

# Densities and Viscosities of Acetone, Diisopropyl Ether, Ethanol, and Methyl Ethyl Ketone with a Five-Component Hydrocarbon Mixture from 288.15 K to 308.15 K

I-Hung Peng and Chein-Hsiun Tu\*

Department of Applied Chemistry, Providence University, Shalu, 433 Taiwan, Republic of China

Densities and viscosities were measured for the systems of four oxygenates (acetone, diisopropyl ether, ethanol, and methyl ethyl ketone) separately with a five-component hydrocarbon mixture at three temperatures (288.15, 298.15, and 308.15) K and atmospheric pressure. The five-component hydrocarbon mixture contains 25 mol % hexane, 10 mol % heptane, 35 mol % 2,2,4-trimethylpentane, 20 mol % toluene, and 10 mol % *p*-xylene. Densities were determined using a vibrating-tube densimeter. Viscosities were measured with an automatic Ubbelohde capillary viscometer. Excess molar volumes  $V^E$  and deviations in viscosity  $\Delta\eta$  for the mixtures were derived from experimental data, and the computed results were fitted to a Redlich–Kister-type equation.

## Introduction

The reformulation of gasoline includes certain oxygenated compounds such as alcohols and ethers. These are commonly methanol, ethanol, propanol, and butanols and methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), and *tert*-amyl methyl ether (TAME). These oxygenated compounds are added to improve the octane rating and pollution-reducing capability of gasoline. MTBE, the primary oxygenated compound currently used in reformulated gasolines, is being phased out because of the ground-water pollution problems. It is important, then, to investigate the possible use of other oxygenates to comply with environmental regulations. In this sense, there has been an increasing interest in the thermodynamic behavior of liquid mixtures of the oxygenated compounds included in a hydrocarbon mixture.<sup>1–6</sup>

To gain some more understanding of the phenomena occurring in these mixtures, we measured the densities and viscosities of acetone, diisopropyl ether, ethanol, and methyl ethyl ketone separately with a five-component hydrocarbon mixture at three temperatures from 288.15 K to 308.15 K and atmospheric pressure. The hydrocarbon mixture contains hexane, heptane, 2,2,4-trimethylpentane, toluene, and *p*-xylene, which are the components that generally appear in gasoline. The experimental data are used to calculate excess molar volumes and viscosity deviations from the mole fraction average. The excess quantities have been fitted to a Redlich–Kister-type equation<sup>7</sup> to estimate the coefficients. By consideration of the six-component mixture as a pseudo-binary system, pseudo-excess volumes and pseudo-deviations in viscosity were derived. These results are used to qualitatively discuss the nature of interactions of the hydrocarbon mixtures in the presence of the mentioned oxygenates.

## Experimental Section

**Materials.** The chemicals used were of analytical grade and obtained from Fisher, Tedia, and Merck. Acetone,

diisopropyl ether, ethanol, and methyl ethyl ketone were dried over molecular sieves (Aldrich, 0.3 nm) and all chemicals were used without further purification. The purity of all chemicals was checked by gas chromatography. The gas chromatographic analysis of pure components showed that the major peak area, which exceeded 99.6%, were used for the experimental investigations. The purity of solvents was further ascertained by comparing their densities, viscosities, and refractive indices at 298.15 K, which agreed well with the corresponding literature values as shown in Table 1. Refractive indices,  $n_D$ , of pure chemicals were measured with a digital refractometer RX-5000 (ATAGO, Tokyo, Japan), with an uncertainty of  $\pm 0.00002$  units.

**Apparatus and Procedure.** Solutions of different composition were prepared by mass in a 50-cm<sup>3</sup> Erlenmeyer flask provided with a joint stopper, using a Mettler AB204 balance with an uncertainty of  $\pm 0.1$  mg. The uncertainty in the mole fraction is believed to be less than  $1 \times 10^{-4}$ . Densities were measured by a DMA-58 vibrating-tube densimeter (Anton-Paar, Graz, Austria) with a stated uncertainty of  $\pm 0.00002$  g·cm<sup>-3</sup>. The temperature in the measuring cell was regulated to  $\pm 0.01$  K. Calibration was performed at atmospheric pressure periodically, in accordance with specifications, using deionized water and dry air. Precautions were taken to avoid evaporation losses and dissolved air during the experimental work. The uncertainty of the density measurements was estimated to be less than  $\pm 1 \times 10^{-4}$  g·cm<sup>-3</sup>. The excess molar volumes were calculated from density data and the uncertainties were estimated to be within  $\pm 1 \times 10^{-2}$  cm<sup>3</sup>·mol<sup>-1</sup>.

The kinematic viscosities were determined with commercial Ubbelohde capillary viscometers (SCHOTT-GERÄTE, Hofheim, Germany) of (0.36, 0.47, 0.53, and 0.63) mm diameter. The viscometer was kept in a LAUDA D20 KP thermostat controlled to  $\pm 0.01$  K with a proportional-integral-differential regulator. A computer-controlled measuring system (LAUDA, Lauda-Königshofen, Germany) with an uncertainty of  $\pm 0.01$  s was used for flow-time measurement. The range of the flow time for the liquids

\* To whom correspondence should be addressed. E-mail: chtu@pu.edu.tw.

**Table 1. Comparison of Measured Densities, Viscosities, and Refractive Indices of Pure Components with Literature Values at 298.15 K**

component	$\rho$ (g·cm <sup>-3</sup> )		$\eta$ (mPa·s)		$n_D$	
	this work	lit.	this work	lit.	this work	lit.
ethanol	0.78549	0.78493 <sup>a</sup> 0.7854 <sup>b</sup>	1.084	1.0826 <sup>a</sup> 1.099 <sup>b</sup>	1.35791	1.35941 <sup>a</sup> 1.3605 <sup>b</sup>
acetone	0.78518	0.78440 <sup>a</sup> 0.78547 <sup>c</sup>	0.305	0.3029 <sup>a</sup>	1.35674	1.35596 <sup>a</sup>
methyl ethyl ketone	0.79975	0.7997 <sup>a</sup>	0.378	0.378 <sup>a</sup>	1.37636	1.37685 <sup>a</sup>
diisopropyl ether	0.71844	0.71854 <sup>a</sup> 0.71813 <sup>d</sup>	0.317	0.319 <sup>a</sup>	1.36542	1.3655 <sup>a</sup> 1.3658 <sup>d</sup>
2,2,4-trimethylpentane	0.68773	0.68781 <sup>a</sup>	0.472		1.38915	1.38898 <sup>a</sup>
<i>n</i> -hexane	0.65489	0.65484 <sup>a</sup>	0.297	0.307 <sup>a</sup>	1.37224	1.37226 <sup>a</sup>
<i>n</i> -heptane	0.67953	0.67946 <sup>a</sup>	0.395	0.3967 <sup>a</sup>	1.38513	1.38511 <sup>a</sup>
toluene	0.86224	0.86219 <sup>a</sup>	0.554	0.5525 <sup>a</sup>	1.49409	1.49413 <sup>a</sup>
<i>p</i> -xylene	0.85657	0.85661 <sup>a</sup>	0.598	0.605 <sup>a</sup>	1.49299	1.49325 <sup>a</sup>

<sup>a</sup>Riddick et al., 1986.<sup>8</sup> <sup>b</sup>Aralaguppi et al., 1999.<sup>9</sup> <sup>c</sup>TRC Tables, 1996.<sup>10</sup> <sup>d</sup>Montón et al., 1999.<sup>11</sup>

investigated is varied from 200 s to 600 s. The kinematic viscosity ( $\nu$ ) was then calculated from the following relationship,

$$\nu \equiv \eta/\rho = k(t - \theta) \quad (1)$$

where  $t$  is the flow time,  $\eta$  is the absolute viscosity, and  $k$  and  $\theta$  are respectively the viscometer constant and the Hagenbach correction. The constant  $k$  for several viscometers was provided by the manufacturer and checked periodically by measurement of the viscosities of pure liquids. The value  $\theta$ , which is dependent on the flow time and the size of the capillary, was taken from the tables supplied by the manufacturer. The accuracy of the flow-time measurement is  $\pm 0.01$  s. Triplicate measurements of flow times were reproducible within  $\pm 0.04\%$ . The uncertainty of the viscosity measurement was estimated to be less than  $\pm 0.8\%$ .

The densities and viscosities of oxygenate + hydrocarbon mixtures were measured at three temperatures (288.15, 298.15, and 308.15) K and atmospheric pressure. The oxygenates were those that have been tested as possible fuel additive candidates, for example, ethanol, acetone, diisopropyl ether, and methyl ethyl ketone. Five hydrocarbons were chosen from the major components shown in a GC analysis of gasoline<sup>12</sup> and the concentration was roughly assigned to each component according to its peak height. The hydrocarbon mixture thus formed for this study consists of 25 mol % hexane, 10 mol % heptane, 35 mol % 2,2,4-trimethylpentane, 20 mol % toluene, and 10 mol % *p*-xylene. This mixture has an average molecular weight of 100.59 and a refractive index of 1.50001 at 298.15 K. An average of at least three measurements was taken for each composition.

## Results and Discussion

The excess molar volumes,  $V^E$ , have been calculated from densities according to the equation

$$V^E = \sum_{i=1}^6 x_i M_i \left\{ (1/\rho) - (1/\rho_i) \right\} \quad (2)$$

where  $x_i$ ,  $M_i$ , and  $\rho_i$  are the mole fraction, molar mass, and density of the components, respectively, and  $\rho$  is the density of the mixture. The experimental densities, viscosities, and excess molar volumes for all of the systems are given in

**Table 2. Experimental Densities ( $\rho$ ), Viscosities ( $\eta$ ), and Excess Molar Volumes ( $V^E$ ) for  $x$  Acetone + (1- $x$ ) Hydrocarbon Mixture<sup>a</sup>**

$x$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$x$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>
$T = 288.15$ K							
0.0000	0.7296	0.450	0.03	0.6000	0.7548	0.372	0.59
0.0500	0.7308	0.441	0.16	0.7000	0.7624	0.362	0.52
0.1001	0.7320	0.433	0.27	0.7999	0.7716	0.352	0.40
0.2000	0.7350	0.420	0.45	0.8498	0.7768	0.347	0.33
0.3000	0.7386	0.407	0.56	0.8999	0.7828	0.343	0.22
0.4000	0.7431	0.395	0.61	0.9500	0.7893	0.339	0.12
0.5000	0.7485	0.384	0.63	1.0000	0.7966	0.335	0.00
$T = 298.15$ K							
0.0000	0.7210	0.404	-0.03	0.6000	0.7445	0.338	0.65
0.0500	0.7220	0.397	0.12	0.7000	0.7519	0.329	0.57
0.1001	0.7230	0.391	0.26	0.7999	0.7608	0.320	0.43
0.2000	0.7258	0.379	0.45	0.8498	0.7659	0.316	0.35
0.3000	0.7292	0.368	0.59	0.8999	0.7717	0.313	0.25
0.4000	0.7335	0.357	0.65	0.9500	0.7780	0.309	0.14
0.5000	0.7385	0.347	0.68	1.0000	0.7852	0.305	0.00
$T = 308.15$ K							
0.0000	0.7123	0.365	-0.07	0.6000	0.7342	0.308	0.71
0.0500	0.7131	0.360	0.10	0.7000	0.7412	0.300	0.63
0.1001	0.7140	0.354	0.26	0.7999	0.7500	0.292	0.46
0.2000	0.7166	0.344	0.47	0.8498	0.7550	0.289	0.36
0.3000	0.7197	0.334	0.63	0.8999	0.7607	0.286	0.24
0.4000	0.7237	0.324	0.70	0.9500	0.7666	0.282	0.15
0.5000	0.7284	0.316	0.74	1.0000	0.7736	0.279	0.00

<sup>a</sup> Hydrocarbon mixture indicates the mixture consists of 25 mol % hexane, 10 mol % heptane, 35 mol % methylcyclohexane, 20 mol % toluene, and 10 mol % *p*-xylene.

Tables 2–5. The deviation of the viscosity from the mole fraction average,  $\Delta\eta$ , is given by

$$\Delta\eta = \eta - \sum_{i=1}^6 x_i \eta_i \quad (3)$$

where  $\eta$  is the absolute viscosities of the mixtures and  $\eta_i$  is the absolute viscosities of the components. The experimental densities, viscosities, and excess molar volumes for all of the systems are given in Tables 2–5.

The  $V^E$  and  $\Delta\eta$  values were fitted as a function of the mole fraction of oxygenate,  $x$ , to a Redlich–Kister-type equation of the form

$$V^E/\text{cm}^3\cdot\text{mol}^{-1} \text{ or } \Delta\eta/\text{mPa}\cdot\text{s} = (1-x) \sum_{i=0}^p a_i (2x-1)^i \quad (4)$$

where  $a_i$  are the adjustable parameters. The values of

**Table 3. Experimental Densities ( $\rho$ ), Viscosities ( $\eta$ ), and Excess Molar Volumes ( $V^E$ ) for  $x$  Diisopropyl Ether + (1- $x$ ) Hydrocarbon Mixture**

$x$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$x$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>
$T=288.15$ K							
0.0000	0.7296	0.450	0.03	0.5999	0.7295	0.386	-0.03
0.0500	0.7297	0.444	0.02	0.6999	0.7294	0.377	-0.03
0.1000	0.7297	0.439	0.01	0.8000	0.7292	0.367	-0.02
0.1999	0.7297	0.428	0.00	0.8499	0.7292	0.362	-0.01
0.3000	0.7296	0.417	-0.02	0.8999	0.7291	0.358	-0.01
0.4000	0.7296	0.407	-0.03	0.9499	0.7290	0.353	-0.01
0.5000	0.7296	0.396	-0.03	1.0000	0.7290	0.349	0.00
$T=298.15$ K							
0.0000	0.7210	0.404	-0.03	0.5999	0.7198	0.346	-0.07
0.0500	0.7209	0.399	-0.04	0.6999	0.7195	0.337	-0.06
0.1000	0.7209	0.394	-0.05	0.8000	0.7192	0.328	-0.05
0.1999	0.7207	0.384	-0.06	0.8499	0.7190	0.324	-0.04
0.3000	0.7205	0.374	-0.07	0.8999	0.7188	0.320	-0.03
0.4000	0.7203	0.364	-0.07	0.9499	0.7186	0.316	-0.01
0.5000	0.7200	0.355	-0.08	1.0000	0.7184	0.312	0.00
$T=308.15$ K							
0.0000	0.7123	0.365	-0.07	0.5999	0.7100	0.313	-0.11
0.0500	0.7122	0.361	-0.09	0.6999	0.7095	0.305	-0.09
0.1000	0.7120	0.356	-0.10	0.8000	0.7090	0.298	-0.07
0.1999	0.7117	0.348	-0.10	0.8499	0.7088	0.294	-0.06
0.3000	0.7113	0.338	-0.11	0.8999	0.7085	0.290	-0.04
0.4000	0.7109	0.330	-0.12	0.9499	0.7082	0.287	-0.02
0.5000	0.7105	0.322	-0.12	1.0000	0.7079	0.283	0.00

**Table 4. Experimental Densities ( $\rho$ ), Viscosities ( $\eta$ ), and Excess Molar Volumes ( $V^E$ ) for  $x$  Ethanol + (1- $x$ ) Hydrocarbon Mixture**

$x$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>
$T=288.15$ K						
0.0000	0.7296	0.450	0.03	0.6001	0.7528	0.698
0.0500	0.7304	0.451	0.14	0.7000	0.7598	0.797
0.1000	0.7317	0.455	0.18	0.8000	0.7686	0.917
0.2000	0.7344	0.474	0.25	0.8500	0.7736	0.991
0.3001	0.7379	0.507	0.27	0.8999	0.7793	1.073
0.4000	0.7421	0.559	0.25	0.9499	0.7860	1.196
0.4999	0.7470	0.619	0.25	1.0000	0.7941	1.311
$T=298.15$ K						
0.0000	0.7210	0.404	-0.03	0.6001	0.7437	0.596
0.0500	0.7217	0.403	0.10	0.7000	0.7508	0.671
0.1000	0.7228	0.406	0.16	0.8000	0.7596	0.768
0.2000	0.7256	0.425	0.24	0.8500	0.7649	0.829
0.3001	0.7290	0.446	0.28	0.8999	0.7707	0.894
0.4000	0.7331	0.485	0.28	0.9499	0.7774	0.977
0.4999	0.7379	0.532	0.27	1.0000	0.7855	1.084
$T=308.15$ K						
0.0000	0.7123	0.365	-0.07	0.6001	0.7347	0.511
0.0500	0.7128	0.363	0.10	0.7000	0.7418	0.575
0.1000	0.7139	0.368	0.18	0.8000	0.7507	0.649
0.2000	0.7166	0.374	0.27	0.8500	0.7559	0.697
0.3001	0.7199	0.398	0.31	0.8999	0.7618	0.750
0.4000	0.7240	0.426	0.30	0.9499	0.7687	0.818
0.4999	0.7289	0.464	0.29	1.0000	0.7768	0.906

coefficients  $a_i$  were determined by a multiple regression analysis based on the least-squares method and are summarized along with the standard deviations of the corresponding fit in Table 6. The standard deviation is defined by

$$\sigma = \left[ \sum_{i=1}^m (Y_i^{\text{exp}} - Y_i^{\text{calc}})^2 / (m - p) \right]^{1/2} \quad (5)$$

where  $m$  is the number of experimental points and  $p$  is the number of adjustable parameters.  $Y^{\text{exp}}$  and  $Y^{\text{calc}}$  are the experimental and fitted values of the respective functions. For the case of  $V^E$ , the  $\sigma$  values lie between  $1.62 \times 10^{-3}$  cm<sup>3</sup>·mol<sup>-1</sup> and  $1.05 \times 10^{-2}$  cm<sup>3</sup>·mol<sup>-1</sup> and the largest  $\sigma$

**Table 5. Experimental Densities ( $\rho$ ), Viscosities ( $\eta$ ), and Excess Molar Volumes ( $V^E$ ) for  $x$  Methyl Ethyl Ketone + (1- $x$ ) Hydrocarbon Mixture**

$x$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$x$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>
$T=288.15$ K							
0.0000	0.7296	0.450	0.03	0.6000	0.7672	0.421	0.30
0.0500	0.7317	0.444	0.14	0.7000	0.7761	0.419	0.27
0.1003	0.7342	0.441	0.18	0.8000	0.7861	0.417	0.20
0.2003	0.7396	0.435	0.25	0.8500	0.7916	0.416	0.16
0.3000	0.7454	0.431	0.30	0.9000	0.7974	0.416	0.11
0.4000	0.7520	0.428	0.32	0.9500	0.8036	0.416	0.06
0.5000	0.7592	0.424	0.32	1.0000	0.8102	0.418	0.00
$T=298.15$ K							
0.0000	0.7210	0.404	-0.03	0.6000	0.7574	0.379	0.33
0.0500	0.7230	0.399	0.09	0.7000	0.7662	0.377	0.29
0.1003	0.7253	0.396	0.15	0.8000	0.7760	0.375	0.22
0.2003	0.7303	0.391	0.27	0.8500	0.7814	0.375	0.18
0.3000	0.7361	0.387	0.32	0.9000	0.7871	0.375	0.13
0.4000	0.7425	0.384	0.34	0.9500	0.7932	0.376	0.07
0.5000	0.7496	0.381	0.34	1.0000	0.7998	0.377	0.00
$T=308.15$ K							
0.0000	0.7123	0.365	-0.07	0.6000	0.7477	0.342	0.35
0.0500	0.7142	0.361	0.05	0.7000	0.7562	0.340	0.31
0.1003	0.7165	0.358	0.14	0.8000	0.7660	0.340	0.23
0.2003	0.7213	0.353	0.26	0.8500	0.7712	0.339	0.18
0.3000	0.7268	0.350	0.33	0.9000	0.7768	0.339	0.14
0.4000	0.7331	0.347	0.35	0.9500	0.7828	0.340	0.07
0.5000	0.7400	0.344	0.36	1.0000	0.7892	0.341	0.00

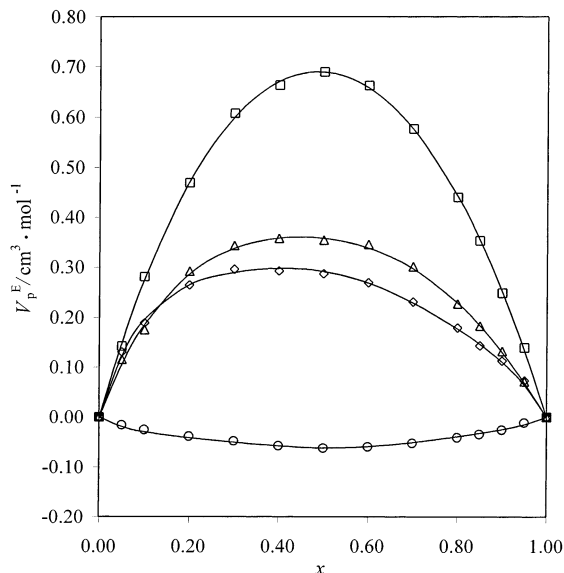
**Table 6. Coefficients of  $V^E$  and  $\Delta\eta$  and Their Standard Deviations**

Y/unit	$T/K$	$a_0$ $\times 10^2$	$a_1$ $\times 10^3$	$a_2$ $\times 10^3$	$a_3$ $\times 10^4$	$a_4$ $\times 10^3$	$\sigma$ $\times 10^5$
Acetone + Hydrocarbon Mixture							
$V^E/$	288.15	125.18	1150.51	83.53	1569.06		412
cm <sup>3</sup> ·mol <sup>-1</sup>	298.15	135.22	1300.67	48.20	1286.77		535
	308.15	147.18	1515.89	69.32	-1776.04	-277.42	1049
$\Delta\eta/\text{mPa}\cdot\text{s}$	288.15	-7.50	-16.44	-4.81	-61.00		51
	298.15	-5.97	-15.93	-6.22	36.75	8.77	30
	308.15	-5.15	-7.76	6.47	-50.91	-8.06	32
Diisopropyl Ether + Hydrocarbon Mixture							
$V^E/$	288.15	-6.35	-109.68	-3.68	770.55	64.38	179
cm <sup>3</sup> ·mol <sup>-1</sup>	298.15	-14.76	-137.00	-35.10	129.18	29.65	162
	308.15	-22.62	-193.82	-72.35	12.61	31.49	190
$\Delta\eta/\text{mPa}\cdot\text{s}$	288.15	-6.34	-8.74	-1.00	15.33		28
	298.15	-5.06	-5.24	-2.08	-22.26		26
	308.15	-4.45	-3.80	3.50	-7.87	-3.58	26
Ethanol + Hydrocarbon Mixture							
$V^E/$	288.15	47.81	270.99	235.32	4058.61		899
cm <sup>3</sup> ·mol <sup>-1</sup>	298.15	53.72	412.38	251.28	2069.05	-189.47	887
	308.15	59.09	516.43	390.35	534.27	-477.39	895
$\Delta\eta/\text{mPa}\cdot\text{s}$	288.15	-57.62	-678.74	-324.61	-2590.90	-93.90	453
	298.15	-46.40	-541.94	-262.24	-2512.16	-113.66	287
	308.15	-38.03	-441.33	-225.91	-2290.99	-105.24	257
Methyl Ethyl Ketone + Hydrocarbon Mixture							
$V^E/$	288.15	63.69	592.67	178.38	-207.71	-206.09	737
cm <sup>3</sup> ·mol <sup>-1</sup>	298.15	69.10	619.62	149.80	1109.22	-136.37	588
	308.15	72.53	680.62	142.82	870.19	-172.54	507
$\Delta\eta/\text{mPa}\cdot\text{s}$	288.15	-7.59	-17.12	-15.62	-171.60		22
	298.15	-6.35	-18.38	-16.71	-114.04	5.19	40
	308.15	-5.65	-16.18	-8.10	-81.55		35

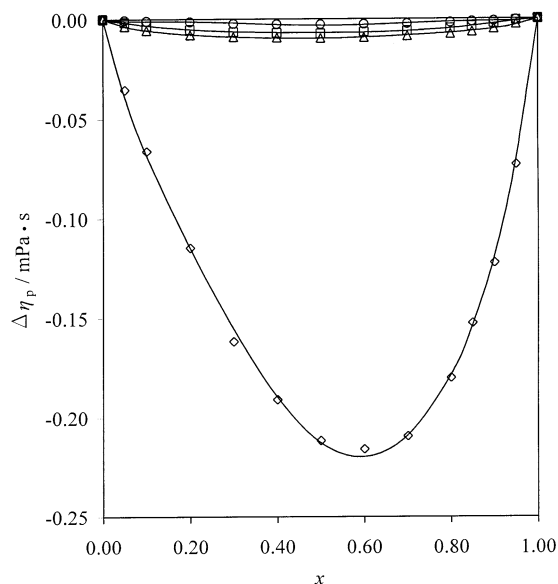
value corresponds to the acetone system at 308.15 K. For the case of  $\Delta\eta$ , the  $\sigma$  values lie between  $2.24 \times 10^{-4}$  mPa·s and  $4.52 \times 10^{-3}$  mPa·s and the largest  $\sigma$  value corresponds to the ethanol system at 288.15 K.

By consideration of the six-component mixture as a pseudo-binary system consisting of a pure component (oxygenates) and a pseudo-pure component (hydrocarbon mixture), the pseudo-excess molar volumes,  $V_p^E$ , can be determined from  $V^E$  data by the following expression

$$V_p^E = V^E - (1 - x)(V^E)_{x=0} \quad (6)$$



**Figure 1.** Variation of pseudo-excess volume with mole fraction for  $x$  oxygenates +  $(1-x)$  hydrocarbon mixture at 298.15 K: (□) acetone; (Δ) methyl ethyl ketone; (◇) ethanol; (○) diisopropyl ether; (—) smoothed.



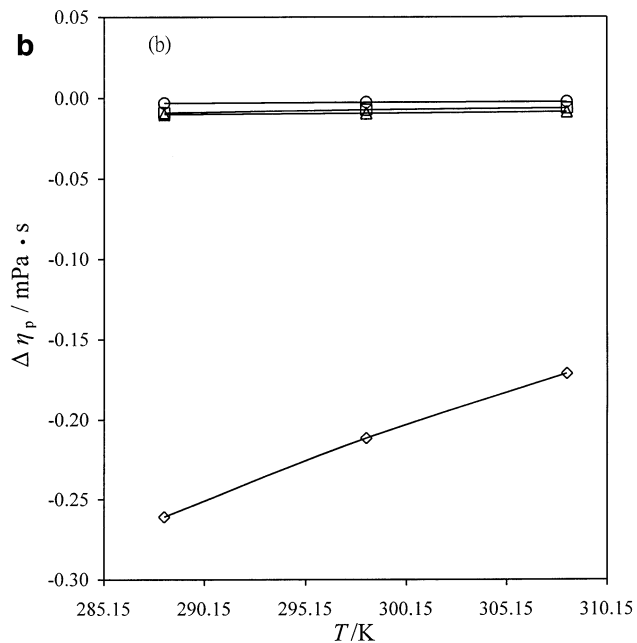
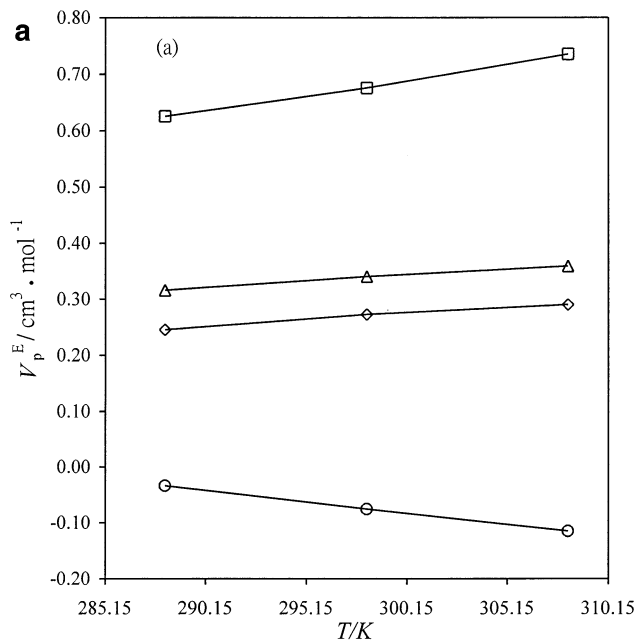
**Figure 2.** Variation of pseudo-viscosity deviation with mole fraction for  $x$  oxygenates +  $(1-x)$  hydrocarbon mixture at 298.15 K: (○) diisopropyl ether; (□) acetone; (Δ) methyl ethyl ketone; (◇) ethanol; (—) smoothed.

where  $x$  is the mole fraction of the oxygenate and  $(V_p^E)_{x=0}$  is the value of  $V_p^E$  at  $x$  to be zero. The pseudo-deviations in viscosity,  $\Delta\eta_p$ , can be determined from  $\Delta\eta$  data from the following equation

$$\Delta\eta_p = \Delta\eta - (1 - x)(\Delta\eta)_{x=0} \quad (7)$$

where  $x$  is the mole fraction of the oxygenate and  $(\Delta\eta)_{x=0}$  is the value of  $\Delta\eta$  at  $x$  to be zero.

Curves of pseudo-excess molar volumes ( $V_p^E$ ) are graphically represented as a function of oxygenate mole fraction for 298.15 K in Figure 1. As can be seen, the systems of acetone, ethanol, and methyl ethyl ketone show positive deviations of  $V_p^E$  over the entire composition range with a maximum at nearly equimolar composition. However, the  $V_p^E$  values are slightly negative for the system of diisopro-



**Figure 3.** Temperature dependence of pseudo-excess molar volume (a) and pseudo-viscosity deviation (b) at  $x = 0.5$  for  $x$  oxygenates +  $(1-x)$  hydrocarbon mixture: (◇) ethanol; (□) acetone; (Δ) methyl ethyl ketone; (○) diisopropyl ether.

pyl ether. The values of  $V_p^E$  at  $x = 0.5$  generally follow the order: acetone > methyl ethyl ketone > ethanol > diisopropyl ether. The systems studied show negative deviations for  $\Delta\eta_p$  in the whole range of composition, with almost zero values for the systems of acetone, methyl ethyl ketone, and diisopropyl ether (Figure 2). The lowest values obtained for the ethanol + hydrocarbon mixture may be explained taking into account the effect of hydrogen bonds between the alcohol species. The values of  $\Delta\eta_p$  at  $x = 0.5$  follow the order: diisopropyl ether > acetone  $\approx$  methyl ethyl ketone > ethanol.

The temperature dependence of  $V_p^E$  and  $\Delta\eta_p$  at  $x = 0.5$  for all of the systems studied is shown in Figure 3a,b. It can be seen that values of  $V_p^E$  increase as the temperature increases for the systems of acetone, ethanol, and methyl ethyl ketone, while decreasing as the temperature in-

creases for the system of diisopropyl ether. The temperature has no significant effect on  $\Delta\eta_p$  for the systems of acetone, diisopropyl ether, and methyl ethyl ketone. However, the  $\Delta\eta_p$  values increase as the temperature increases for the systems of ethanol. The observed  $V_p^E$  or  $\Delta\eta_p$  may be discussed in terms of several opposing effects. Some authors<sup>13–15</sup> explain both composition and temperature dependence of  $V^E$  or  $\Delta\eta$  of 1-alkanol + alkane mixtures as a balance between positive contributions (hydrogen bond rupture and dispersive interactions between unlike molecules) and negative contributions (dipole–dipole interactions and geometrical fitting between components). In addition, the dilution of dipoles affects excess volumes considerably and Marsh<sup>16</sup> showed the evidence of this effect for nitromethane + and nitroethane + each of several nonpolar liquids.

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