1394 *J. Chem. Eng. Data* **2006,** *51,* 1394−1397

Surface Tension of Dimethoxymethane and Methyl *tert*-Butyl Ether

Xiaopo Wang, Jiang Pan, Jiangtao Wu,* and Zhigang Liu

State Key Laboratory of Multiphase Flow and Power Engineering, Xi’an Jiaotong University, Xi’an, Shaanxi 710049, People’s Republic of China

The surface tension of dimethoxymethane was measured at temperatures from (238 to 388) K with a differential capillary rise method (DCRM), together with the surface tension of methyl *tert*-butyl ether measured at temperatures from (243 to 393) K. The uncertainty of temperature is less than ± 10 mK (ITS-90). The uncertainty of surface tension measurements was estimated to be within ± 0.2 mN·m^{-1}. The results were correlated as a function of temperature, and the average absolute deviations were 0.059 mN·m^{-1} for dimethoxymethane and 0.050 mN·m^{-1} for methyl *tert*-butyl ether, respectively.

Introduction

In recent research, it was found that using dimethoxymethane ($CH_3-O-CH_2-O-CH_3$) as a fuel additive can provide great improvement in diesel oil and petrol combustion properties. It is regarded as a good fuel additive and a potential alternative fuel in the future. High-purity dimethoxymethane is also used in cosmetics and pharmaceuticals. For those applications, the thermophysical property data of dimethoxymethane are important. In our previous work, the thermal conductivity, density, viscosity, and vapor pressure of dimethoxymethane were measured.[1−3] In this work, the surface tension of dimethoxymethane was measured at temperatures from (238 to 388) K along the saturation line.

Recently, branched alkyl ethers have been used as fuel additives. Methyl *tert*-butyl ether was one of those substances. It was widely used as a gasoline additive to improve the octane rating and reduce exhaust pollution. However, because of the high water solubility and the health risk caused by the contamination of drinking water, methyl *tert*-butyl ether has become a very controversial gasoline additive. To find an environmentally friendly replacement of methyl *tert*-butyl ether, its thermophysical properties should be known. This paper also presents the surface tension data of methyl *tert*-butyl ether for temperatures ranging from (243 to 393) K along the saturation line.

Experimental Section

Materials. The sample of dimethoxymethane was provided by Shanghai Yongfu Aerosol Manufacturing Co. Ltd. The sample was further purified with sodium wire, followed fractional distillation from sodium.[4] Finally, the mass fraction purity of dimethoxymethane was better than 99.93 %, as indicated by analysis with the Agilent 6890N gas chromatograph. A thermal conductivity detector (TCD) and a capillary column (DB-WAX, model: Agilent 125-7032) were used for the analysis using hydrogen as the carrier gas at 20.0 mL/min. The oven temperature and the detector temperature were (473 and 523) K, respectively.

The sample of methyl *tert*-butyl ether was used as made by Nanjing Fubang Chemical Co. Ltd. The final purity was checked by gas chromatograph (Agilent 6890N), the mass fraction purity of methyl *tert*-butyl ether was better than 99.70 %.

Apparatus and Procedure. The differential capillary rise method was used for the surface tension measurement. The experimental apparatus and procedure have been described in detail in previous work[5,6] and are only briefly described here.

During the experiment, the capillary rise difference Δh_0 is measured, and the surface tension can be calculated using the following expression as

$$\sigma = \frac{(\rho_L - \rho_g)g}{2(1/r_1 - 1/r_2)}(\Delta h_0 + r_1/3 - r_2/3) \qquad (1)$$

where σ is the surface tension; g is the local gravitational acceleration (this work, $g = 9.7965$ m·s^{-2}); ρ_L and ρ_g are the densities of saturated liquid and vapor, respectively. Δh_0 is height difference of the meniscus bottom of the two capillaries. r_1 and r_2 are the radii of two different capillaries used in the experiment, respectively.

In general, the capillary constant a^2 is defined in order to learn the accuracy of the apparatus itself:

$$a^2 = \frac{\Delta h_0 + r_1/3 - r_2/3}{1/r_1 - 1/r_2} \qquad (2)$$

The inner radii of two capillaries used in this work are $r_1 = (0.2270 \pm 0.0004)$ mm, $r_2 = (0.3292 \pm 0.0003)$ mm.

The capillaries were placed in a small pressure cell with observation windows, and the pressure cell was placed in a thermostat bath with the maximum temperature stability of the thermostat bath within ± 10 mK in 2 h. Alcohol and silicon oil were chosen as the working medium depending on the temperature range.[5,7] The temperature measurement system consisted of an ASL F18 thermometry bridge and two 25 Ω standard platinum resistance thermometers (Beijing Const Technology Co. Ltd.) and a 100 Ω reference resistor. One thermometer (no. 68033) can be used from (83.8058 to 273.16) K, and another (no. 68115) can be used from (273.15 to 933.473) K. The thermometers were calibrated on ITS-90 at the National Institute of Metrology of China. The total standard uncertainty of temperature was better than ± 1.0 mK. The total uncertainty of temperature for surface tension was less than ± 10 mK on ITS-90. The capillary rise difference was measured with a

---

* Corresponding author. E-mail: jtwu@mail.xjtu.edu.cn. Fax: +86-29-82668789.

10.1021/je060097q CCC: $33.50

Table 1. Experimental Data of Dimethoxymethane

T/K	ρ_l/kg·m^{-3}	ρ_g/kg·m^{-3}	Δh_0/mm	a^2/mm^2	σ/mN·m^{-1}
238.067	931.023	0.080	8.47	6.1657	28.116
243.119	924.356	0.112	8.32	6.0561	27.417
248.130	917.810	0.153	8.18	5.9538	26.762
253.118	911.272	0.205	8.07	5.8734	26.211
258.115	904.697	0.271	7.95	5.7856	25.631
263.083	898.133	0.353	7.76	5.6468	24.832
268.087	891.492	0.454	7.63	5.5518	24.231
273.086	884.822	0.578	7.50	5.4567	23.635
278.080	878.124	0.727	7.39	5.3763	23.106
283.073	871.386	0.905	7.22	5.2521	22.394
288.079	864.587	1.117	7.07	5.1425	21.750
293.051	857.787	1.364	6.89	5.0109	21.021
298.040	850.913	1.654	6.73	4.8940	20.358
303.163	843.797	1.999	6.57	4.7770	19.697
308.150	836.811	2.388	6.39	4.6455	18.987
313.162	829.725	2.836	6.25	4.5431	18.401
318.164	822.584	3.347	6.06	4.4043	17.674
323.155	815.385	3.925	5.94	4.3166	17.157
328.134	808.124	4.577	5.79	4.2069	16.558
333.159	800.710	5.318	5.61	4.0754	15.878
338.159	793.240	6.147	5.47	3.9730	15.318
343.150	785.686	7.074	5.29	3.8415	14.651
348.137	778.031	8.108	5.12	3.7172	14.019
353.151	770.221	9.267	4.93	3.5784	13.338
358.152	762.308	10.555	4.80	3.4834	12.827
363.151	754.264	11.987	4.65	3.3737	12.266
368.155	746.070	13.579	4.45	3.2275	11.580
373.146	737.742	15.344	4.29	3.1106	11.007
378.148	729.227	17.311	4.10	2.9717	10.363
383.134	720.558	19.494	3.93	2.8475	9.778
388.145	711.644	21.941	3.75	2.7159	9.175

cathetometer with an uncertainty ± 0.02 mm. In this work, the maximum uncertainty of surface tension was estimated to be within ± 0.2 mN·m^{-1}.

Results and Discussion

Dimethoxymethane. The surface tension of liquid dimethoxymethane was measured along the saturation line from (238 to 388) K. The experimental data are listed in Table 1. The saturated liquid densities of dimethoxymethane were from ref 2. The gas densities were calculated from the Peng−Robinson equation, where the critical temperature (T_c), the critical pressure (P_c), and the Pitzer acentric factor (ω) were 480.60 K, 3736.4 kPa, and 0.267, respectively.[3] At each temperature, the capillary rise difference was measured at least three times.

The capillary constant a^2 was fitted to the functional form:[8]

$$a^2 = a_0^{\;2}\tau^{0.935}(1 + a_1\tau) \tag{3}$$

where τ is the reduced temperature $(T_c - T)/T_c$, and the critical temperature $T_c = 480.60$ K was used in this work; a_0^2 and a_1 are the fitted parameters. The exponent 0.935 was taken from the theoretical analysis and is believed to be asymptotically correct near T_c. On the basis of the present results, the values of a_0^2 and a_1 were fitted to the data to give 13.2856 mm^2 and −0.2347, respectively. The measured values of capillary constant a^2 and the fitted curves are shown in Figure 1, and the deviations are shown in Figure 2. As can be seen in Figures 1 and 2, eq 3 fits the data within the precision of the measurements, and the maximum deviation is 0.75 %.

The surface tension is normally correlated as a function of temperature by a van der Waals type correlation:

$$\sigma = \sigma_0\left(1 - \frac{T}{T_c}\right)^n \tag{4}$$

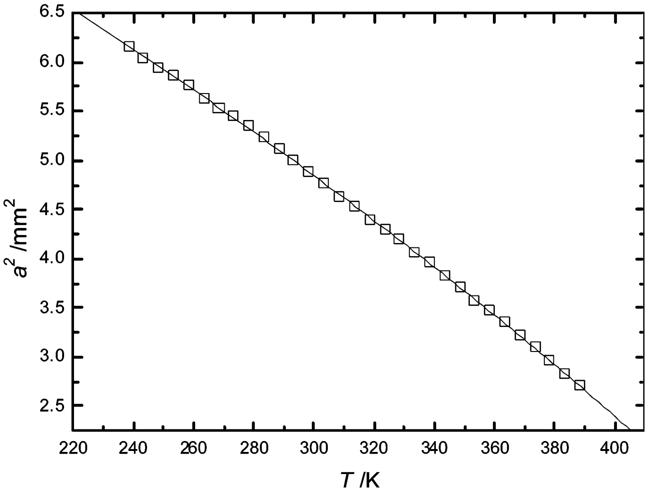

Figure 1. Relation between temperature and capillary constant for dimethoxymethane.

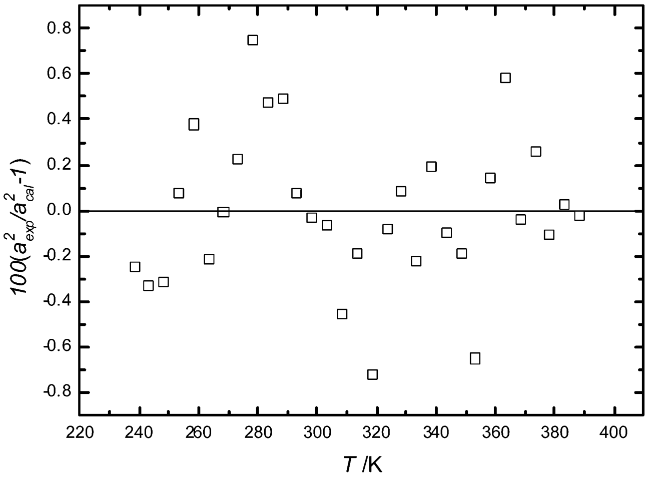

Figure 2. Deviation of capillary constant for dimethoxymethane from the fit to eq 3.

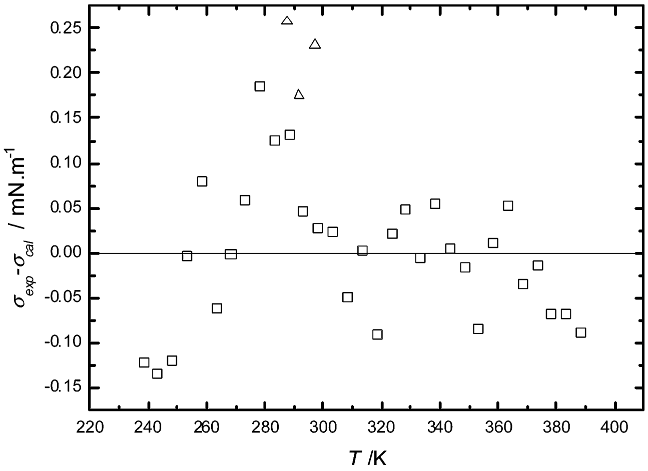

Figure 3. Comparison of the surface tension results and literature data for dimethoxymethane from eq 4: □, this work; △, Vogel.[9]

where σ_0 and n are the fitted parameters. With the measurements of this work, σ_0 and n are determined, and the values are 62.211 mN·m^{-1} and 1.155, respectively. The average absolute and maximum deviations of eq 4 are 0.059 mN·m^{-1} and 0.186 mN·m^{-1}. There was only three points of surface tension data of liquid dimethoxymethane to be found in previous literature[9] as shown in Figure 3, where the maximum deviation of literature data from eq 4 was 0.26 mN·m^{-1}. It was indicated that these data had the agreement under the measurement uncertainties.

Table 2. Experimental Data of Methyl *tert*-Butyl Ether

T/K	ρ_l/kg·m^{-3}	ρ_g/kg·m^{-3}	Δh_0/mm	a^2/mm^2	σ/mN·m^{-1}
243.077	789.965	0.089	8.55	6.2227	24.076
248.010	785.253	0.118	8.37	6.0912	23.425
253.106	780.349	0.155	8.21	5.9771	22.842
258.129	775.478	0.202	8.08	5.8777	22.321
263.103	770.617	0.260	7.88	5.7374	21.650
268.129	765.665	0.332	7.69	5.5941	20.971
273.163	760.663	0.420	7.57	5.5094	20.516
278.108	755.708	0.526	7.43	5.4041	19.990
283.120	750.642	0.654	7.24	5.2667	19.348
288.132	745.528	0.807	7.14	5.1965	18.956
293.072	740.441	0.986	7.03	5.1147	18.526
298.079	735.234	1.199	6.79	4.9364	17.749
303.106	729.953	1.450	6.64	4.8282	17.229
308.147	724.601	1.741	6.49	4.7200	16.712
313.160	719.220	2.076	6.36	4.6265	16.252
318.106	713.851	2.456	6.16	4.4803	15.612
323.159	708.301	2.898	6.01	4.3663	15.086
328.136	702.767	3.392	5.83	4.2376	14.517
333.155	697.115	3.955	5.68	4.1295	14.021
338.158	691.405	4.587	5.55	4.0301	13.558
343.135	685.647	5.290	5.40	3.9190	13.060
348.135	679.777	6.078	5.22	3.7874	12.498
353.130	673.823	6.953	5.04	3.6558	11.942
358.151	667.743	7.926	4.92	3.5740	11.551
363.127	661.615	8.991	4.71	3.4161	10.920
368.127	655.349	10.168	4.59	3.3313	10.528
373.124	648.969	11.459	4.39	3.1851	9.946
378.125	642.458	12.874	4.26	3.0916	9.534
383.116	635.823	14.418	4.06	2.9425	8.956
388.139	628.997	16.113	3.92	2.8372	8.518
393.129	622.053	17.947	3.74	2.7057	8.006

Methyl tert-Butyl Ether. Thirty-one experimental data points were report here in the temperature range from (243 to 393) K. The experimental data are listed in Table 2. The saturated liquid densities of methyl *tert*-butyl ether were from ref 9. The gas densities were also calculated from the Peng−Robinson equation, where the critical temperature (T_c), the critical pressure (P_c), and the Pitzer acentric factor (ω) were 497.1 K, 3434.9 kPa, and 0.265, respectively.[10]

The capillary constant a^2 was fitted to the form of eq 3. The critical temperature $T_c = 497.1$ K was used. The values of $a_0{}^2$ and a_1 are 11.7847 mm^2 and -0.0281, respectively. The measured values of capillary constant a^2 and the fitted curves are shown in Figure 4, and the deviations are shown in Figure 5. The maximum deviation is 0.96 %.

The experimental data were also correlated as a function of temperature by a van der Waals-type correlation. The fitted parameters σ_0 and n are 54.522 mN·m^{-1} and 1.223, respectively.

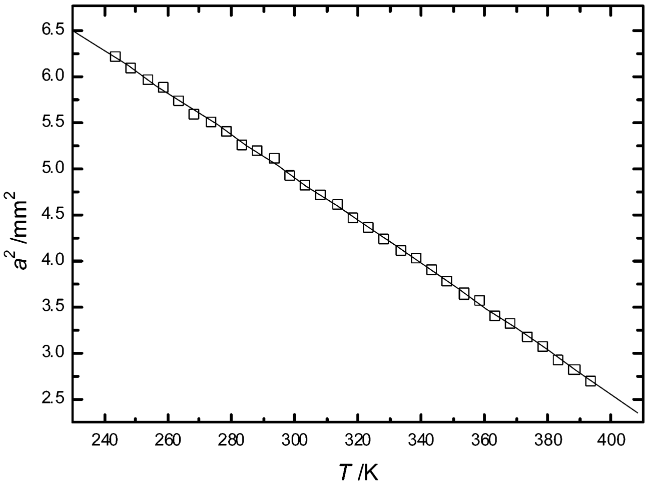

Figure 4. Relation between temperature and capillary constant for methyl *tert*-butyl ether.

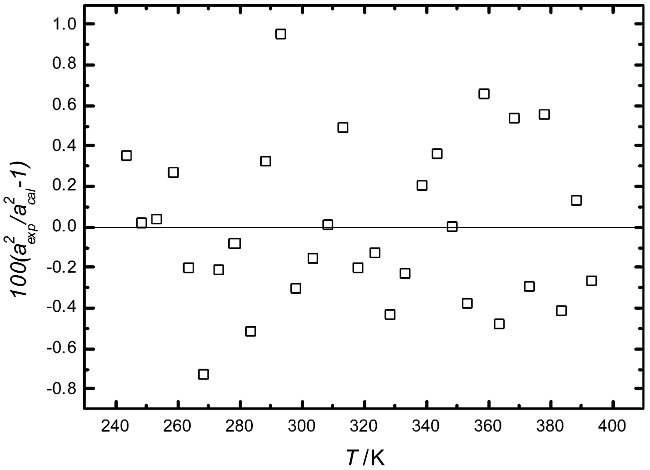

Figure 5. Deviation of capillary constant for methyl *tert*-butyl ether from the fit to eq 3.

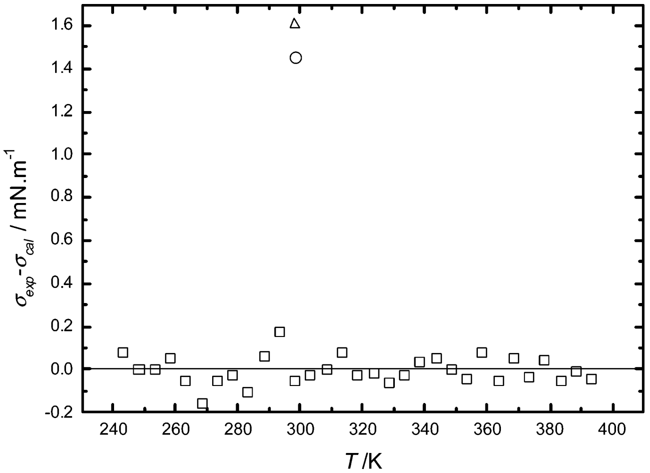

Figure 6. Comparison of the surface tension results and literature data for methyl *tert*-butyl ether from eq 4: □, this work; △, Csikoset al.;[11] ○, Ouyang et al.[12]

The average absolute and maximum deviations are 0.050 mN·m^{-1} and 0.180 mN·m^{-1}.

To our knowledge, there are no surface tension data of methyl *tert*-butyl ether to be found in the published literatures except refs 11 and 12 provided its surface tension data at 298.15 K. Compared to refs 11 and 12, the absolute deviations of eq 4 are 1.607 mN·m^{-1} and 1.457 mN·m^{-1}, respectively. The details are shown in Figure 6. The discrepancies between the previous data and this work are obvious. Furthermore, to check the reliability and reproducibility of this work, the surface tension of methyl *tert*-butyl ether was re-measured with two other capillaries, of which the inner radii were (0.2218 ± 0.0002) mm and (0.3269 ± 0.0001) mm. The deviations of the experimental data using the different set capillaries were within 0.2 mN·m^{-1}. Hence, it could be learned that the present experiment was reliable. The reason for the discrepancy may be caused from the measurement method and condition. For example, the pendant-drop method was used in ref 12, and the surface tension data of methyl *tert*-butyl ether were measured at atmosphere condition. However, in this work, the surface tension data were measured along the saturation line with the differential capillary rise method.

Conclusion

The surface tension of dimethoxymethane was measured over a wide temperature range from (238 to 388) K and that of methyl *tert*-butyl ether was measured at a temperature range from (243 to 393) K using the differential capillary rise method. The uncertainty of surface tension measurements was estimated to be within ± 0.2 $\mathrm{mN \cdot m^{-1}}$. On the basis of the present results, the equations of surface tension for dimethoxymethane and methyl *tert*-butyl ether as a function of temperature have been proposed. The capillary constant and its correlation were also presented.

Literature Cited

(1) Pan, J.; Wu, J. T.; Liu, Z. G. Measurement of the thermal conductivity of liquid dimethoxymethane from 240 to 362 K. *Int. J. Thermophys.* **2004**, *25*, 701−707.

(2) Wu, J. T.; Xu, Z. Y.; Liu, Z. G.; Wang, B. Density and viscosity of saturated liquid dimethoxymethane from (218.15 to 383.15) K. *J. Chem. Eng. Data* **2005**, *50*, 966−968.

(3) Pan, J.; Wu, J. T.; Liu, Z. G. Vapor pressure of dimethoxymethane and 1,1,1,3,3-pentafluoropropane. *J. Chem. Eng. Data* **2006**, *51*, 186−189.

(4) Perrin, D. D.; Armarego. W. L. F. *Purification of Laboratory Chemicals*, 4th ed.; World Publishing Co. Ltd.: Beijing, 2000.

(5) Wu, J. T. Development of the new thermophysical properties measurement system and research of thermophysical properties of dimethyl ether. Ph.D. Dissertation, Xi’an Jiaotong University, Xi’an, China, 2003.

(6) Wu, J. T.; Liu, Z. G.; Wang, F. K.; Ren, C. Surface tension of dimethyl ether from (213 to 368) K. *J. Chem. Eng. Data* **2003**, *48*, 1571−1573.

(7) Wu, J. T.; Liu, Z. G.; Pan, J. Development of fluid thermophysical property measurement system with high accuracy. *J. Xi’an Jiaotong Univ.* **2004**, *38*, 937−942.

(8) Chae, H. B.; Schmidt, J. W.; Moldover, M. R. Alternative refrigerants R123a, R134, R141b, R142b, and R152a: critical temperature, refractive index, surface tension, and estimates of liquid, vapor, and critical densities. *J. Phys. Chem.* **1990**, *94*, 8840−8845.

(9) Vogel, A. I. Physical properties and chemical constitution. Part XII. Ethers and acetals. *J. Chem.* Soc. **1948**, 616−624.

(10) Ihmels, E. C.; Gmehling. J. Compressed liquid densities of methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), and diisopropyl ether (DIPE). *J. Chem. Eng. Data* **2002**, *47*, 1307−1313.

(11) Csikos, R.; Pallay, I.; Laky, J. Low-lead fuel with MTBE and C4 alcohols. *Hydrocarbon Process.* **1976**, *55*, 121−125.

(12) Ouyang, G. F.; Lu, G. Z.; Pan, C. R.; Yang, Y. Y.; Huang, Z. Q.; Kang, B. S. Excess molar volumes and surface tensions of xylene with isopropyl ether or methyl *tert*-butyl ether at 298.15 K. *J. Chem. Eng. Data* **2004**, *49*, 732−734.

Received for review March 3, 2006. Accepted May 3, 2006. This work was supported by the National Science Foundation of China (Grant 50336020) and the National Basic Research Priorities Program of Ministry of Science and Technology of China (Grant 2001CB209208).

JE060097Q