

# Densities, Surface Tensions, and Viscosities of Diesel–Oxygenate Mixtures at the Temperature 301.15 K

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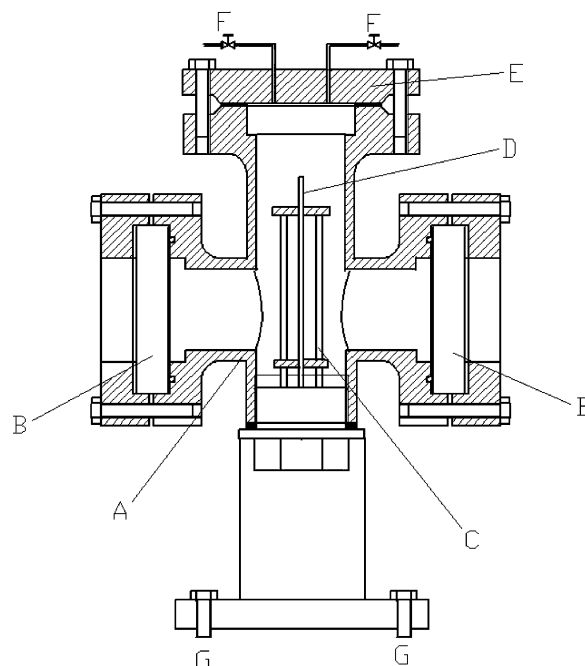
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The densities, surface tensions, and viscosities were measured at 301.15 K for the blends of {diesel plus diethyl adipate (DEA)}, {diesel plus diethyl carbonate (DEC)}, {diesel plus diglyme (DGM)}, {diesel plus dimethyl carbonate (DMC)}, and {diesel plus dimethoxymethane (DMM)}. On the basis of the experimental data, the excess thermodynamic properties, including excess densities, excess surface tensions, and excess viscosities, were determined as functions of mass fractions over the entire composition range. Furthermore, polynomial correlations were fitted for the excess thermodynamic properties.

## Introduction

As we know, automobiles are one of the major contributors of air pollutants, such as carbon monoxide (CO), nitrogen oxide (NO<sub>x</sub>), particulate matters (PM), and other harmful gases. With the increasing concern of the environment, more strict government regulations on exhaust emissions have been provided gradually. At present, the reduction of engine emissions is a major objective of vehicle improvement.

Recently, it was found that oxygenic additives,<sup>1–4</sup> such as diethyl adipate (DEA),<sup>5,6</sup> diethyl carbonate (DEC),<sup>6,7</sup> diglyme (DGM),<sup>8,9</sup> dimethyl carbonate (DMC),<sup>10,11</sup> and dimethoxymethane (DMM),<sup>12,13</sup> could provide great improvement in fuel properties and reduce engine emissions. When an engine operates with diesel–oxygenate blends, PM decreases markedly without the increase of NO<sub>x</sub>. Generally speaking, it is difficult to reduce PM and NO<sub>x</sub> simultaneously, owing to the tradeoff between NO<sub>x</sub> and PM.<sup>14</sup> Therefore, DEA, DEC, DGM, DMC, and DMM are regarded as good fuel additives and potential alternative fuels in the future. For the applications of oxygenic additives,



**Figure 1.** Experimental apparatus of the surface tension: (A) pressure-resistant metallic cell, (B) observation window, (C) capillary bracket, (D) capillary, (E) flange plate, (F) valves, and (G) adjusting bolts.

thermophysical properties are indispensable. Unfortunately, reliable thermophysical property data for the mixtures of diesel and oxygenic additives are scarce at present. In this work, densities, surface tensions, and viscosities of diesel with different oxygenic additives were measured at ambient pressure.

## Experimental Section

**Materials.** The samples of diesel fuel provided by China Petroleum and Chemical Corporation were the 0 number. The samples of five oxygenate compounds, including DEA, DEC, DGM,

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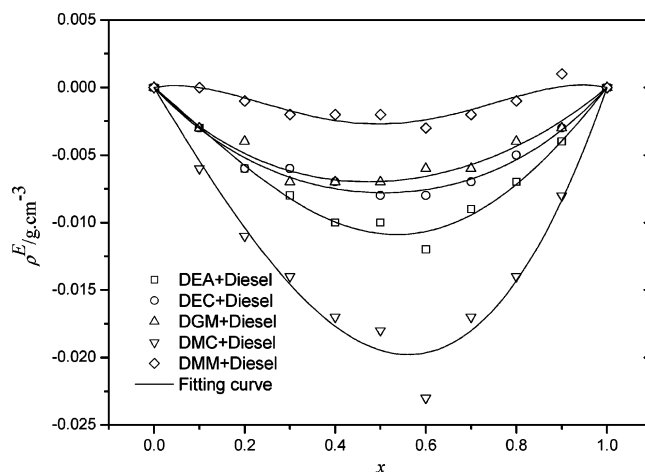
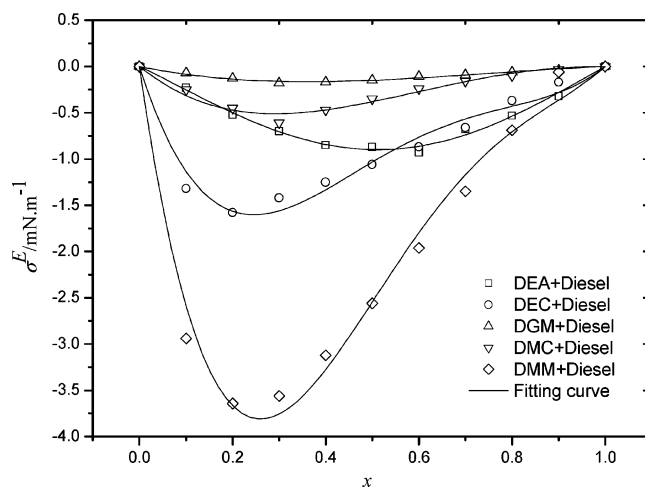
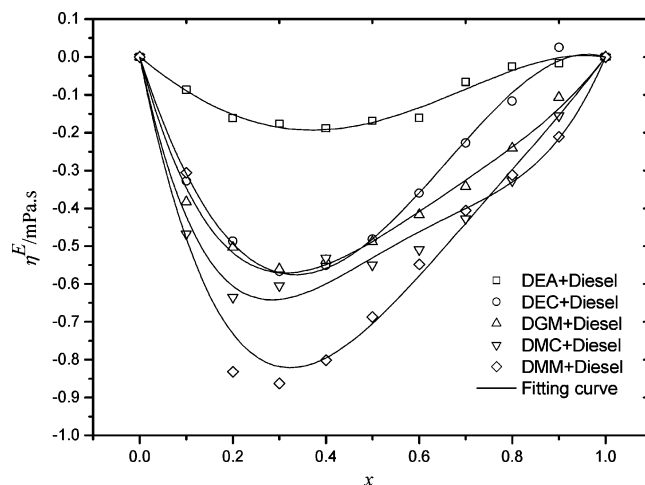
**Table 1.** Densities, Surface Tensions, and Viscosities of Diesel–Oxygenate Mixtures ( $T = 301.15$  K)

$x$	$\rho$ (g cm <sup>-3</sup> )	$\rho^E$ (g cm <sup>-3</sup> )	$\sigma$ (mN m <sup>-1</sup> )	$\sigma^E$ (mN m <sup>-1</sup> )	$\eta$ (mPa s)	$\eta^E$ (mPa s)
{ $x$ DEA plus (1 - $x$ ) Diesel}						
0.00	0.826	0.000	28.6	0.0	2.744	0.000
0.10	0.840	-0.003	28.7	-0.2	2.664	-0.087
0.20	0.855	-0.006	28.7	-0.5	2.595	-0.162
0.30	0.870	-0.008	28.8	-0.7	2.588	-0.177
0.40	0.886	-0.010	29.0	-0.9	2.582	-0.189
0.50	0.903	-0.010	29.3	-0.9	2.608	-0.169
0.60	0.918	-0.012	29.5	-0.9	2.624	-0.161
0.70	0.938	-0.009	30.1	-0.7	2.724	-0.067
0.80	0.958	-0.007	30.5	-0.5	2.773	-0.026
0.90	0.978	-0.004	31.0	-0.3	2.788	-0.017
1.00	0.999	0.000	31.7	0.0	2.812	0.000
{ $x$ DEC plus (1 - $x$ ) Diesel}						
0.00	0.826	0.000	28.6	0.0	2.744	0.000
0.10	0.837	-0.003	27.0	-1.3	2.215	-0.328
0.20	0.848	-0.006	26.5	-1.6	1.855	-0.487
0.30	0.862	-0.006	26.4	-1.4	1.573	-0.567
0.40	0.875	-0.007	26.3	-1.3	1.388	-0.551
0.50	0.888	-0.008	26.2	-1.1	1.256	-0.481
0.60	0.902	-0.008	26.2	-0.9	1.176	-0.360
0.70	0.917	-0.007	26.1	-0.7	1.108	-0.227
0.80	0.932	-0.005	26.1	-0.4	1.017	-0.117
0.90	0.948	-0.003	26.1	-0.2	0.958	0.025
1.00	0.965	0.000	26.0	0.0	0.732	0.000
{ $x$ DGM plus (1 - $x$ ) Diesel}						
0.00	0.826	0.000	28.6	0.0	2.744	0.000
0.10	0.834	-0.003	28.5	-0.1	2.177	-0.383
0.20	0.844	-0.004	28.4	-0.1	1.872	-0.503
0.30	0.852	-0.007	28.4	-0.2	1.630	-0.560
0.40	0.863	-0.007	28.3	-0.2	1.468	-0.538
0.50	0.873	-0.007	28.3	-0.2	1.334	-0.488
0.60	0.885	-0.006	28.3	-0.1	1.221	-0.417
0.70	0.896	-0.006	28.3	-0.1	1.112	-0.342
0.80	0.909	-0.004	28.3	-0.1	1.029	-0.241
0.90	0.921	-0.003	28.3	0.0	0.979	-0.107
1.00	0.935	0.000	28.3	0.0	0.901	0.000
{ $x$ DMC plus (1 - $x$ ) Diesel}						
0.00	0.826	0.000	28.6	0.0	2.744	0.000
0.10	0.844	-0.006	28.3	-0.3	2.064	-0.467
0.20	0.862	-0.011	28.0	-0.5	1.684	-0.635
0.30	0.881	-0.014	27.7	-0.6	1.502	-0.604
0.40	0.902	-0.017	27.8	-0.5	1.363	-0.531
0.50	0.924	-0.018	27.8	-0.4	1.132	-0.549
0.60	0.943	-0.023	27.8	-0.2	0.960	-0.509
0.70	0.972	-0.017	27.8	-0.2	0.828	-0.427
0.80	0.998	-0.014	27.8	-0.1	0.716	-0.327
0.90	1.028	-0.008	27.8	0.0	0.676	-0.155
1.00	1.059	0.000	27.7	0.0	0.618	0.000
{ $x$ DMM plus (1 - $x$ ) Diesel}						
0.00	0.826	0.000	28.6	0.0	2.744	0.000
0.10	0.828	0.000	24.8	-2.9	2.197	-0.306
0.20	0.830	-0.001	23.2	-3.6	1.431	-0.832
0.30	0.831	-0.002	22.4	-3.6	1.161	-0.862
0.40	0.833	-0.002	22.0	-3.1	0.981	-0.801
0.50	0.835	-0.002	21.7	-2.6	0.855	-0.687
0.60	0.837	-0.003	21.4	-2.0	0.754	-0.548
0.70	0.840	-0.002	21.1	-1.4	0.655	-0.406
0.80	0.843	-0.001	20.9	-0.7	0.510	-0.312
0.90	0.847	0.001	20.7	-0.1	0.370	-0.211
1.00	0.849	0.000	19.8	0.0	0.341	0.000

DMC, and DMM, were provided by Chaoyang Chemical Co. Ltd. The mass purities of the five oxygenate compounds were all better than 99.0%, as indicated by analysis with the Agilent 6890N gas chromatograph, and no further purification was performed in this experiment.

**Measurements.** In this experiment, all solvent mixtures were made by weight, with a balance of the accuracy  $\pm 0.1$  mg, and stabilized to within  $\pm 0.02$  K with a thermal bath of water. Every measurement was repeated 3 times and could be generally reproducible to within the accuracies. Finally, the average values were reported.

Densities of the blended fuels with various oxygenate components at 301.15 K were measured with a pycnometer, in which a balance (AB204-N made by Mettler Toledo Co.) with the precision

**Figure 2.** Experimental values of the excess density  $\rho^E$  and fitting.**Figure 3.** Experimental values of the excess surface tension  $\sigma^E$  and fitting.**Figure 4.** Experimental values of the excess viscosity  $\eta^E$  and fitting.

of  $\pm 0.1$  mg was used. Ultrapure water and benzene were used for the calibration, and the accuracy of density thus obtained was about  $\pm 0.002$  g cm<sup>-3</sup>.

Surface tensions at the air–sample interface of the various mixtures were measured at atmospheric pressure and temperature of 301.15 K with the differential capillary rise method (DCRM). The inner radii of the two capillaries used in this work are  $r_1 = (0.22697 \pm 0.0004)$  mm and  $r_2 = (0.32920 \pm 0.0003)$  mm, determined by the mercury line method. From direct observation, the capillary wall was completely wetted by the samples, and thus,

Table 2. Parameters  $A_i$  of eq 4 and AAD of Experimental Results with eq 4

function	mixture	$A_0$	$A_1$	$A_2$	AAD
$\rho^E$ (g cm <sup>-3</sup> )	{x DEA plus (1 - x) diesel}	-0.0433	-0.007 32	0.007 85	0.000 306
	{x DEC plus (1 - x) diesel}	-0.031 18	-0.000 76	-0.004 97	0.000 303
	{x DGM plus (1 - x) diesel}	-0.027 86	0.002 78	-0.002 79	0.000 344
	{x DMC plus (1 - x) diesel}	-0.077 88	-0.020 45	0.001 83	0.000 815
	{x DMM plus (1 - x) diesel}	-0.010 78	0.000 51	0.017 33	0.000 352
$\sigma^E$ (mN m <sup>-1</sup> )	{x DEA plus (1 - x) diesel}	-3.594	-0.202 02	0.965 47	0.023 292
	{x DEC plus (1 - x) diesel}	-4.138 24	5.914 14	-5.838 03	0.074 511
	{x DGM plus (1 - x) diesel}	-0.600 65	0.406 57	-0.031 64	0.007 221
	{x DMC plus (1 - x) diesel}	-1.526 26	2.068 18	-0.507 09	0.026 487
	{x DMM plus (1 - x) diesel}	-10.1791	15.401 52	-9.688 71	0.128 805
$\eta^E$ (mPa s)	{x DEA plus (1 - x) diesel}	-0.691 55	0.603 54	0.285 41	0.008 921
	{x DEC plus (1 - x) diesel}	-1.922 13	2.076 26	0.233 72	0.009 115
	{x DGM plus (1 - x) diesel}	-1.948 54	1.455 05	-1.142 91	0.011 804
	{x DMC plus (1 - x) diesel}	-2.122 37	1.430 05	-2.227 98	0.030 586
	{x DMM plus (1 - x) diesel}	-2.816 68	2.256 06	-1.106 09	0.043 244

the liquid-glass contact angle was treated as 0, which was valid in that condition. The apparatus was calibrated with ultrapure water and ethanol, and the accuracy was  $\pm 0.2$  mN m<sup>-1</sup>. The experiment apparatus was shown in Figure 1, and more details about the surface-tension measurement can be referred to in ref 15.

Viscosities of the various mixtures were measured at atmospheric pressure and temperature of 301.15 K with a capillary viscometer calibrated with ultrapure water and benzene. The accuracy of viscosity measurements was of the order of  $\pm 0.002$  mPa s, and more details about the viscosity measurement can be referred to in ref 16.

### Results and Discussion

The densities, surface tensions, and viscosities of mixtures of {diesel plus DEA}, {diesel plus DEC}, {diesel plus DGM}, {diesel plus DMC}, and {diesel plus DMM} were listed in Table 1. In this work, the excess thermodynamic functions of the mixtures were calculated with the following equations:

$$\rho^E = \rho_m - x\rho_1 - (1 - x)\rho_2 \quad (1)$$

$$\sigma^E = \sigma_m - x\sigma_1 - (1 - x)\sigma_2 \quad (2)$$

$$\eta^E = \eta_m - x\eta_1 - (1 - x)\eta_2 \quad (3)$$

where  $\rho^E$ ,  $\sigma^E$ , and  $\eta^E$  represent excess density, excess surface tension, and excess viscosity, respectively.  $\rho$ ,  $\sigma$ , and  $\eta$  represent density, surface tension, and viscosity, respectively. Subscript m, 1, and 2 represent the mixture, component 1 and component 2, respectively.  $x$  represents the mass fraction of component 1. The excess densities, excess surface tensions, and excess viscosities were also given in Table 1, and the details of excess thermodynamic properties versus components were shown in Figures 2–4. All excess thermodynamic functions ( $\rho^E$ ,  $\sigma^E$ , and  $\eta^E$ ) were fitted to the Redlich–Kister equation:

$$Y^E = x(1 - x) \sum_{i=0}^n A_i (2x - 1)^i \quad (4)$$

where  $Y$  represents the density, surface tension, or viscosity and  $A_i$  values are fitting parameters. The values of the adjustable parameters  $A_i$  and the average absolute deviation (AAD) of eq 4 are summarized in Table 2. The fitting curves of the

excess thermodynamic functions are also shown in Figures 2–4. In addition, it can be learned from the experimental data that the variations of densities for the five mixtures are weak. With respect to surface tensions, the mixtures of {DMM plus diesel} have a lower surface tension even though the fractions of DMM are small, while the surface tensions of the other four mixtures keep almost constant. In the case of viscosities, there is a little increase of viscosity values for {DEA plus diesel} and a significant decrease for the rest of the mixtures. With a lower surface tension and viscosity, the fuel can be pumped and atomized more easily. Subsequently, spray and combustion processes will be improved markedly, and namely, the fuel properties are improved by the oxygenic additions.

To our knowledge, there are some surface-tension data of pure dimethyl carbonate<sup>15</sup> and dimethoxymethane.<sup>17</sup> In comparison to the results of ref 15, the absolute deviation of pure dimethyl carbonate at 301.15 K was 0.17 mN m<sup>-1</sup>. The absolute deviation of pure dimethoxymethane between this work and ref 17 at 301.15 K was 0.11 mN m<sup>-1</sup>. Hence, it can be learned that the results of the present experiment are reliable. For the discrepancies of the dimethyl carbonate and dimethoxymethane data between this work and the literature, the reason may be caused by the different experimental conditions. For example, in refs 15 and 17, the surface-tension data were measured along the saturation line. However, in this work, the surface-tension data were measured at atmosphere conditions.

### Conclusion

The densities, surface tensions, and viscosities were measured at 301.15 K for {diesel plus DEA}, {diesel plus DEC}, {diesel plus DGM}, {diesel plus DMC}, and {diesel plus DMM}. For the measurement of densities, surface tensions, and viscosities, the accuracies were  $\pm 0.02$  g cm<sup>-3</sup>,  $\pm 0.2$  mN m<sup>-1</sup>, and  $\pm 0.002$  mPa s, respectively. The excess densities, excess surface tensions, and excess viscosities were determined as functions of mass fractions, and polynomial regressions were fitted.

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