Viscosities of Six 1-Alkanols at Temperatures in the Range 298–348 K and Pressures up to 200 MPa

S. Matsuo[1] and T. Makita[1]

Viscosities of six higher 1-alkanols (1-hexanol, 1-octanol, 1-decanol, 1-dodecanol, 1-tetradecanol, and 1-hexadecanol) have been determined at temperatures from 298 to 348 K and pressures up to 200 MPa. The viscosity measurements were performed using a falling-body viscometer with an uncertainty of ±5%. Simple equations are presented to express the experimental viscosities as a function of temperature and pressure within the experimental uncertainty. The relationship between the viscosity and the density of these alkanols is discussed in terms of the significant structure theory extended to high pressures.

KEY WORDS: decanol; dodecanol; falling-body viscometer; free volume; hexadecanol; hexanol; high pressure; octanol; significant structure theory; tetradecanol; viscosity.

1. INTRODUCTION

Reliable experimental data of liquid viscosities under high pressures are quite limited because of the difficulty in the measurements in spite of the increasing needs in both scientific and industrial fields. The primary objective of this work is, therefore, to study directly the variations of viscosities of 1-alkanols with temperature and pressure.

In the past three decades, a number of theoretical and semi-empirical free volume equations [1–5] have been proposed in order to analyze the experimental viscosity data. Although they have been successful for some restricted groups of liquids including the application to high pressures [6–7], there is no generalized equation which can be used to predict the liquid viscosity without any adjustable parameter. In this work, the signifi-

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[1] Department of Chemical Engineering, Kobe University, Kobe 657, Japan.

cant structure theory, which has been used successfully to correlate both thermodynamic and transport properties of liquids, has been applied to correlate the experimental viscosities of 1-alkanols with those molar volumes obtained in a previous paper [8].

2. EXPERIMENTAL

2.1. Measurements at Atmospheric Pressure

Viscosity measurements at atmospheric pressure were performed at 11 temperatures from 298 to 348 K at an interval of 5 K using an Ostwald viscometer calibrated against pure water.

2.2. Measurements Under High Pressures

High-pressure viscosities were measured at 298, 323, and 348 K and pressures up to 200 MPa or freezing pressures using a falling-body viscometer newly constructed for highly viscous liquids. A schematic diagram of the high-pressure apparatus is given in Fig. 1. The apparatus consists of a mirror-finished stainless-steel tube, B (length, 108.2 mm; outer diameter, 12.4 mm; inner diameter, 9.85 mm), and a permeable stainless-steel falling-body, A (length, 39.40 mm; diameter, 9.75 mm), contained in a

to Strain Gauge

A: Falling Body
B: Stainless Steel Tube
C: Differential Transformer
D: Thermocouple
E: Electrode
F: High Pressure Vessel
G: Band Heater
H: Oil Inlet
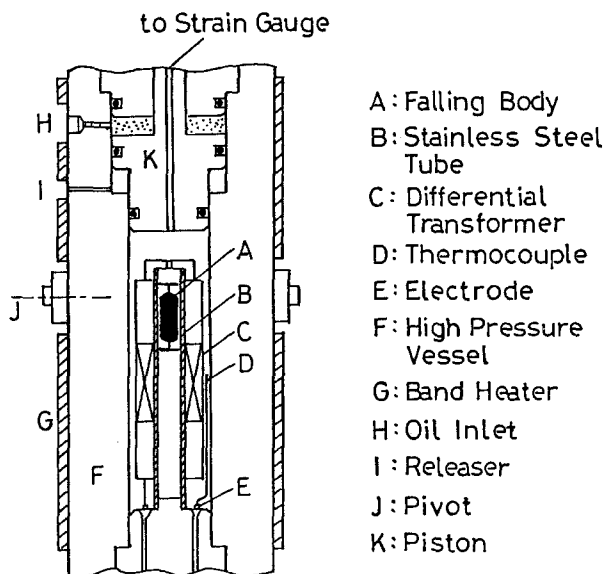I: Releaser
J: Pivot
K: Piston

Fig. 1. Schematic diagram of the experimental apparatus.

high-pressure vessel, F. The body has cross-shaped stabilizers projecting from both ends of the cyclindrical body to prevent flutter when it falls. The falling body is taken to the position shown in Fig. 1 by turning the entire vessel upside down. The position of the body can be detected by a displacement meter connected to a differential transformer, C, which is placed around the tube. Using a time interval counter, the falling time was determined as the time which the body takes to fall through a fixed distance (about 10 mm) at the middle of the tube in the terminal velocity. The sample liquid contained in the vessel was regulated thermostatically within ± 0.2 K by an electric band heater, G, placed around the vessel. Pressure generated by a semiautomatic hydraulic oil pump is transmitted to the sample liquid through the piston, K, which acts as both a pressure intensifier and a sample separator. Temperature and pressure were determined by an alumel–chromel thermocouple, D, inserted in the vessel through the electrodes, E, within ± 0.1 K and a strain gauge calibrated against a pressure balance within ± 0.5 MPa, respectively.

The measuring principle of the falling-body viscometer is based on Stokes law, and the liquid viscosity η can be determined by the following equation:

$$\eta = K(\rho_b - \rho_s)t \tag{1}$$

where ρ_s and ρ_b are the densities of the sample liquid and falling body, respectively, t is the falling time, and K is the cell constant, which depends mainly on the dimensions of the instrument. In this work, the constant K has been determined at atmospheric pressure using the experimental viscosity and density data of the sample alcohols measured by an Ostwald viscometer and a glass pycnometer. As the estimated pressure dependence of the cell constant is less than 0.1% even at the highest pressure (200 MPa), this effect has been neglected.

2.3. Materials

The sample materials were obtained from Tokyo Chemical Industry Co., Ltd., with guaranteed purities greater than 99% except for 1-octanol (97%). These are the same samples as in the density measurements and have been used without any further purification.

2.4. Uncertainty

Judging from the precision of our temperature and pressure control and the purities of the sample materials, the estimated uncertainties of the

viscosities obtained at atmospheric pressure and high pressures should be within ±1.0 and ±5.0%, respectively.

3. RESULT

3.1. Viscosity at Atmospheric Pressure

The viscosities obtained at atmospheric pressure are given in Table I together with some literature values. As shown in this table, the viscosity of each alkanol decreases monotonously with temperature and increases according to the carbon number. In the comparison with the literature values of 1-hexanol at 298 K, the present result agrees with the datum by Iwahashi et al. [9] and the selected value by Rathovics and Salamon [10] within the combined experimental uncertainties. Data obtained by Singh and Singh [11] show fairly large discrepancies at some temperatures.

In order to correlate the experimental viscosities with temperature, the following empirical equation, which is often applied to associated liquids, has been adopted:

$$\eta_0 = A \exp(B/T + C/T^2) \tag{2}$$

where η_0 is the viscosity at atmospheric pressure in mPa·s and T is the temperature in K. Empirical coefficients A, B, and C determined as the

Table I. Viscosities of 1-Alkanols at Atmospheric Pressure in mPa·s

Temp. (K)	Hexanol	Octanol	Decanol	Do-decanol	Tetra-decanol	Hexa-decanol	Hexanol (lit.)
298.15	4.51	7.24	11.05	15.91			4.551[a]
							4.592[b]
							4.590[c]
303.15	3.90	6.01	9.20	13.08			3.765[c]
308.15	3.36	5.10	7.71	10.84			
313.15	2.89	4.37	6.47	9.02	12.18		2.934[c]
318.15	2.52	3.76	5.53	7.57	10.11		
323.15	2.21	3.25	4.69	6.45	8.50		2.169[c]
328.15	1.95	2.84	4.07	5.48	7.19	9.03	
333.15	1.73	2.49	3.52	4.71	6.11	7.61	1.655[c]
338.15	1.54	2.19	3.07	4.07	5.24	6.52	
343.15	1.38	1.94	2.70	3.55	4.56	5.61	
348.15	1.24	1.72	2.37	3.11	3.95	4.85	

[a] From Ref. 9.
[b] From Ref. 10.
[c] From Ref. 11.

Table II. Coefficients in Eqs. (2a), (2b), and (2c)

$10^2 a_1$	a_2	$10^2 a_3$	b_1	b_2	b_3	$10^{-5} c_1$	$10^{-3} c_2$
7.101	-0.3400	1.132	-286.3	179.92	-5.333	3.010	5.74

parameters of a least-squares fitting for each alkanol were found to be satisfactorily correlated with the carbon number of sample alkanol C_n by the following equations:

$$A = a_1 \exp(a_2 C_n + a_3 C_n^2) \qquad (2a)$$

$$B = b_1 + b_2 C_n + b_3 C_n^2 \qquad (2b)$$

$$C = c_1 + c_2 C_n \qquad (2c)$$

Parameters in Eqs. (2a) to (2c) are given in Table II. The average and maximum deviations of the experimental data from Eq. (2) are 0.30 and 0.73%, respectively, and within the experimental uncertainty except for that of 1-octanol, whose purity is a little inferior to those of other 1-alkanols (1.23 and 1.56%, respectively).

3.2. Viscosity Under High Pressures

Pressure effects on the viscosities of 1-alkanols at 348 K are shown in Fig. 2. As each isotherm in this figure shows an exponential curvature, the following equations has been adopted to represent the experimental results:

$$\eta_P = \eta_0 \exp[m_1(P - P_0) + m_2(P - P_0)^2] \qquad (3)$$

where η_P is the viscosity under high pressures in mPa·s, and P_0 and P are the atmospheric pressure and a high pressure in MPa, respectively. The experimental constants m_1 and m_2 were determined using the smoothed η_0 calculated by Eq. (2). As m_2 was independent of both temperature and sample material within the experimental uncertainty, m_1 has been redetermined using the following average value of m_2:

$$m_2 = -1.10 \times 10^{-5} \qquad (3a)$$

The optimum values of m_1 are given in Table III together with the average and maximum deviations of experimental data from Eq. (3). The relative viscosities η_P/η_0 calculated from Eq. (3) at each temperature increase monotonously with the carbon number and the consistency of the experimental results has been confirmed.
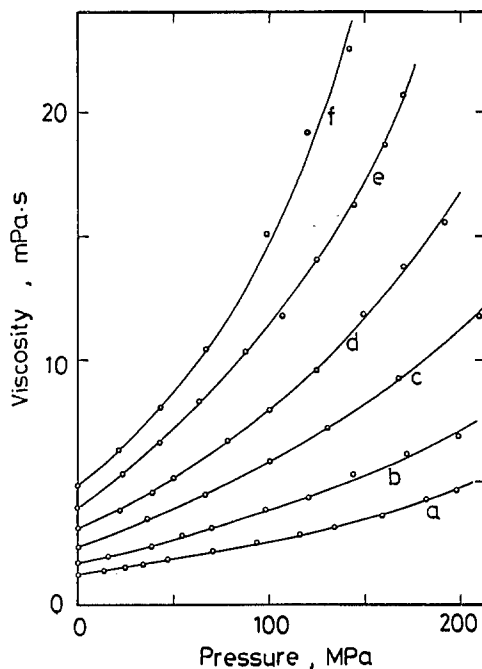
Fig. 2. Viscosities of 1-alkanols at 348.15 K as a function of pressure. (a) $C_6H_{13}OH$; (b) $C_8H_{17}OH$; (c) $C_{10}H_{21}OH$; (d) $C_{12}H_{25}OH$; (e) $C_{14}H_{29}OH$; (f) $C_{16}H_{33}OH$.

Table III. Optimum Coefficients m_1 in Eq. (3)

	Temp. (K)	$10^3 m_1$	Ave. dev. (%)	Max. dev. (%)
$C_6H_{13}OH$	298.15	9.585	2.03	3.75
	323.15	9.245	1.95	4.18
	348.15	8.656	2.06	3.99
$C_8H_{17}OH$	298.15	10.475	1.55	2.35
	323.15	9.951	0.46	1.30
	348.15	9.287	1.65	3.01
$C_{10}H_{21}OH$	298.15	11.070	1.45	3.22
	323.15	10.583	0.85	1.74
	348.15	10.043	1.57	4.33
$C_{12}H_{25}OH$	323.15	10.948	2.18	3.54
	348.15	10.538	0.96	1.67
$C_{14}H_{29}OH$	323.15	11.982	1.21	3.22
	348.15	11.633	2.53	5.29
$C_{16}H_{33}OH$	348.15	12.424	1.89	4.01

4. DISCUSSION

In order to represent the liquid viscosity, some successful free volume equations were proposed based on the quasicrystalline liquid structure model. Among these equations the significant structure theory by Eyring has been applied to the present experimental results.

4.1. Application at Atmospheric Pressure

According to the significant structure theory, liquid viscosity at atmospheric pressure η_0 is expressed as follows:

$$\eta_0 = \frac{T^{1/2}}{V - V_{SO}} \exp \left[A_0 + \frac{B_0 V_{SO}}{(V - V_{SO}) T} \right] \tag{4}$$

$$A_0 = \frac{(\pi m k)^{1/2} N}{2\kappa} l_f \tag{4a}$$

$$B_0 = a' \frac{Z\phi(a)}{2k} \tag{4b}$$

where V and V_{SO} are the molar volume of liquid and that of the solid-like structure in $cm^3 \cdot mol^{-1}$, l_f is the free length between nearest neighbors, κ is the transmission coefficient, a' is a dimensionless constant, $\phi(a)$ is an intermolecular potential, Z is the number of nearest molecules, k is Boltzmann's constant, m is the molecular mass, and N is Avogadro's number. Since some unknown physical properties are involved in Eq. (4), A_0, B_0, and V_{SO} were determined as the adjustable parameters for each alkanol. As the ratio of V_{SO} to the van der Waals volume V_W calculated by the group contribution suggested by Bondi [12] has shown very little dependence of the sample materials, A_0 and B_0 were redetermined using the following fixed V_{SO}:

$$V_{SO} = 1.388 \, V_W \tag{4c}$$

The optimum values of A_0 and B_0 are given in Table IV together with V_{SO} calculated by Eq. (4c). The average and maximum deviations of experimental results from Eq. (4) are 0.26 and 0.67%, respectively.

Table IV. Coefficients in Eq. (4)

	$C_6H_{13}OH$	$C_8H_{17}OH$	$C_{10}H_{21}OH$	$C_{12}H_{25}OH$	$C_{14}H_{29}OH$	$C_{16}H_{33}OH$
A_0	−1.791	−1.589	−1.301	−1.084	−0.935	−0.751
B_0	258.7	270.6	276.4	283.8	294.4	299.5
V_{SO}	101.13	129.53	157.93	186.33	214.72	243.12

It is of interest to compare the molar volume of the solid-like structure V_{SP} with that of the solid. Since the compressions of solid for sample alkanols have not been found, those of ethanol and 1-butanol by Bridgman have been referred to and are shown in Fig. 3 for comparison. The ratios of the hypothetical solid molar volumes extrapolated to the atmospheric pressure $V_{0(solid)}$ to Bondi's van der Waals volume V_W are 1.35 ± 0.02 in ethanol and 1.38 ± 0.01 in 1-butanol. Although V_{S0} is not the molar volume of the crystallized solid but that of the randomly distributed solid-like structure, (V_{S0}/V_W) is quite comparable to $[V_{0(solid)}/V_W]$, while the pressure dependences of V_{S0} and $V_{0(solid)}$ are different from each other as shown in Fig. 3. It is considered that this difference would arise from the incompleteness of the approximations which were introduced in order to extend the significant structure theory to high pressures.

5. CONCLUSION

Experimental viscosities of six 1-alkanols (1-hexanol, 1-octanol, 1-decanol, 1-dodecanol, 1-tetradecanol, and 1-hexadecanol) are presented at temperatures from 298 to 348 K and pressures up to 200 MPa. Using a semiempirical equation based on the significant structure theory, the experimental viscosities at atmospheric pressure have been successfully represented. Furthermore, it was found that this equation could be extended to high pressures by adding some adequate approximations concerning the packing of solid-like molecules and its pressure dependence. This successful application of the significant structure theory indicates the probability of predicting the liquid viscosity covering wide ranges of temperature and pressure.

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