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Viscosity of Saturated Liquid Dimethyl Ether from (227 to 343) K

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Measurements of the viscosity of saturated liquid dimethyl ether are reported over the temperature range from (227 to 343) K along the saturation line made with a calibrated capillary viscometer. The results were correlated as a function of temperature. The standard deviation and the maximum deviation of the experimental results from the correlation equation are 0.5% and 1.3%, respectively.

1. Introduction

As a chemical raw material, dimethyl ether plays an important role in the synthesis of chemicals. At the same time, it is often used as a propellant gas, assist solvent, vesicant, fuel additive, of liquefied petroleum gas substitute. Also, it can be used as a refrigerant and vesicant. Especially, in recent research of clean alternative fuels, it has been discovered that dimethyl ether and its mixtures are possible alternatives for diesel oil in the future.[1] Hence, the thermophysical property data of dimethyl ether are important. In the design of the feed and ejection systems of combustion processes, the viscosity data are indispensable, but there are few data on the viscosity of dimethyl ether. In this work, the viscosity of dimethyl ether was measured with a sealed gravitational capillary viscometer at temperatures between (227 and 343) K along the saturation line.

2. Experimental Method

According to the Hagen−Poiseuille principle, if a fluid flows through a capillary under a gravity head, then, often accounting for the kinetic-energy correction and the end correction, the viscosity of the fluid can be expressed by

$$\eta = \frac{\pi g h(\rho_L - \rho_V)R^4}{8V(L + nR)}t - \frac{m\rho_L V}{8\pi(L + nR)t} \tag{1}$$

where η is the fluid dynamic viscosity, V is the volume of flow through the capillary for a given time t, m is the kinetic energy factor, L is the capillary length, R is the capillary radius, ρ_L is the saturated liquid density of the sample, ρ_V is the saturated vapor density, h is the height of fluid in the capillary, g is the acceleration of gravity, and n is the end-correction factor. Equation 1 could be rewritten as

$$\nu = \frac{\eta}{\rho_L} = kAt - B/t \tag{2}$$

where

$$k = \frac{\rho_L - \rho_V}{\rho_L} \tag{3}$$

$$A = \frac{\pi g h R^4}{8V(L + nR)} \tag{4}$$

$$B = \frac{mV}{8\pi(L + nR)} \tag{5}$$

where ν is the kinematic viscosity. A and B are temperature independent and constant, while k generally decreases as the temperature increases. When the relative measurement method is applied, L, V, R, h, and g are constants for the specific viscometer at a site, and then A and B are constants, which are also called instrument constants. In this work, L and R equal 120 ± 0.1 mm and 0.165 ± 0.01 mm, respectively, and the uniformity of the capillary is better than 0.05 mm; h equals L is assumed in our experiment. The k value can be regarded as 1.0, if the temperature is far less than the critical temperature. But when the temperature is close to the critical temperature, the k value has to be taken into account. In this work, the temperature range is limited and far less than the critical temperature. Therefore, if the time of liquid flowing through the capillary is measured, and the values of A and B are known, the kinematic viscosity could be obtained.

From eq 2, the following equation can be derived:

$$\epsilon_E = \frac{B/t}{kAt} = \frac{mV^2}{\pi^2 kghR^4}\frac{1}{t^2} = \frac{\xi}{t^2} \tag{6}$$

where

$$\xi = \frac{mV^2}{\pi^2 kghR^4} \tag{7}$$

ξ is a constant for a specific viscometer; ϵ_E is in inverse proportion to the square of t. It is proved that the value of ϵ_E for the viscometer used in this research is less than 0.5%, if $t > 900$ s. Thus, if the term B/t is ignored, the maximum deviation will be less than 0.5%, when the time of liquid flow through the capillary is more than 900 s. And then

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eq 2 can be written as

$$v = At \tag{8}$$

On the basis of the above discussion, pure water and ethanol were selected as reference liquids to calibrate the constant A. In this instrument, the flow time of water and ethanol is longer than 900 s at ambient temperature. In this work, with eq 8 and the experimental data, A is fitted by using the least-squares method.

The kinetic-energy factor and end-correction factor are related to the Reynolds number and shape of the end of the capillary,[2,3] and there are some different ways to obtain B.

From the ref 2, in the range of Reynolds numbers $46 \le Re \le 1466$, the values of m are 1.08 to 1.16, while the end-correction factor n is 0.57, and B can be calculated from

$$B = \frac{mghR^4}{64A(L + nR)^2} \tag{9}$$

because A, L, R, g, h, m, and n are constants for the specific viscometer at a site and then B is a constant.

From ref 3, in the range of Reynolds number $80 \le Re \le 500$, the kinetic-energy factor m can be calculated from the empirical correlation

$$m = 0.037Re^{0.5} \tag{10}$$

For this instrument, the Reynolds number Re can be approximated by

$$Re = \frac{2V}{\pi RkAt^2} \tag{11}$$

and then B can be calculated as follows:

$$B = 0.00117\frac{V^{1.5}}{(kA)^{0.5}R^{0.5}(L + nR)} \tag{12}$$

The value of V is calculated from eq 4.

In this paper, both methods were applied. The results indicated that the B calculated from eq 9 is more workable than that from eq 12 for this instrument, if the buoyancy of the vapor is neglected and the k value is regarded as 1.0. Hence, eq 9 was used to obtain the kinematic viscosity of dimethyl ether in this work.

3. Experiment Apparatus and Procedures

The apparatus is shown in Figure 1.

Three valves, which are shown in Figure 1, are necessary for the experiment. Before the experiment, the liquid sample is injected into the pressure vessel through valve A. During the experiment, valve A is always closed, and the sample remains at its vapor pressure. Prior to each measurement, the liquid must be forced through the bypass tube to the upper bulbs. When raising the liquid, valve B is closed; at the same time valve C is open and connects to the atmosphere. When the saturation pressure in the vessel is higher than atmospheric pressure, the liquid will be raised naturally. When the saturation pressure in the vessel is less than atmospheric pressure, the vacuum pump must be used to draw the liquid into the upper volume. During each measurement, valve C is closed and valve B is opened, so the vapor inside and outside the capillary are connected. Due to its weight, the liquid will flow down. The details of the instrument could be found in ref 4.

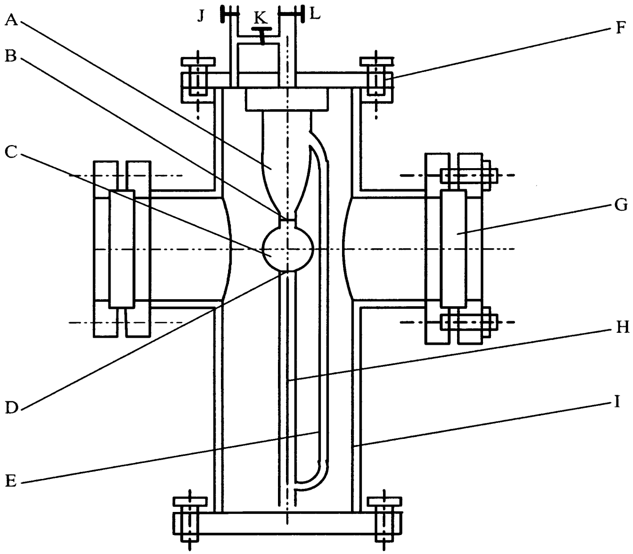

Figure 1. Viscometer schematic: (A) additional volume; (B) upper mark; (C) flow volume; (D) lower mark; (E) bypass tube; (F) flange plate; (G) observation window; (H) capillary; (I) pressure vessel; (J) valve A; (K) valve B; (L) valve C.

Table 1. Flow Times and Viscosities of Ethanol and Water

liquid	T/K	t/s	ρ/kg·m^{-3}	v/mm^2·s^{-1}	η/μPa·s	refs
water	315.052	1276.28	991.444	0.6358	630.314	
	325.109	1099.31	987.111	0.5363	529.348	6
	335.207	924.72	982.105	0.4605	452.257	
ethanol	309.946	2346.35	774.775	1.1230	870.065	
	319.786	1921.90	766.068	0.9586	734.355	7, 8
	330.124	1622.93	756.700	0.8210	621.245	

The viscometer was placed in a thermostat bath, for which temperature can be varied from (220 to 500) K, and the stability of the temperature in the bath is better than ±4 mK·h^{-1}. The total uncertainty of temperature is less than ±5 mK (ITS-90). The details about the thermostat bath and temperature measurement have been described in ref 5. A stopwatch was used to measure the flow time, and the accuracy is 0.01 s.

4. Calibration

Ethanol and water were used to calibrate the instrument; the mass purity of ethanol is 99.7%, and the electrical resistance of water is no less than 40 MΩ. The specifications were provided by the producer, and no further purifications were carried out. Their kinematic viscosity and density data were cited from refs 6−8. The calibration results are listed in Table 1. The flow times given in Table 1 are the average times, and three to five flow times were measured at each temperature. The repeatability of flow time is better than 1.0% (= (measured time − average time)/average time) and usually is about 0.5%.

With the method discussed above, A was determined ($A = 4.937 \times 10^{-10}$ mm^2·s^{-2}), and B depended on the fitted method. If eq 9 was used, $B = 2.142 \times 10^{-6}$ mm^2·s, and if eq 12 was applied, the B value depends on the shape of the capillary.

To test the reliability and proper operation of the instrument, the viscosity of HFC152a was measured. The sample was from Hangzhou First Chemical Co. Ltd., and its mass purity was 99.95% and was analyzed with gas chromatography before the measurement.

The viscosities of HFC152a are listed in Table 2. The dynamic viscosity and density data were cited from refs 8

Table 2. Experimental Viscosities for Saturated Liquid HFC152a

					$k = 1.0$				$k = (\rho_L - \rho_g)/\rho_L$			
					B eq 9		*B* eq 12		*B* eq 9		*B* eq 12	
T/K	t/s	ρ_L/kg·m^{-3}	ρ_g/kg·m^{-3}	v_{ref}/mm^2·s^{-1}	v_{exp}/mm^2·s^{-1}	Δ^a/%	v_{exp}/mm^2·s^{-1}	Δ/%	v_{exp}/mm^2·s^{-1}	Δ/%	v_{exp}/mm^2·s^{-1}	Δ/%
244.397	632.18	1020.63	2.76	0.3168	0.3087	2.55	0.3109	1.85	0.3079	2.81	0.3101	2.12
253.460	571.75	1001.96	4.03	0.2799	0.2788	0.50	0.2808	−0.32	0.2774	0.91	0.2797	0.08
263.913	497.10	979.64	6.02	0.2465	0.2414	2.20	0.2435	1.23	0.2396	2.81	0.2420	1.84
271.620	464.24	962.58	7.93	0.2269	0.2249	1.03	0.2270	−0.03	0.2227	1.87	0.2251	0.80
281.749	425.72	939.27	11.14	0.2062	0.2055	0.50	0.2076	−0.68	0.2027	1.71	0.2051	0.53
293.103	391.58	911.77	15.89	0.1878	0.1883	−0.02	0.1902	−1.29	0.1845	1.78	0.1869	0.51
303.082	362.46	886.21	21.32	0.1745	0.1735	0.83	0.1753	−0.49	0.1687	3.30	0.1710	1.98
315.345	343.25	852.59	30.03	0.1601	0.1637	−1.98	0.1654	−3.37	0.1573	1.75	0.1595	0.36
315.347	342.47	852.58	30.03	0.1601	0.1633	−1.73	0.1650	−3.12	0.1569	1.99	0.1591	0.60
325.328	321.53	822.00	39.26	0.1489	0.1526	−2.10	0.1542	−3.50	0.1445	2.98	0.1466	1.59
325.132	319.41	823.60	39.06	0.1492	0.1515	−1.22	0.1531	−2.61	0.1435	3.79	0.1456	2.41

[a] $\Delta = 100(v_{exp} - v_{ref})/v_{ref}$.

Table 3. Experimental Viscosities for Saturated Liquid Dimethyl Ether

T/K	t/s	ρ/kg·m^{-3}	v/mm^2·s^{-1}	η/μPa·s
227.218	697.97	757.655	0.3418	258.928
232.277	653.91	751.053	0.3198	240.191
237.471	610.59	744.185	0.2982	221.920
243.152	583.05	736.565	0.2845	209.520
248.297	558.50	729.561	0.2722	198.576
253.138	537.55	722.876	0.2617	189.180
258.153	512.65	715.848	0.2492	178.413
263.141	493.59	708.749	0.2397	169.869
268.154	477.41	701.498	0.2316	162.432
273.157	460.82	694.138	0.2232	154.939
278.156	446.20	686.654	0.2159	148.215
283.151	433.68	679.035	0.2095	142.287
288.152	424.89	671.258	0.2051	137.681
293.145	411.36	663.333	0.1983	131.523
298.157	403.91	655.205	0.1945	127.443
303.162	393.08	646.900	0.1890	122.282
308.148	379.40	638.426	0.1821	116.252
312.534	370.02	630.790	0.1773	111.857
317.518	363.50	621.888	0.1740	108.217
322.498	352.54	612.733	0.1684	103.205
327.501	345.44	603.246	0.1648	99.423
332.493	341.74	593.455	0.1629	96.688
337.467	336.30	583.340	0.1601	93.419
342.448	332.98	572.801	0.1584	90.759

and 9. To check the feasibility of the assumption $k = 1.0$, both results ($k = 1.0$ and $(\rho_L - \rho_g)/\rho_L$) were given. It can be found that if *B* is obtained with eq 9, the results of $k = 1.0$ are better than those of $k = (\rho_L - \rho_g)/\rho_L$, and the maximum deviation and the average deviation are 2.55% and 1.33%, respectively. If *B* is obtained with eq 12, the results of $k = (\rho_L - \rho_g)/\rho_L$ are better than those of $k = 1.0$, and the maximum deviation and the average deviation are 2.41% and 1.16%, respectively.

On the basis of the above discussion and the similarity of HFC152a and dimethyl ether, the assumption $k = 1.0$ and eq 9 are used in the viscosity measurements of dimethyl ether. Another reason is that information on the vapor density of dimethyl ether is currently lacking.

5. Results and Analysis

The sample of dimethyl ether was provided by Zhongshan Fine Chemical Co. Ltd. Its mass purity was better than 99.95%, and no further purification was needed.

The viscosity of liquid dimethyl ether was measured along the saturation line from (227 to 343) K. The experimental data are listed in Table 3. The saturated liquid densities of dimethyl ether are cited from ref 10. At each temperature, the flow time is measured three to five times, and the repeatability of the flow time is better than 1.0%.

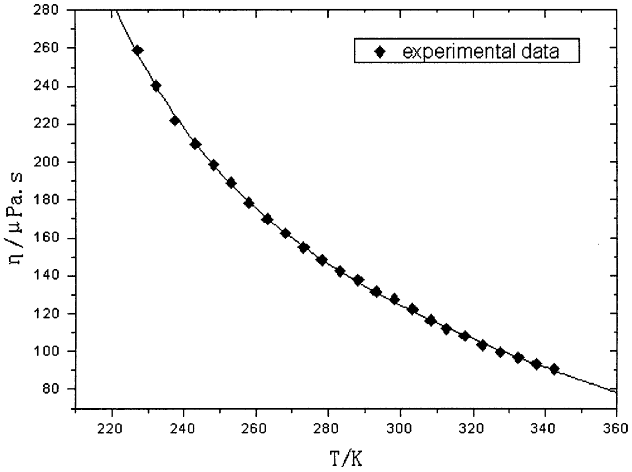

Figure 2. Saturated liquid viscosity of dimethyl ether as a function of temperature: —, calculation; ◆, experimental data.

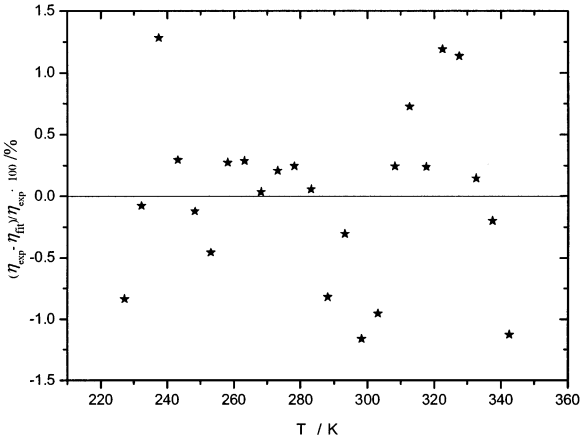

Figure 3. Deviations of experimental data from eq 14.

The experimental results listed in Table 3 were correlated as a function of temperature using the following equation:

$$\log_{10}(\eta/\text{mPa·s}) = -5.7282 + 631.031/(T/\text{K}) + (1.4530 \times 10^{-2})(T/\text{K}) - (1.8225 \times 10^{-5})(T/\text{K})^2 \quad (13)$$

where the viscosity is in mPa·s and temperature is in K. The standard deviation and the maximum deviation of the experimental results from eq 13 are 0.5% and 1.3%, respectively. Figure 2 shows the viscosity of dimethyl ether as a function of temperature, and Figure 3 shows the deviations of the experimental data from eq 13.

6. Conclusion

In this work, the viscosity of dimethyl ether was measured with a capillary viscometer at temperatures between (227 and 343) K along the saturation line. The repeatability of the flow time is better than 1.0% at a certain temperature, and the total relative uncertainty of the kinematic viscosity is better than 3.0%. The results were correlated as a function of temperature. The standard deviation and the maximum deviation of the experimental results from the equation are 0.5% and 1.3%.

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