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Experimental Measurement and Modeling of the Viscosity of Dimethyl Ether

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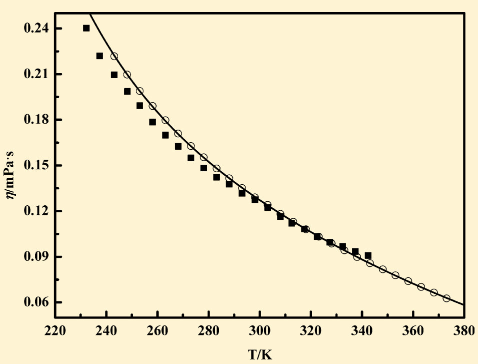
ABSTRACT: The viscosities of dimethyl ether in the temperature range of (243 to 373) K from saturated pressure up to 30 MPa are reported. These new experimental data were measured with a vibrating-wire viscometer. The combined expanded uncertainty of the results with a level of confidence of 0.95 (k = 2) is about ± 2.0 % over all ranges of temperature and pressure. The experimental data are used to develop correlations for the viscosity, including a saturated liquid equation and a multiparameter formulation covering liquid and vapor region. On the basis of the uncertainty of and comparisons with the experimental data, the estimated uncertainty of viscosity correlation is 2 % in the liquid phase and 3 % in the gas region.



■ INTRODUCTION

Dimethyl ether (DME, CAS number 115-10-6) is an important chemical raw material which is widely used for pharmaceutical, alternative fuel, pesticide, and chemical applications. In recent decades, dimethyl ether is accepted as a promising alternative fuel for its lager oxygen content and lower emissions of SO_x, NO_x, and particulates than conventional fuel when burning as well as its high-efficiency and nonpetroleum-based character.[1] In addition, dimethyl ether, named as RE170, has been considered as a potential green refrigerant with an ozone depletion potential equal to 0 and a global warming potential equal to 0.1 (over 100 years, CO_2 = 1). The thermophysical properties of dimethyl ether are essential in practically designing unit operations, and many researchers have measured its properties. In recent years, the authors' group has launched a systematic study on the thermophysical properties of dimethyl ether, including vapor pressure, critical properties, pvT properties, surface tension, viscosity, thermal conductivity, and so on.[2−11]

Nevertheless, only a limited number of data sets of the viscosity of dimethyl ether could be available. Wu et al.[2] measured the viscosity of dimethyl ether over the temperature range from (227 to 343) K along the saturation line with a calibrated capillary viscometer; Wang et al.[11] reported the viscosity of gaseous dimethyl ether in the range of temperature from (299 to 396) K at pressures up to 1.2 MPa, obtained with an oscillating disk viscometer. Tomida et al.[12] also presented the gaseous viscosity of dimethyl ether with an oscillating disk viscometer at temperatures from (298.15 to 423.15) K and at pressures up to 4.97 MPa. To the knowledge of the authors, for dimethyl ether, no viscosity measurements could be found in the literature for the compressed liquid region. Therefore, the present work provides measurements of viscosity of dimethyl ether with a vibrating-wire viscometer at temperatures from (243 to 373) K and from saturated pressure up to 30 MPa.

■ EXPERIMENTAL SECTION

Fluid Samples. The dimethyl ether was manufactured by Shandong Jiutai Chemical Co., Ltd., China, with a stated mass fraction purity of 99.9 %. The sample was purified several times before use by freeze−pump−thaw cycles using liquid nitrogen and a high vacuum pump (<0.01 Pa) to eliminate the effect of gaseous impurities.

Apparatus. The measurements were carried out with the steady state vibrating-wire viscometer described earlier.[13] This instrument employed a tungsten wire with a nominal radius of 50 μm and a nominal length of 62 mm, supplied by Goodfellow (Cambridge, UK) with a mass fraction purity greater than 99.95 %. The wire was clamped at one end between two stainless steel pieces with screws. The other end of the wire was attached to a mass for about 24 h, and then we tightened the lower clamp carefully and removed the mass. The two clamps were separated from each other by a machinable glass ceramic tube with an outer diameter of 10 mm and an inner diameter of 6 mm. The magnetic fields were generated by two rectangular samarium−cobalt magnets, with a length of about L_B = 38 mm so that the ratio L/L_B = 1.63 was sufficient to eliminate the third harmonic mode oscillation. The vibrating-wire was assembled in a pressure vessel, fabricated from stainless steel vessel with a maximum operating pressure of 70 MPa. The electrical connections through the pressure vessel to the wire were obtained from Conax Buffalo (model: MHC1). A sinusoidal voltage was achieved by a function generator (model: 33220A, Agilent). The in-phase and quadrature voltages of the signal were detected by the lock-in amplifier (model: SR830, Stanford Research Systems) over the frequency range. By fitting the experimental complex voltages

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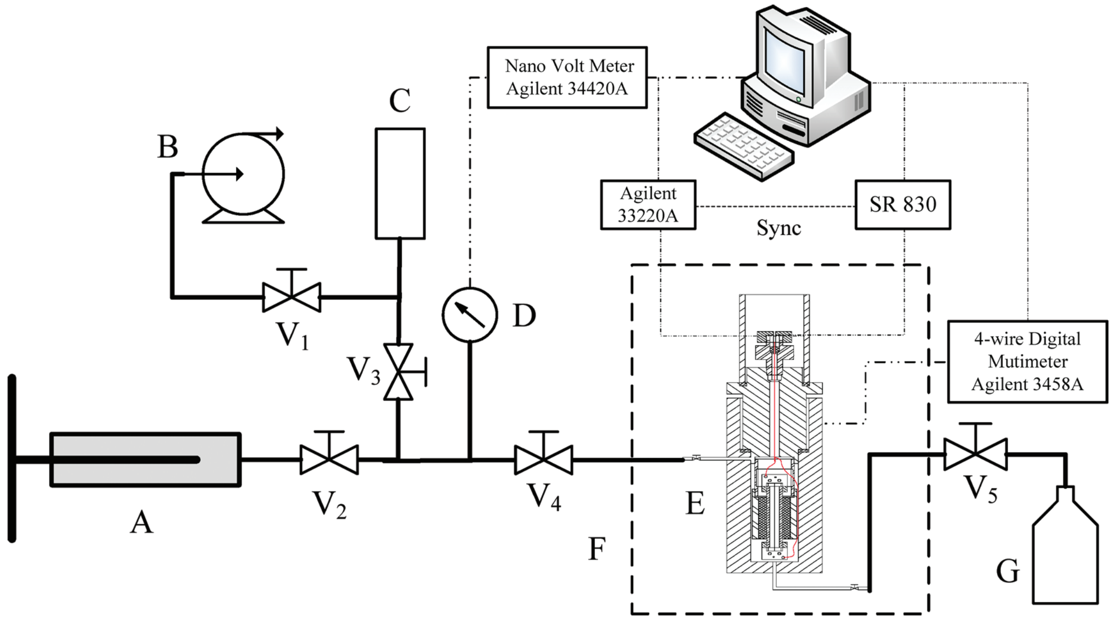

Figure 1. Schematic diagram of experimental system: (A) manual piston pump; (B) vacuum pump; (C) sample container; (D) pressure transducer; (E) vibrating wire viscometer; (F) thermostatic bath; (G) wasting recycle; (V_1–V_5) valves.

to working equations, the viscosity can be obtained if the density is known.

The internal damping and the radius of tungsten wire were determined by calibration. The vacuum measurement was used to obtained the internal damping, while the wire radius was experimentally determined in toluene at T_{ref} = 298.15 K and p_{ref} = 0.1 MPa. The detailed calibration procedures were described in our previous work.[13]

A thermostatic bath (model: 7037, Fluke) was used to maintain the constant temperature of the apparaturs. The temperature of the thermostatic bath was measured with a 100 Ω platinum resistance thermometer. The combined expanded uncertainty of temperature with level of confidence of 0.95 (k = 2) is $U_c(T)$ = 12 mK. Pressure was generated with a manual piston pump (model: 50-6-15, HIP) and measured by a high pressure transducer (model: P3MB, HBM) with the combined expanded uncertainty of $U_c(p)$ = 0.13 MPa (k = 2). A diagram of the experimental system is shown in Figure 1.

The same procedure of uncertainty analysis of the measurements was performed as our previous work.[13] By taking into account the uncertainties of temperature, pressure, repeatability of measurement, regression procedure, and the density of fluid, the combined expanded uncertainty of viscosity with level of confidence of 0.95 (k = 2) is better than ± 2.0 %.

■ RESULTS AND CORRELATION

The viscosity of liquid dimethyl ether both along the saturation line and in compressed region was measured. The experimental results in saturated liquid phase, listed in Table 1, cover a temperature range of (243 to 373) K. The viscosity of compressed liquid dimethyl ether was obtained along 13 isotherms over the temperature range from (253 to 373) K and at pressures from (5 to 30) MPa, shown in Table 2. The density values, required to obtain the viscosity from the working equations, were calculated from the equation of state of Wu et al.[14] The estimated uncertainty of density for dimethyl ether is 0.05 % in the saturated liquid phase and 0.1 % in the liquid region.

Table 1. Measurements of Viscosity for Saturated Liquid Dimethyl Ether[a]

T	ρ	η
K	$kg \cdot m^{-3}$	mPa·s
243.150	742.245	0.22169
248.155	735.407	0.20967
253.147	728.489	0.19885
258.143	721.485	0.18894
263.151	714.387	0.17961
268.138	707.189	0.17092
273.142	699.884	0.16275
278.134	692.463	0.15524
283.136	684.916	0.14792
288.142	677.233	0.14143
293.139	669.402	0.13506
298.140	661.409	0.12897
303.138	653.239	0.12399
308.141	644.874	0.11808
313.142	636.294	0.11291
318.120	627.475	0.10803
323.125	618.390	0.10314
328.124	609.006	0.09861
333.126	599.283	0.09419
338.127	589.175	0.08983
343.129	578.624	0.08575
348.126	567.558	0.08166
353.124	555.886	0.07777
358.130	543.489	0.07388
363.132	530.211	0.07014
368.135	515.834	0.06636
373.129	500.046	0.06256

[a]The combined expanded uncertainties U_c are $U_c(T)$ = 12 mK, $U_c(p)$ = 0.13 MPa, and $U_c(\eta)$ = 0.02η (level of confidence = 0.95).

Table 2. Measurements of Viscosity of Dimethyl Ether at Temperature T and Pressure p^a

T	p	ρ	η
K	MPa	kg·m^{-3}	mPa·s
253.146	5	734.28	0.20444
	10	739.73	0.21247
	15	744.86	0.21987
	20	749.69	0.23143
	25	754.29	0.24212
	30	758.66	0.25406
263.151	5	720.73	0.18364
	10	726.74	0.19112
	15	732.34	0.19887
	20	737.60	0.20679
	25	742.57	0.21556
	30	747.27	0.22516
273.141	5	706.84	0.16690
	10	713.48	0.17416
	15	719.62	0.18160
	20	725.35	0.18896
	25	730.72	0.19596
	30	735.79	0.20347
283.140	5	692.52	0.15205
	10	699.90	0.15903
	15	706.65	0.16575
	20	712.91	0.17238
	25	718.73	0.17908
	30	724.21	0.18575
293.141	5	677.72	0.13949
	10	685.96	0.14555
	15	693.14	0.15267
	20	700.26	0.15860
	25	706.59	0.16516
	30	712.50	0.17089
303.138	5	662.34	0.12762
	10	671.61	0.13402
	15	679.88	0.14015
	20	687.39	0.14635
	25	694.28	0.15209
	30	700.68	0.15842
313.138	5	646.26	0.11652
	10	656.77	0.12352
	15	666.00	0.12940
	20	674.27	0.13548
	25	681.79	0.14153
	30	688.72	0.14734
323.123	5	629.37	0.10696
	10	641.41	0.11385
	15	651.76	0.11986
	20	660.90	0.12623
	25	669.12	0.13157
	30	676.63	0.13703
333.123	5	611.38	0.09797
	10	625.38	0.10494
	15	637.07	0.11113
	20	647.21	0.11700
	25	656.23	0.12312
	30	664.39	0.12839
343.126	5	592.02	0.08951
	10	608.56	0.09664
	15	621.88	0.10364
	20	633.19	0.10961
	25	643.11	0.11514
	30	651.98	0.12043
353.121	5	570.83	0.08119
	10	590.80	0.08899
	15	606.14	0.09590
	20	618.82	0.10169
	25	629.75	0.10753
	30	639.42	0.11274
363.134	10	571.84	0.08181
	15	589.73	0.08877
	20	604.04	0.09499
	25	616.13	0.10097
	30	626.68	0.10655
373.132	5	518.81	0.06522
	10	551.43	0.07506
	15	572.59	0.08237
	20	588.84	0.08883
	25	602.25	0.09475
	30	613.78	0.09991

[a]The combined expanded uncertainties U_c are $U_c(T)$ = 12 mK, $U_c(p)$ = 0.13 MPa, and $U_c(\eta) = 0.02\eta$ (level of confidence = 0.95).

The obtained experimental data were used to correlate the equations of viscosity. To assess the performances of the correlations, the average absolute percentage deviation, AAD, the maximum absolute percentage deviation, MAD, and the average percentage deviation, Bias, are defined as follows

$$\mathrm{AAD} = \frac{1}{N_b}\sum_{i=1}^{i=N_b}\left|\frac{\eta_{i,\mathrm{exp}} - \eta_{i,\mathrm{cal}}}{\eta_{i,\mathrm{exp}}}\right| \tag{1}$$

$$\mathrm{MAD} = \max\left(\left|\frac{\eta_{i,\mathrm{exp}} - \eta_{i,\mathrm{cal}}}{\eta_{i,\mathrm{exp}}}\right|\right) \tag{2}$$

$$\mathrm{Bias} = \frac{1}{N_b}\sum_{i=1}^{i=N_b}\frac{\eta_{i,\mathrm{exp}} - \eta_{i,\mathrm{cal}}}{\eta_{i,\mathrm{exp}}} \tag{3}$$

The saturated liquid visocosity of dimethyl ether were correlated using the following equation,

$$\log_{10}(\eta) = A + \frac{B}{T} + CT + DT^2 \tag{4}$$

where η is the viscosity in mPa·s, T is the absolute temperature in K, and A, B, C, and D are the coefficients. Only the measurements of this work were used for correlation, and the AAD, MAD, and Bias of the experimental data from the correlation are listed in Table 3, together with the values of the coefficients.

On the basis of literature data and our own measurements, we developed a correlation of the viscosity of dimethyl ether based on the residual viscosity concept. The viscosity $\eta(T, \rho)$ was correlated in terms of density ρ and temperature T with the form[15]

$$\eta(T, \rho) = \eta^0(T) + \Delta\eta_r(T, \rho) + \Delta\eta_c(T, \rho) \tag{5}$$

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Table 3. Coefficients and Deviations of Equation 4 for Dimethyl Ether

parameter	value		
A	-6.4543	AAD/%	0.15
B	$6.7942\cdot10^{2}$	MAD/%	0.47
C	$1.8293\cdot10^{-2}$	Bias/%	0.075
D	$-2.4377\cdot10^{-5}$		

where the viscosity of a real pure fluid, $\eta(T, \rho)$, is considered as a sum of three contributions. $\eta^0(T)$ represents the dilute-gas viscosity, the term $\Delta\eta_r\ (T, \rho)$ is the residual contribution of the real fluid, and $\Delta\eta_c\ (T, \rho)$ represents the critical enhancement of the viscosity, which was set to zero in this work. The density of dimethyl ether was calculated from the fundamental equation of state.[14]

For the dilute-gas viscosity, $\eta^0(T)$, an engineering form was adopted

$$\eta^0(T) = \frac{0.021375\sqrt{MT}}{\sigma^2\vartheta^*_\eta(T^*)} \quad (6)$$

in which M is the molecular mass in g·mol^{-1}, T is the absolute temperature in K, σ is the length scaling parameter in nm, $\vartheta^*\eta$ is the reduced effective collision cross section, and η^0 is in units of μPa·s. The effective collision cross section is usually expressed in the functional form

$$\ln \vartheta^*_\eta = \sum_{i=0}^{n} a_i(\ln T^*)^i \quad (7)$$

where $T^* = kT/\varepsilon$ is the reduced temperature, and ε/k is the energy scaling parameter in K. ε/k, σ, and the coefficients, a_i, are listed in Table 4.

Table 4. Coefficients for the Representation of the Viscosity of Dimethyl Ether

Molar Mass			
$M = 46.06844$ g·mol^{-1}			
Critical Constants[14]			
$T_c = 400.378$ K		$\rho_c = 5.94$ mol·L^{-1}	
Scaling Factors			
$\varepsilon_0/k = 317.937$ K		$\sigma = 0.446704$ nm	
Coefficients a_i of eq 7			
$a_0 = 0.294261$		$a_1 = -0.377826$	
$a_2 = -0.491673$			
Coefficients n_i, t_i, d_i and p_i of eq 8			
$n_0 = -2.70002$	$t_0 = -5.92$	$d_0 = 3$	
$n_1 = 4.44583$	$t_1 = -4.36$	$d_1 = 3$	
$n_2 = -104.998$	$t_2 = -2.93$	$d_2 = 3$	$p_2 = 1$
$n_3 = 78.27474$	$t_3 = -1.64$	$d_3 = 4$	$p_3 = 1$
$n_4 = 41.3751$	$t_4 = -7.86$	$d_4 = 5$	$p_4 = 2$
$n_5 = -175.055$	$n_5 = -4.25$	$d_5 = 2$	$p_5 = 1$
$n_6 = 62.81975$	$t_6 = -4.79$	$d_6 = 2$	$p_6 = 1$
$n_7 = 0.21302$	$t_7 = -5.87$	$d_7 = 5$	$p_7 = 0$
$n_8 = 112.3219$	$t_8 = -3.11$	$d_8 = 2$	$p_8 = 2$
$n_9 = 6.50681$	$t_9 = -0.45$	$d_9 = 1$	$p_9 = 0$

The residual viscosity $\Delta\eta_r\ (T, \rho)$ in μPa·s is given by

$$\Delta\eta_r(T, \rho) = \sum_{i=0}^{1} n_i\tau^{t_i}\delta^{d_i} + \sum_{i=2}^{6} n_i\tau^{t_i}\delta^{d_i}e^{-\delta^{p_i}} \quad (8)$$

where the dimensionless parameters are defined as $\tau = T/T_c$ and $\delta = \rho/\rho_c$. The coefficients and exponents were regressed from experimental data, as given in Table 4. The distribution on the $p-T$ plane of the available experimental data of viscosity for dimethyl ether was shown in Figure 2. The results of Wang et al.,[11] Tomida et al.,[12] and this work were considered in the regression of the correlation.

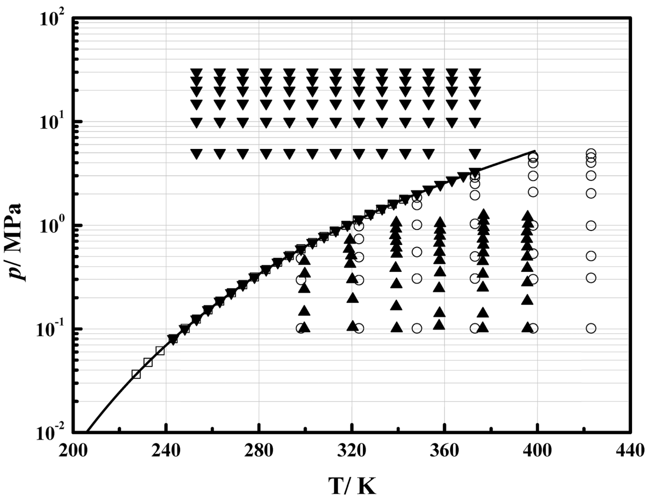

Figure 2. Distribution of the viscosity experimental data for dimethyl ether in the pressure−temperature plane. The solid line represents the saturation line. □, Wu et al.; ○, Tomida et al.; ▲, Wang et al.; ▼, this work.

■ DISCUSSION

Figure 3 shows the saturated liquid viscosity of dimethyl ether as a function of temperature. The relative deviations of experimental results from the values calculated from eq 4 are shown in Figure 4. The deviation of this work from the correlation does not exceed 0.47 %, and the average absolute deviation is 0.15 %. The measurements from ref 2 seem to exhibit a systematical deviation with temperature increasing, which reaches to 5.03 % at 342.45 K from −6.04 % at 243.15 K.

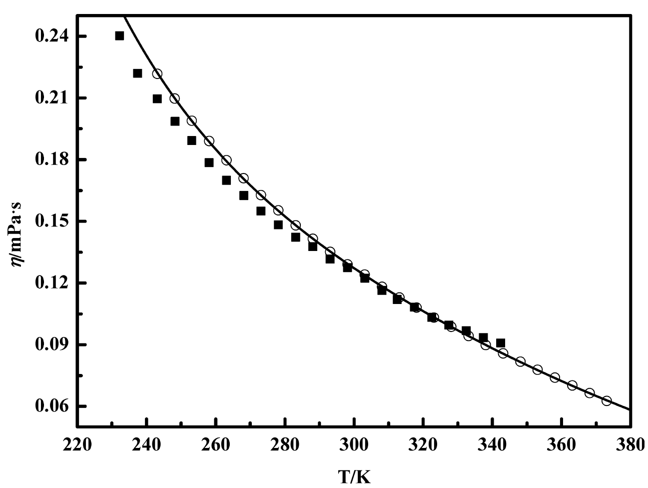

Figure 3. Saturated liquid viscosity of dimethyl ether as a function of temperature. ○, this work; ■, Wu et al.; —, correlation.

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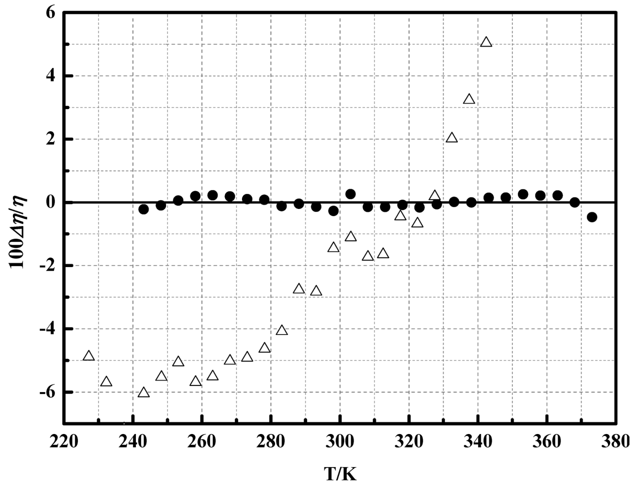

Figure 4. Fractional deviations $\Delta\eta/\eta = (\eta_{exptl} - \eta_{calcd})/\eta_{exptl}$ of the saturated viscosities η_{exptl} of dimethyl ether from values η_{calcd} obtained from eq 4 as a function of temperature. ●, this work; △, Wu et al.

The new viscosity equation for dimethyl ether covering the gas and liquid phase has been validated in detail with respect to all available experimental data. The deviations between eq 5 and the experimental data are shown in the Figure 5 as a function of temperature. Our measurements show a good agreement with the correlation, and the AAD is 0.5 %. The results of Tomida et al.[12] are represented well with an AAD of 1.33 % and a MAD of 2.83 %. There is satisfactory agreement between eq 5 and the results of Wang et al.[11] The measurements along saturation line from ref 2 show greater deviations especially at low temperatures, and the MAD is −7.47 % at 237.47 K. In addition, the plot of viscosity versus temperature at different pressures has been presented in Figure 6. As shown in Figure 6, the plot is very flat, and no abnormal behavior was found, which verified the reasonability of the developed equation.

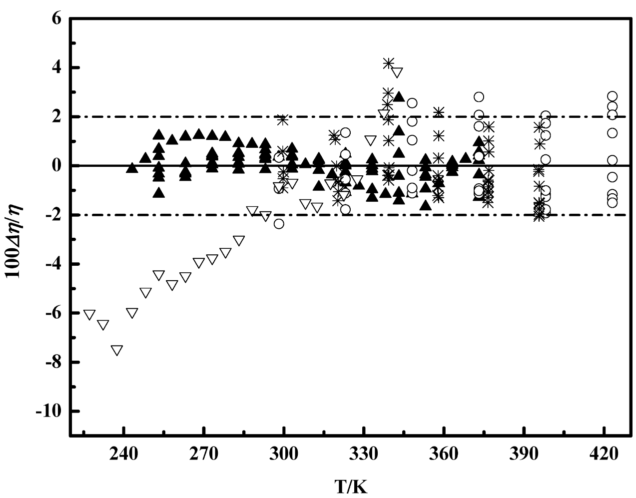

Figure 5. Fractional deviations $\Delta\eta/\eta = (\eta_{exptl} - \eta_{calcd})/\eta_{exptl}$ of the viscosities η_{exptl} for dimethyl ether from values η_{calcd} obtained from eqs 5 to 8 as a function of temperature. ▲, this work; ○, Tomida et al.; *, Wang et al.; ▽, Wu et al.

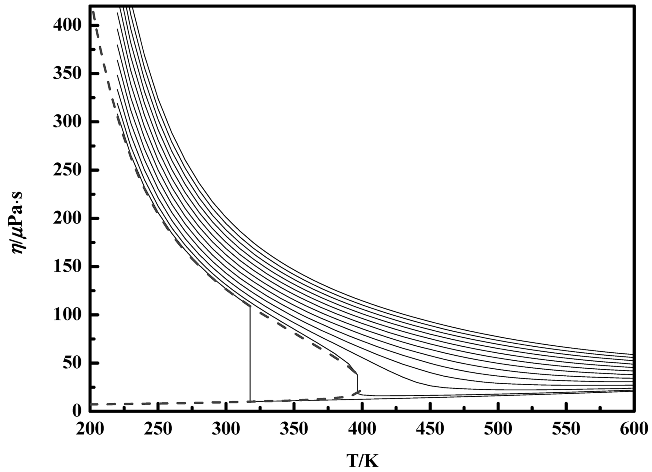

Figure 6. Viscosity versus temperature. Isobars are shown at pressures of (1, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, and 60) MPa. The dashed line represents the saturation line.

CONCLUSIONS

In this work, we measured the viscosity of dimethyl ether in the temperature range of (243 to 373) K and from saturated pressure up to 30 MPa with a vibrating-wire viscometer. The combined expanded uncertainty of the results with level of confidence 0.95 ($k = 2$) is about ± 2.0 %. New correlations of viscosity for dimethyl ether were developed. The saturated liquid viscosity results were correlated as a function of temperature. The multiparameter equation was developed successfully with an estimated uncertainty of 2 % in the liquid phase and 3 % in the gas phase.

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Notes

The authors declare no competing financial interest.

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