Surface Tension of Diethyl Ether, Diisopropyl Ether, and Dibutyl Ether

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The surface tension of diethyl ether, diisopropyl ether, and dibutyl ether were measured with a differential capillary rise method over the temperature range from (258 to 373) K, (248 to 373) K, and (263 to 373) K, respectively. The uncertainties of measurements for the temperature and surface tension were estimated to be within ± 10 mK and ± 0.2 mN·m^{-1}. The results were correlated as a function of temperature, and the average absolute deviations were 0.053 mN·m^{-1} for diethyl ether, 0.041 mN·m^{-1} for diisopropyl ether, and 0.063 mN·m^{-1} for dibutyl ether, respectively.

Introduction

In recent research, oxygenated additives have been recognized as a safe, efficient, and cost-effective way to reduce the emission levels and improve combustion.[1] Ethers, such as diethyl ether, diisopropyl ether, and dibutyl ether, are regarded as ideal potential fuel alternatives or additives, which have good combustion characteristics. The investigation on the thermophysical properties is very important for the increased applications of oxygenated fuels or fuel additives. In our previous work, the liquid density and viscosity of diethyl ether, diisopropyl ether, and dibutyl ether were measured.[2,3] In this work, their surface tensions were measured along the saturation line.

Experimental Section

Materials. Diethyl ether was provided by Tianjin Dongliqu Tianda Chemical Reagent Factory, and nominal mass fraction purity is 99.5 %. Diisopropyl ether and dibutyl ether were purchased from Alfa Aesar, and the purities are better than 98 % and 99 %, respectively. The fluid samples were introduced in the measuring cell without any further treatment.

Apparatus and Procedure. The differential capillary rise method was used for the surface tension measurement. The same experimental apparatus and procedure has been used to measure the surface tensions of some oxygenated fuels in our previous work.[4,5]

During the experiment, the capillary rise difference Δh_0 was 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 is 9.7965 m·s^{-2}), and ρ_L and ρ_g are the densities of saturated liquid and vapor, respectively. Δh_0 is the 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 as

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

The bore radii of two capillaries used in this work are r_1 = (0.1490 ± 0.0001) mm and r_2 = (0.2340 ± 0.0001) mm. Their radii were determined by partially filling the capillaries with plugs of mercury. The plugs were weighed, and their lengths were measured with a traveling microscope. The procedure was repeated at least six times for each capillary with different plugs of mercury.

The capillaries were placed in a small pressure cell with observation windows, and the pressure cell was placed in a thermostatic bath in which the temperature stability was within ± 10 mK in 2 h. Silicon oil was chosen as the working fluid. The temperature measurement system consisted of an Agilent 3458A and two 25 Ω standard platinum resistance thermometers. One thermometer (no. 68033) is used in the temperature range of (83.8058 to 273.16) K, and another (no. 68115) is used in the temperature range of (273.15 to 933.473) K. The thermometers were calibrated on ITS-90 at the National Institute of Metrology of China. The total uncertainty of the temperature was less than ± 10 mK. The capillary rise difference was measured with a cathetometer with an uncertainty of ± 0.02 mm. In this work, the maximum uncertainty of surface tension was estimated to be within ± 0.2 mN·m^{-1}.

Table 1. Surface Tension of Heptane

T / K	ρ_l[a] / kg·m^{-3}	ρ_g[a] / kg·m^{-3}	σ / mN·m^{-1}	$(\sigma - \sigma_r)$ / mN·m^{-1}
298.135	679.516	0.248	20.003	−0.024
303.179	675.241	0.312	19.577	0.078
308.123	671.029	0.388	18.967	−0.015
313.180	666.698	0.481	18.414	−0.045
318.169	662.400	0.589	17.973	0.028
323.198	658.039	0.717	17.481	0.050
328.150	653.716	0.864	16.916	−0.012

[a] Density values from ref 6.

Table 2. Parameter in Equation 3 for Diethyl Ether, Diisopropyl Ether, and Dibutyl Ether

sample	A_1	$A_2 \cdot 10^{-2}$	$A_3 \cdot 10^{-7}$	$A_4 \cdot 10^{-19}$	$A_5 \cdot 10^{-21}$
diethyl ether	0.163	−1.368	−2.008	−1.750	2.657
diisopropyl ether	0.211	−2.044	−3.960	3.187	−10.820
dibutyl ether	0.339	−3.7344	−7.735	−10.380	4.4188

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Table 3. Surface Tension of Diethyl Ether, Diisopropyl Ether, and Dibutyl Ether

sample	T (K)	ρ_l ($kg \cdot m^{-3}$)	ρ_g ($kg \cdot m^{-3}$)	Δh_0 (mm)	a^2 (mm^2)	σ ($mN \cdot m^{-1}$)
diethyl ether	258.167	752.840	0.597	14.24	5.829	21.487
	263.167	747.508	0.763	13.86	5.673	20.759
	268.178	742.121	0.966	13.54	5.542	20.127
	273.181	736.693	1.209	13.30	5.444	19.619
	278.182	731.214	1.499	12.96	5.304	18.966
	283.181	725.676	1.841	12.72	5.206	18.464
	288.175	720.078	2.243	12.38	5.066	17.820
	293.160	714.420	2.709	12.02	4.919	17.153
	298.100	708.737	3.243	11.72	4.796	16.578
	303.170	702.822	3.873	11.42	4.673	16.003
	308.111	696.971	4.575	11.12	4.55	15.435
	313.192	690.858	5.396	10.82	4.427	14.868
	318.160	684.784	6.305	10.40	4.254	14.143
	323.163	678.562	7.336	10.12	4.139	13.614
	328.125	672.283	8.482	9.74	3.984	12.957
	333.175	665.776	9.784	9.48	3.877	12.462
	338.174	659.213	11.218	9.18	3.754	11.919
	343.170	652.528	12.807	8.80	3.598	11.278
	348.172	645.703	14.563	8.50	3.475	10.746
	353.190	638.719	16.502	8.18	3.344	10.194
	358.184	631.624	18.621	7.80	3.188	9.575
	363.160	624.408	20.929	7.46	3.048	9.014
	368.180	616.973	23.470	7.12	2.909	8.459
	373.167	609.429	26.216	6.78	2.769	7.914
diisopropyl ether	248.070	767.676	0.063	14.74	6.034	22.697
	253.231	762.674	0.089	14.42	5.903	22.058
	258.100	757.946	0.120	14.18	5.805	21.555
	263.175	753.006	0.161	13.92	5.698	21.020
	268.331	747.969	0.214	13.68	5.600	20.517
	273.462	742.935	0.281	13.38	5.477	19.929
	278.500	737.967	0.362	13.02	5.329	19.260
	283.175	733.332	0.454	12.80	5.239	18.813
	288.175	728.344	0.571	12.54	5.132	18.301
	293.160	723.336	0.711	12.30	5.034	17.823
	298.100	718.335	0.876	12.00	4.911	17.263
	303.170	713.159	1.075	11.74	4.804	16.762
	308.080	708.101	1.301	11.42	4.673	16.183
	313.270	702.701	1.578	11.14	4.558	15.658
	318.167	697.553	1.881	10.82	4.427	15.089
	323.188	692.217	2.237	10.54	4.312	14.577
	328.124	686.911	2.636	10.28	4.205	14.099
	333.118	681.477	3.094	10.06	4.115	13.678
	338.109	675.978	3.611	9.76	3.992	13.151
	343.100	670.407	4.192	9.42	3.852	12.575
	348.103	664.746	4.845	9.16	3.746	12.111
	353.099	659.012	5.573	8.84	3.614	11.573
	358.155	653.125	6.391	8.50	3.475	11.012
	363.173	647.192	7.292	8.24	3.368	10.561
	368.170	641.193	8.282	7.92	3.237	10.039
	373.170	635.095	9.372	7.74	3.163	9.698
dibutyl ether	263.171	792.950	0.004	16.21	6.637	25.789
	268.176	788.779	0.006	16.02	6.559	25.352
	273.183	784.618	0.008	15.78	6.461	24.840
	278.191	780.465	0.012	15.58	6.379	24.394
	283.196	776.319	0.016	15.34	6.281	23.890
	288.189	772.185	0.023	15.22	6.231	23.577
	293.181	768.051	0.031	14.96	6.125	23.049
	298.106	763.968	0.042	14.74	6.034	22.588
	303.170	759.763	0.056	14.58	5.969	22.219
	308.046	755.703	0.074	14.34	5.870	21.735
	313.180	751.414	0.097	14.10	5.772	21.249
	318.129	747.263	0.125	13.80	5.649	20.680
	323.200	742.988	0.160	13.60	5.567	20.262
	328.199	738.751	0.203	13.34	5.460	19.760
	333.180	734.503	0.255	13.18	5.395	19.408
	338.179	730.210	0.318	12.86	5.263	18.824
	343.174	725.888	0.393	12.60	5.157	18.331
	348.181	721.519	0.482	12.36	5.058	17.871
	353.165	717.132	0.587	12.16	4.976	17.472
	358.180	712.674	0.711	11.88	4.861	16.959
	363.185	708.180	0.856	11.66	4.771	16.536
	368.185	703.642	1.023	11.42	4.673	16.087
	373.170	699.065	1.215	11.08	4.533	15.501

Table 4. Parameter in Equations 4 and 5 for Diethyl Ether, Diisopropyl Ether, and Dibutyl Ether

sample	a_0^2 (mm^2)	a_1	σ_0 ($mN \cdot m^{-1}$)	n
diethyl ether	12.65236	−0.0502	57.96694	1.23089
diisopropyl ether	11.23556	0.04164	53.39562	1.2484
dibutyl ether	12.28797	−0.09037	53.01078	1.19636

Results and Analysis

Before the experiment, the surface tension of pure heptane was measured along the saturation line from (298 to 328) K to test the reliability of the experimental apparatus. The heptane was supplied by Xi'an Fuli Chemical Reagent Factory, China, and its nominal mass purity is 99 %. The experimental data were listed in Table 1 and compared with the calculated data from NIST REFPROP 8.0.[6] The results indicated that the maximum deviation was 0.08 $mN \cdot m^{-1}$.

The surface tension of diethyl ether, diisopropyl ether, and dibutyl ether was measured along the saturation line over the temperature range from (258 to 373) K, (248 to 373) K, and (263 to 373) K, respectively. Their saturated liquid densities were cited from previous work.[2,3] The gas densities were calculated from the Design Institute for Physical Property Data (DIPPR),[7] where the second virial coefficient B was:

$$B = A_1 + A_2/T + A_3/T^3 + A_4/T^8 + A_5/T^9 \qquad (3)$$

where T is temperature, K; a_i (i = 1 to 5) are the fitted parameters listed in Table 2. The saturated vapor pressure of diethyl ether, diisopropyl ether, and dibutyl ether were cited from ref 8, ref 9, and ref 10, respectively.

At each temperature, the capillary rise difference was measured at least three times. The experimental data are listed in Table 3.

The capillary constants a^2 were fitted to the functional form:

$$a^2 = a_0^2 \tau^{0.935}(1 + a_1 \tau) \qquad (4)$$

where τ is the reduced temperature $(T_c - T)/T_c$, and T_c is the critical temperature; a_0^2 and a_1 are the fitted parameters. The critical temperatures are 466.7 K for diethyl ether,[11] 500.3 K for diisopropyl ether,[12] and 584 K for dibutyl ether.[11] The values of a_0^2 and a_1 have been fitted and listed in Table 4.

The determined values of capillary constant a^2 and the fitted curves are shown in Figure 1. The average deviation between the determined values and the calculated data for the fitted eq 4 is 0.023 mm^2 for the diethyl ether, 0.025 mm^2 for the diisopropyl ether, and 0.013 mm^2 for the dibutyl ether.

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

$$\sigma = \sigma_0 \left(1 - \frac{T}{T_c}\right)^n \qquad (5)$$

where σ_0 and n are the fitted parameters. With the measurements of this work, σ_0 and n are determined and listed in Table 4.

Figure 2 shows the relation of temperature and surface tension. The average absolute and maximum deviations between the experimental data and the calculated data from eq 5 are 0.05 $mN \cdot m^{-1}$ and 0.12 $mN \cdot m^{-1}$ for the diethyl ether, 0.04 $mN \cdot m^{-1}$ and 0.09 $mN \cdot m^{-1}$ for the diisopropyl ether, and 0.06 $mN \cdot m^{-1}$ and 0.17 $mN \cdot m^{-1}$ for the dibutyl ether.

There were several data of surface tension for liquid diethyl ether found in previous literature[13−16] which are shown in Figure 3, where the maximum deviation of literature data from eq 5 was 0.15 $mN \cdot m^{-1}$. Ouyang et al.[17] and Bonnet

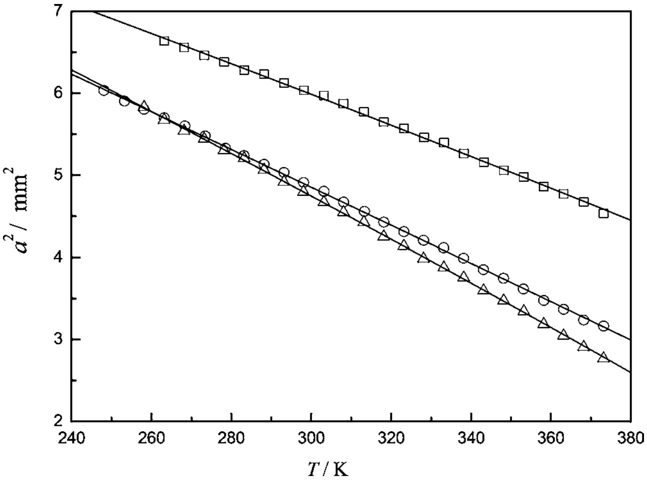

Figure 1. Relation between the temperature and the capillary constant for diethyl ether, diisopropyl ether, and dibutyl ether. Δ, Diethyl ether; ○, diisopropyl ether; □, dibutyl ether.

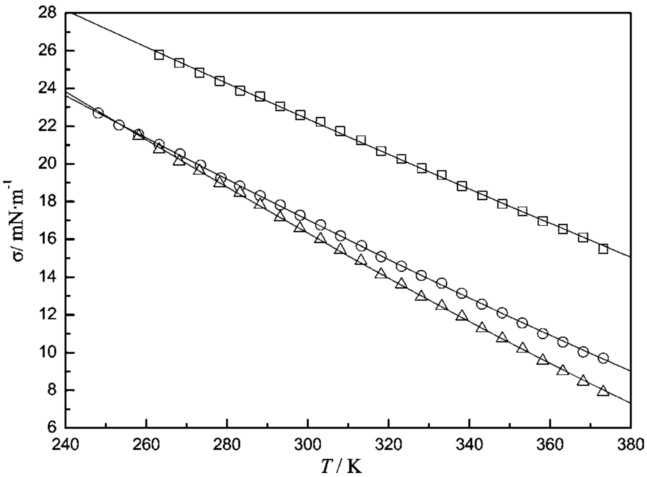

Figure 2. Relation between the temperature and the surface tension for diethyl ether, diisopropyl ether, and dibutyl ether. Δ, Diethyl ether; ○, diisopropyl ether; □, dibutyl ether.

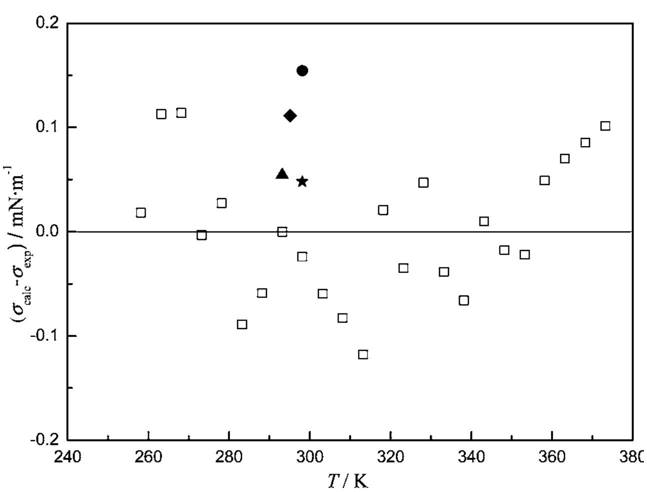

Figure 3. Comparison of the surface tension results and literature data for diethyl ether from eq 5: □, this work; ●, ref 13; ▲, ref 14; ◆, ref 15; ★, ref 16.

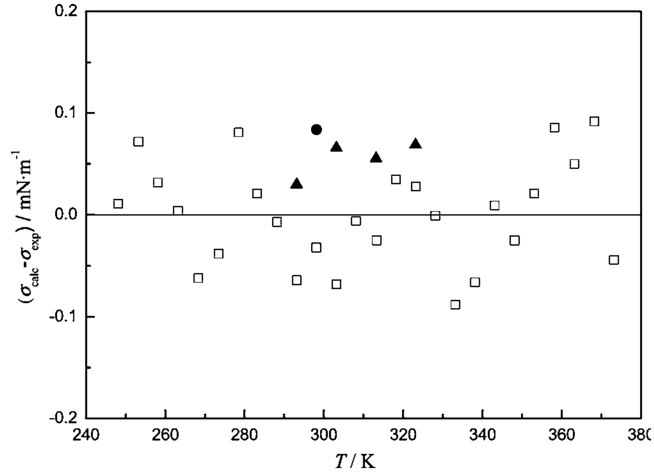

Figure 4. Comparison of the surface tension results and literature data for diisopropyl ether from eq 5: □, this work; ●, ref 17; ▲, ref 18.

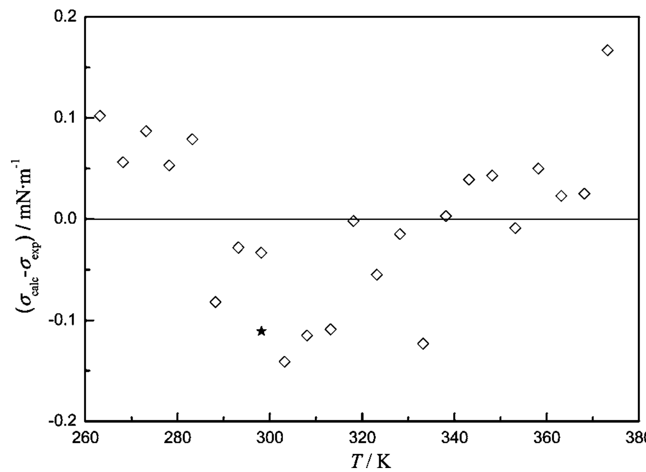

Figure 5. Comparison of the surface tension results and literature data for dibutyl ether from eq 5: □, this work; ★, ref 19.

and Pike[18] have measured the liquid surface tension of the diisopropyl ether, which were compared with eq 5 showed in Figure 4, and the maximum deviation was 0.08 mN·m^{-1}. There was only one surface tension datum of liquid diisopropyl ether found in previous literature,[15] which is shown in Figure 5, where the deviation of literature data from eq 5 was −0.11 mN·m^{-1}.

Conclusion

The surface tension of diethyl ether, diisopropyl ether, and dibutyl ether were measured using the differential capillary rise method. The uncertainty of surface tension measurements was estimated to be within ± 0.2 mN·m^{-1}. On the basis of the present results, the equations of surface tension for diethyl ether, dissopropyl ether, and dibutyl ether as a function of temperature have been proposed.

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