Viscosity of Methanol and 2-Methyl-2-Propanol Mixtures Under High Pressures

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A new capillary viscometer has been constructed and the viscosities of methanol, 2-methyl-2-propanol, and their mixtures have been measured at two temperatures, 303 and 323 K, and at pressures up to 30 MPa. Simple empirical equations are given to represent the pressure and composition dependences of the viscosity within the experimental uncertainty of $\pm 2\%$.

1. INTRODUCTION

In spite of the increasing needs for liquid viscosity in both scientific and industrial fields, reliable experimental data for liquids at high pressures are quite limited because of the technical difficulties in making the measurements. Among the numerous types of viscometers, a capillary viscometer has the advantage of having a rigorous theoretical background [1, 2] and that it can be used over a wide range of temperatures and pressures. Therefore, a new semiautomatic capillary viscometer has been designed and constructed, suitable for temperature and pressure ranges up to 373 K and 200 MPa, respectively.

In our previous works [3–5], the densities and viscosities of some aqueous solutions of alcohols had been measured using a high-pressure burette method [6] which is categorized into the variable-volume method and a falling-cylinder method [7], respectively. Anomalous behavior resulting from their complicated molecular interactions had been observed in the composition dependence of the viscosity, the isothermal

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compressibility, and the partial molar volume. As a continuation of the earlier work, the viscosity of mixtures of methanol and 2-methyl-2-propanol has been measured with a new capillary viscometer at 303 and 323 K and at pressures up to 30 MPa.

2. EXPERIMENTAL

Viscosities of methanol, 2-methyl-2-propanol, and their eight mixtures were determined at atmospheric pressure and two temperatures, 303 and 323 K, with an Ubbelhode viscometer calibrated against pure water.

Measurements of viscosities at high pressures were performed with a capillary-tube viscometer schematically shown in Fig. 1. The main portion of the viscometer consists of a capillary unit (D), bellows cells (F), an electric circulating pump (P), and flow-detecting electrodes (B). As shown in the drawing, the stainless-steel capillary, L (length, 105 mm; inner diameter, 0.143 mm; outer diameter, 1.59 mm), is located in a coaxial thicker tube (K) of the same material (length, 95 mm; inner diameter, 2.35 mm; outer diameter, 6.35 mm). The sample liquid permeates into the narrow gap between these tubes due to the imperfect welding at one end of the capillary. Therefore, the same pressure is applied to both the inside and the outside of the capillary and the change of the dimensions of the capillary with pressure is minimized. With a set of polytetrafluoroethylene bellows, the sample liquid is separated from the ethanol which serves as a

A : Oil Pump
B : Electrodes
C : Water Bath
D : Capillary-Tube Unit
E : Digitized Bourden Gauge
F : Bellows Cells
G : Mercury U-cut
H : T.I.Counter
I : Interface
J : Mercury Holder
K : Outer-tube
L : Capillary-tube
M : Micro-computer
N : Solenoid
P : Circulating Pump
R : Magnetic Piston
S : Quartz Sensor
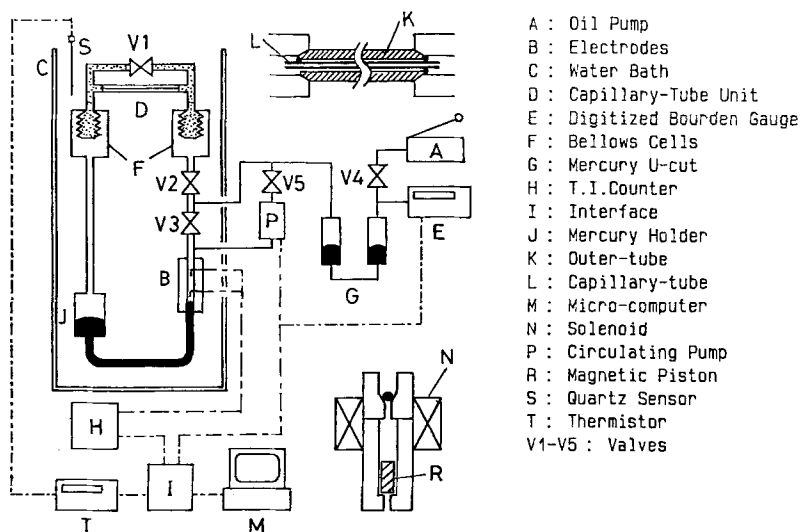T : Thermistor
V1-V5 : Valves

Fig. 1. Schematic diagram of the experimental apparatus.

pressure medium, so as to ensure a perfect contact of mercury with the electrodes. Furthermore, the ethanol is separated by the mercury trap (G) from the secondary pressure medium, hydraulic oil. The main portion of the viscometer is placed in a water bath (C) which is regulated thermostatically within ± 10 mK. Temperatures and pressures are measured with a quartz thermometer, T (Tokyo Denpa DMT 610), to within ± 10 mK and by a digitized precise Bourdon gauge, E (Heise 901B), to within ± 0.2 MPa, respectively.

The operational procedure is as follows.

(1) Pressure generated by a hydraulic oil pump is transmitted to a sample liquid through the two kinds of pressure media.

(2) After closing valves V1 and V3, the mercury in the holder is raised to a somewhat higher position than the upper electrode by a computer-controlled circulating pump and then valve V5 is closed.

(3) After thermal equilibration, valve V3 is opened so that the sample begins to flow through the capillary tube.

(4) the time interval in which the mercury falls between a pair of electrodes is measured and recorded, together with the temperature and pressure, by a computer.

The measuring principle of a capillary viscometer is based on the Hagen–Poiseuille law for laminar flow, and the fluid viscosity is given by the following equation:

$$\eta = \frac{\pi a^4 \Delta P t}{8LV} - \frac{m\rho V}{8\pi Lt} = C_1 \Delta P t + \frac{C_2 \rho}{t} \tag{1}$$

where a and L are the inner radius and the length of the capillary, respectively, ΔP is the pressure difference across the capillary, V the fluid volume which passes through the capillary during a period t, ρ the fluid density, m the Hagenbach constant accounting for both the acceleration and the deceleration in the entrace and exit region, and C_1 and C_2 are the cell constants [1]. In this work, the second term of Eq. (1) has been neglected because of its very small contribution of 0.011%. In the present work, the pressure difference ΔP steadily decreases from about 42 to 34 kPa during the time interval t according to the drop of the mercury level in the electrode's cell. Therefore, the flow in the capillary is not strictly steady-state flow and ΔP should be replaced by a mean value. But the viscosity of the sample liquid can be given by the following equation when the viscometer is used on a relative basis:

$$\eta = \eta_{H_2O} \frac{t}{t_{H_2O}} \tag{2}$$

where η_{H_2O} is the viscosity of pure water, which is used for the reference measurements covering the entire range of temperature and pressure; t and t_{H_2O} are the falling times of mercury when the viscometer is filled with the sample liquid and pure water, respectively.

The sample alcohols, which were obtained from Wako Pure Chemical Industry Ltd. with guaranteed purities more than 99.9%, were dried with a molecular sieve and then purified several times by fractional distillation. The sample mixtures were prepared by weighing and their composition should be accurate to within ±0.01%.

Judging from the above sources of experimental errors and the reproducibility of the measurements, the estimated uncertainties of the viscosities obtained should be within ±1 and ±2%, at atmospheric pressure and at high pressures, respectively.

3. RESULTS

3.1. Viscosity at Atmospheric Pressure

The viscosities obtained at atmospheric pressure are presented in Table I together with some literature values for the pure components. The

Table I. Viscosity (in mPa · s) of Methanol + 2-Methyl-2-Propanol Mixtures at Atmospheric Pressure. x = Mole-fraction of 2-Methyl-2-Propanol

	T (K)		
	303.15	323.15	
x	(obs.)	(obs.)	(lit.)
0	0.512	0.392	0.395[a]
			0.396[b]
			0.399[c]
0.0546	0.588	0.443	
0.1247	0.710	0.516	
0.2518	0.967	0.664	
0.3661	1.267	0.812	
0.4988	1.702	0.994	
0.6163	2.130	1.153	
0.7496	2.656	1.308	
0.8651	3.089	1.397	
1.0	3.380	1.406	1.414[a]

[a] Source: Ref. 4.
[b] Source: Ref. 8.
[c] Source: Ref. 9.

viscosity of this system deviates very little from the mole-fraction averaged values and any viscosity maximum, which exists in (water + primary alcohol) mixtures, is not observed.

In order to correlate the experimental viscosity η_0 at atmospheric pressure with the concentration, the following empirical equation was adopted:

$$\eta_0 = (1 - x)\eta_{M,0} + x\eta_{B,0} + x(1 - x) \sum_{i=1}^{3} d_i(1 - 2x)^{i-1} \qquad (3)$$

where $\eta_{M,0}$ and $\eta_{B,0}$ are the viscosities of pure methanol and 2-methyl-2-propanol in mPa's and where x is the mole fraction of 2-methyl-2-propanol. The empirical coefficients d_i determined from the best fit to the experimental viscosities are presented in Table II. As shown in Table II the average and maximum deviations of the experimental data from Eq. (3) are within the experimental uncertainty of $\pm 1\%$.

3.2. Viscosity at High Pressures

The viscosities obtained at high pressures are presented in Table III. The relative viscosity at 323 K, i.e., the ratio of the viscosity at high pressures to that at atmospheric pressure, is given in Fig. 2 in order to elucidate the pressure effect on the viscosity for this system. As shown in this figure, the relative viscosity of pure methanol increases almost linearly with increasing pressure. The concave curvature becomes clear gradually with increasing concentration of 2-methyl-2-propanol. A similar behavior is observed at 303 K. Since each isotherm shows a gentle curvature, a quadratic equation was adopted to represent the experimental results.

$$\eta_P = \eta_0\{1 + e_1(P - P_0) + e_2(P - P_0)^2\} \qquad (4)$$

where η_P and η_0 are the viscosity in mPa's under high pressure P and that at atmospheric pressure P_0 in MPa. The coefficients e_1 and e_2 are given in Table IV together with the average and maximum deviations.

Table II.   Coefficients d_i in Eq. (3)

T (K)	d_1	d_2	d_3	Dev. (%) (Ave.)	Dev. (%) (Max.)
303.15	−0.98695	−1.4540	1.1405	0.41	0.52
323.15	−3.8811	−0.7511	0.28027	0.10	0.30

Table III. Viscosity (in mPa·s) of Methanol + 2-Methyl-2-Propanol
Mixtures at High Pressures. x = Mole-fraction of 2-Methyl-2-Propanol

P (MPa)	x				
	0	0.2514	0.5003	0.7449	1.0
			303.15 K		
0.10	0.512	0.964	1.701	2.648	3.380
2.50	0.519	0.981	1.743	2.747	3.551
5.00	0.523	1.001	1.783	2.859	3.718
7.50	0.529	1.014	1.834	2.948	3.899
10.00	0.535	1.031	1.898	3.064	4.087
12.50	0.540	1.059	1.942	3.186	4.265
15.00	0.547	1.080	1.999	3.297	4.441
17.50	0.555	1.106	2.035	3.419	4.663
20.00	0.562	1.131	2.079	3.535	4.895
22.50	0.568	1.151	2.127	3.665	5.159
25.00	0.575	1.168	2.191	3.795	
27.50	0.581	1.201	2.236	3.923	
30.00	0.587	1.219	2.294	4.057	
			323.15 K		
0.10	0.392	0.663	0.997	1.304	1.406
2.51	0.397	0.675	1.015	1.342	1.467
5.07	0.401	0.690	1.047	1.383	1.525
7.51	0.406	0.703	1.067	1.426	1.590
9.99	0.412	0.718	1.105	1.461	1.657
12.51	0.416	0.732	1.123	1.504	1.720
14.99	0.421	0.747	1.154	1.546	1.794
17.48	0.426	0.762	1.185	1.603	1.876
19.92	0.432	0.780	1.212	1.651	1.955

In the comparison with the literature values, the present results for pure methanol at 323 K agree with our own previous data [4], with those of Isdale et al. [8] and with those of Isakova and Oshueva [9] to within 0.4, 1.0, and 2.0%, respectively. For pure 2-methyl-2-propanol, our previous data are slightly larger by 1.3% but are still within the combined uncertainties of the measurements. Reference data at high pressures are not available for the viscosity of (methanol + 2-methyl-2-propanol) mixtures.

3.3. Composition Dependence of Molar Volume and Viscosity

It is of interest to examine the relationship between the liquid molar volume and its viscosity. In this work, the molar volume of the sample
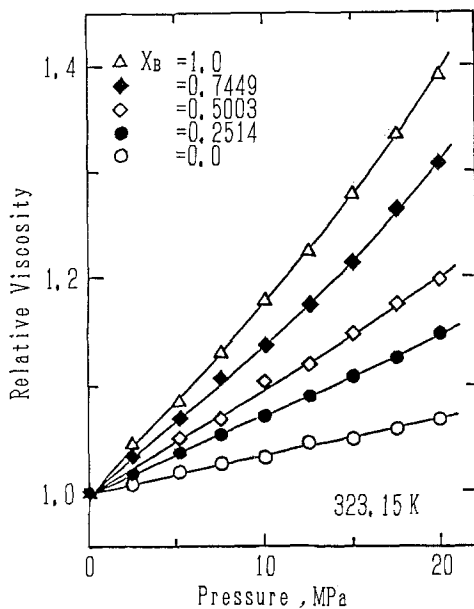
Fig. 2. Relative viscosity of (methanol + 2-methyl-2-propanol) mixture at 323.15 K as a function of pressure. x, mole-fraction of 2-methyl-2-propanol.

Table IV. Coefficients e_i in Eq. (4)

	x				
	0	0.2514	0.5003	0.7449	1.0
	303.15 K				
$10^3 e_1$	4.4035	7.2473	10.943	15.123	18.661
$10^5 e_2$	1.8749	5.7888	2.1516	8.9707	20.025
$AD^a(\%)$	0.15	0.29	0.29	0.10	0.34
$MD^b(\%)$	0.34	0.71	0.63	0.32	0.66
	323.15 K				
$10^3 e_1$	4.6293	7.7553	9.5392	11.280	16.188
$10^5 e_2$	2.4425	5.2041	6.9385	10.213	17.014
$AD^a(\%)$	0.09	0.08	0.24	0.19	0.15
$MD^b(\%)$	0.20	0.16	0.65	0.40	0.34

[a] AD: Average Deviation.
[b] MD: Maximum Deviation.

mixture was measured with a high-pressure burette method [6]. The molar volumes obtained were represented by the Tait equation:

$$V = V_0 \left(1 - C \ln \frac{B+P}{B+P_0} \right) \tag{5}$$

where V and V_0 are the molar volumes at high pressure P and atmosphezric pressure P_0 in $cm^3 \cdot mol^{-1}$. V_0 and the coefficients B and C were found to be satisfactorily correlated with the mole fraction of 2-methyl-2-propanol x by the following equations:

$$V_0 = x V_{B,0} + (1-x) V_{M,0} + x(1-x) \sum_{i=1}^{4} a_i (1-2x)^{i-1} \tag{5a}$$

$$B = b_1 + b_2 x + b_3 x^2 \tag{5b}$$

$$C = c_1 + c_2 x \tag{5c}$$

The molar volume of pure methanol, $V_{M,0}$, and that of 2-methyl-2-propanol, $V_{B,0}$, and the parameters in Eqs. (5a) to (5c) are given in Table V. The maximum deviations of the experimental molar volumes from Eq. (5) are 0.05% at 303 K and 0.06% at 323 K within the experimental uncertainty of $\pm 0.09\%$.

To represent the composition dependence of the molar volume and viscosity, excess values Y_E are shown in Figs. 3 and 4, with Y_E defined by

$$Y_E = Y - \{ x Y_B + (1-x) Y_M \} \tag{6}$$

Table V. Molar Volumes at Atmospheric Pressure and the Coefficients in Eqs. (5a) to (5b)

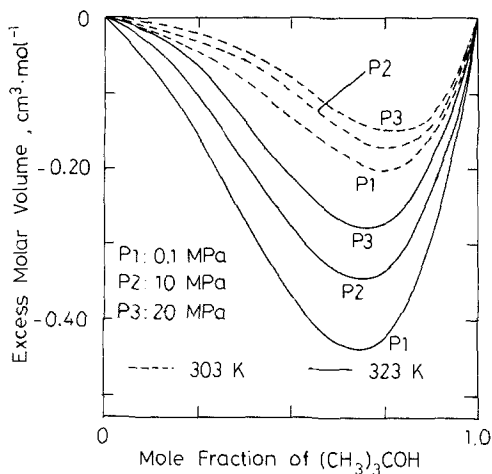|	T (K)	
	303.15	323.15
$V_{B,0}$ ($cm^3 \cdot mol^{-1}$)	95.556	98.252
$V_{M,0}$ ($cm^3 \cdot mol^{-1}$)	40.986	41.984
a_1	−0.51146	−1.46801
a_2	0.79741	1.42793
a_3	−0.57867	−0.30540
$10^2 a_4$	2.7909	3.3187
b_1	803.24	680.39
b_2	−55.420	98.441
b_3	−117.04	−235.41
$10^2 c_1$	9.8745	9.7683
$10^2 c_2$	−2.0032	−1.5015

Fig. 3. Excess molar volume of (methanol + 2-methyl-2-propanol) system at various pressures.
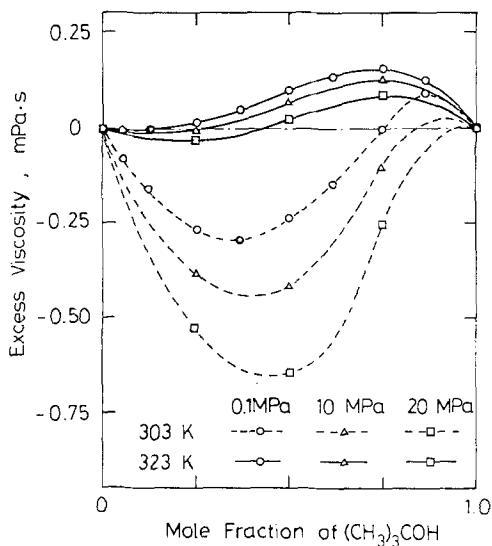

Fig. 4. Excess viscosity of (methanol + 2-methyl-2-propanol) system at various pressures.

Here Y, Y_M, and Y_B are the properties of the mixture, of pure methanol, and of pure 2-methyl-2-propanol, respectively. As shown in Fig. 3, the excess molar volume calculated with the Tait equation [Eq. (5)] is negative in the entire range of the measurements. With increasing temperature or decreasing pressure, the excess molar volume becomes more negative and the location of the minimum shifts slightly to the lower concentration of 2-methyl-2-propanol. Furthermore, it is found that each isobar has a inflexion point in a methanol rich region.

For the excess viscosity, shown in Fig. 4, it was found that the isobars at 303 K have distinct minima near $x = 0.4$, whereas those at 323 K show gentle maxima near $x = 0.7$. But the composition dependence of the present mixture is much less than those of aqueous alcohol solutions, which are much more highly associated due to the hydrogen bonds.

4. CONCLUSION

The viscosities of methanol, 2-methyl-2-propanol, and their mixtures were determined at 303 and 323 K and at pressures up to 30 MPa by a newly constructed capillary viscometer. The composition dependences of the excess viscosities and those of the excess molar volumes were determined. Simple empirical equations are given to represent the temperature and pressure effects on the viscosity within the experimental uncertainty.

ACKNOWLEDGMENTS

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