6502	0.8772	4.0821
15	0.8890	0.9638	0.8845	1.2196	0.8815	1.5618	0.8763	2.3561	0.8732	3.5740
20	0.8848	0.8945	0.8800	1.1201	0.8771	1.4120	0.8724	2.1120	0.8691	3.1519
25	0.8795	0.8278	0.8754	1.0337	0.8725	1.2834	0.8682	1.9067	0.8649	2.7895
30	0.8743	0.7718	0.8708	0.9584	0.8680	1.1870	0.8641	1.7316	0.8611	2.4907
35	0.8696	0.7219	0.8660	0.8906	0.8638	1.0897	0.8599	1.5755	0.8570	2.2437
40	0.8650	0.6792	0.8615	0.8279	0.8594	1.0053	0.8558	1.4429	0.8533	2.0346
45	0.8600	0.6383	0.8568	0.7783	0.8550	0.9393	0.8517	1.3341	0.8494	1.8624
50	0.8551	0.5998	0.8526	0.7196	0.8506	0.8747	0.8475	1.2307	0.8452	1.7023
55	0.8502	0.5669	0.8481	0.6763	0.8461	0.8176	0.8433	1.1408	0.8413	1.5640
60	0.8462	0.5358	0.8435	0.6440	0.8417	0.7650	0.8392	1.0603	0.8375	1.4438
65	0.8410	0.5082	0.8382	0.6106	0.8374	0.7195	0.8352	0.9891	0.8335	1.3380
70	0.8361	0.4831	0.8339	0.5747	0.8328	0.6782	0.8309	0.9253	0.8295	1.2455
75	0.8315	0.4624	0.8292	0.5437	0.8282	0.6392	0.8267	0.8696	0.8254	1.1581
80	0.8260	0.4400	0.8244	0.5156	0.8235	0.6052	0.8222	0.8162	0.8212	1.0827

[a] Density = d (g/cm^3).
[b] Viscosity = η (cp^{-1}).

TABLE 2

Parameters for the Equation, d = k + lT(K) for Methyl n-Alkanoate

Carbon number	k	l/x 10^{-4}	Correlation coefficient
C_6	1.16761	−9.6635	−0.99991
C_7	1.15005	−9.2135	−0.99995
C_8	1.13688	−8.8635	−0.99997
C_{10}	1.11569	−8.3008	−0.99998
C_{12}	1.10211	−7.9479	−0.99997

TABLE 3

Parameters for the Equation, $\log_{10}\eta = m + n/(T - T_o)$ for Methyl n-Alkanoate

Carbon number	m	n	T_o/K	max. error in log η
C_6	−1.8414	518.50	3.96	0.0071
C_7	−1.6973	438.05	42.23	0.0058
C_8	−1.3454	273.30	110.57	0.0044
C_{10}	−1.5888	416.28	75.36	0.0056
C_{12}	−1.2989	306.51	121.55	0.0032

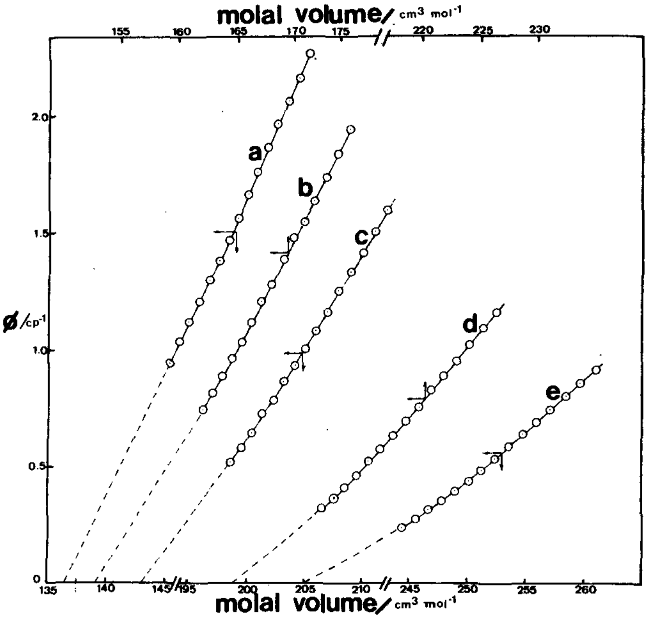

FIG. 1. Plots of the fluidities against the molal volumes (cm^3/mole) of (a) methyl hexanoate, (b) methyl heptanoate, (c) methyl octanoate, (d) methyl decanoate and (e) methyl dodecanoate.

TABLE 4

Values of V_0 for Methyl Esters

Carbon number	C_6	C_7	C_8	C_{10}	C_{12}
V_0/cm^3	136.3	153.0	170.1	203.2	235.8

a modified Hildebrand equation as follows. For a nonassociated liquid, the parameter B is a constant related to the capacity of the molecules to resist externally imposed momentum by reason of mass, softness or rotational inertia. For these liquids, the value of V_0 is determined by the intercept at $\phi = 0$ in the plot of ϕ *vs* V. For the methyl esters, the values of V_0 were estimated by extrapolation of the curves of ϕ *vs* V to $\phi = 0$, as shown in Figure 1. These values are tabulated in Table 4. It is seen that the V_0 values obtained are linearly related to the carbon numbers of the acids.

The B values for the esters at different temperatures were then calculated by using the V_0 value from Table 4 and the molal volume obtained from V = M/d, where M is the molecular weight of the ester and d is given by Equation 2.

The values of B so calculated are shown in Table 5.

TABLE 5

Values of B Calculated from Equation 1 and the Parameters for the Equation ln B = ln A − E/T(K)

	B				
Temp (°C)	C_6	C_7	C_8	C_{10}	C_{12}
10	13.87	12.49	11.46	9.19	6.72
15	13.98	12.50	11.56	9.22	6.80
20	13.96	12.54	11.67	9.29	6.91
25	14.04	12.60	11.79	9.36	7.07
30	14.08	12.65	11.78	9.45	7.22
35	14.12	12.72	11.91	9.58	7.37
40	14.13	12.84	12.05	9.71	7.51
45	14.19	12.85	12.07	9.78	7.63
50	14.29	13.12	12.19	9.92	7.79
55	14.34	13.21	12.28	10.05	7.94
60	14.42	13.16	12.40	10.18	8.09
65	14.47	13.19	12.49	10.31	8.23
70	14.52	13.35	12.59	10.44	8.36
75	14.50	13.46	12.71	10.54	8.52
80	14.58	13.57	12.79	10.68	8.66
A	17.839	19.102	19.763	20.025	24.804
E	71.59	123.20	155.15	225.06	373.22
Correlation coefficient	−0.9890	−0.9774	−0.9949	−0.9903	−0.9985

TABLE 6

Comparison of Calculated and Experimental Fluidities

	C_6 (Φ)		C_7 (Φ)		C_8 (Φ)		C_{10} (Φ)		C_{12} (Φ)	
Temp (°C)	exp	cal	exp	cal	exp	cal	exp	cal	exp	cal
10	0.949	0.948	0.751	0.743	0.574	0.572	0.377	0.371	0.245	0.242
15	1.038	1.033	0.820	0.817	0.640	0.639	0.424	0.422	0.280	0.280
20	1.118	1.119	0.893	0.893	0.708	0.707	0.474	0.474	0.317	0.319
25	1.208	1.207	0.967	0.971	0.779	0.776	0.525	0.527	0.359	0.360
30	1.296	1.296	1.043	1.050	0.842	0.847	0.578	0.582	0.402	0.403
35	1.385	1.387	1.122	1.130	0.918	0.920	0.635	0.639	0.446	0.447
40	1.472	1.479	1.208	1.213	0.995	0.994	0.693	0.696	0.492	0.493
45	1.567	1.573	1.285	1.296	1.065	1.070	0.750	0.756	0.537	0.540
50	1.667	1.668	1.389	1.382	1.143	1.148	0.813	0.817	0.587	0.590
55	1.764	1.765	1.479	1.469	1.223	1.227	0.877	0.879	0.639	0.640
60	1.866	1.863	1.553	1.557	1.307	1.307	0.943	0.943	0.693	0.693
65	1.968	1.963	1.634	1.647	1.390	1.389	1.011	1.009	0.747	0.747
70	2.070	2.064	1.740	1.739	1.474	1.473	1.081	1.075	0.803	0.803
75	2.163	2.166	1.839	1.832	1.564	1.558	1.150	1.144	0.864	0.860
80	2.273	2.271	1.939	1.927	1.652	1.645	1.225	1.213	0.924	0.919
Average error	0.003		0.006		0.003		0.004		0.002	

These values increase with increase in temperature for the same ester. The increase is nearly linear with temperature, especially at temperature higher than 30°C. Nevertheless, to conform to the Andrade equation (14) and other theoretical expressions (15), the values were fitted to the temperatures with the following expression (Equation 4):

$$\ln B = \ln A - E/T(K) \qquad [4]$$

The values of ln A and E and the correlation coefficient of the fit are also shown in Table 5. It is noted that the decrease in the value of B is approximately linear with the increase in carbon number in the homologous series, similar to the n-alkanoic acid series (7).

By substitutions of Equations 2 and 4 into Equation 1, we obtained the fluidities expression for a particular ester at different temperatures (Equation 5):

$$\phi = Ae^{-E/T} \left(\frac{M}{(k + lT)V_0} - 1\right) \qquad [5]$$

From Equation 5, with the values of M, the molecular weight, A and E from Table 5, k and l from Table 2 and V_0 from Table 4, the values of ϕ at different temperatures were calculated and compared with the experimental values in Table 6. The maximum error between the calculated values and the experimental fluidities is less than 1%, which is comparable to the experimental error.

Equation 5 contains five parameters. The parameters k and l were determined independently and are not adjustable. Although it is possible to best fit the experimental data to the equation with the three remaining parameters, we deliberately chose to determine the V_0 values graphically to implicate its physical significance. The calculated fluidities in Table 6 are thus the result of a two-parameter best fit.

Equation 5 is consistent with the Andrade equation in terms of the concept of the "activation energy for flow." It is also consistent with the Batschinski and Hildebrand equation and the experimental fact that fluidity is dependent upon the free volume of the liquids. It is similar to the theoretical equation of Eyring (15) although not in details. It is thus concluded that the modified Equation 5 is a reasonable representation of viscous flow for methyl esters of n-alkanoic acids at varying temperatures.

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REFERENCES

1. Reid, R.C., J.M. Prausnitz and T.K. Sherwood, *The Properties of Gases and Liquids*, McGraw Hill, New York, NY, 1977, pp. 435–456.
2. Van Velzen, D., R.L. Cardozo and H. Lengenkamp, *Ind. Eng. Chem. Fundam. 11 (1)*:20 (1972).
3. Makhija, R.C., and R.A. Stairs, *Can. J. Chem. 48*:1214 (1970).
4. Batschinski, A.J., *Z. Physik Chem. 84*:643 (1913).
5. Hildebrand, J.H., *Science 174*:493 (1971).
6. Hildebrand, J.H., *Ind. Eng. Chem. Fundam. 16(4)*:492 (1977).
7. Liew, K.Y., C.E. Seng and E.K. Lau, *J. Am. Oil Chem. Soc. 68(7)*:488 (1991).
8. Gouw, T.H., J.C. Vlugter and C.J.A. Roelands, *Ibid. 43*:433 (1966).
9. Gouw, T.H., and J.C. Vlugter, *Ibid. 41*:142 (1964).
10. Gros, A.T., and R.O. Feuge, *Ibid. 29*:313 (1952).
11. Bonhorst, C.W., P.M. Althouse and H.O. Triebold, *Ind. Eng. Chem. 40(12)*:2379 (1948).
12. American Society for Testing and Materials, A.S.T.M. Standards D341-77, Philadelphia, PA.
13. Watson, K.M., J.L. Wien and G.B. Murphy, *Ind. Eng. Chem. 28*:605 (1936).
14. Andrade, E.N. daC., *Nature 125*:309 (1930).
15. Jhon, M.S., and H. Eyring in *Physical Chemistry—An Advance Treatise*, Vol. VIII A, edited by G.H. Eyring, Academic Press, New York, NY, 1971, pp. 361–364.

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