Densities, Viscosities, and Refractive Indices for Binary and Ternary Mixtures of Diisopropyl Ether, Ethanol, and 2,2,4-Trimethylpentane

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Densities, viscosities, and refractive indices of the ternary system diisopropyl ether + ethanol + 2,2,4-trimethylpentane at $T = 298.15$ K and the binary systems diisopropyl ether + ethanol and diisopropyl ether + 2,2,4-trimethylpentane were measured at $T =$ (288.15, 298.15, and 308.15) K and atmospheric pressure over the whole composition range. Densities were determined using a vibrating-tube density meter. Viscosities were measured with an automatic Ubbelohde capillary viscometer, and refractive indices were measured using a digital Abbe-type refractometer. Excess molar volumes (V^E), deviations in the viscosity from mole fraction average ($\Delta\eta$), and deviations in the refractive index from volume fraction average (Δn_D) for the mixtures were derived from experimental data. The binary and ternary data of V^E, $\Delta\eta$, and Δn_D were correlated with liquid composition by using the Redlich−Kister and the Cibulka equations.

Introduction

The reformulation of gasoline includes certain oxygenated compounds such as alcohols and ethers. These oxygenated compounds are added to improve the octane rating and pollution-reducing capability of gasoline. This work has been carried out as a part of the project to investigate the thermophysical behavior of liquid mixtures of the oxygenated compounds included in a hydrocarbon mixture.[1−8] The main purpose of the present paper is to investigate the thermophysical properties for binary and ternary systems formed by two oxygenated compounds, such as ethanol and diisopropyl ether, and a hydrocarbon liquid, such as 2,2,4-trimethylpentane. The hydrocarbon liquid is the component that generally appears in gasoline. In this work, we measured the densities, viscosities, and refractive indices of the ternary mixture (diisopropyl ether + ethanol + 2,2,4-trimethylpentane) at 298.15 K and of its constituent binary mixtures (diisopropyl ether + ethanol and diisopropyl ether + 2,2,4-trimethylpentane) at 288.15 K, 298.15 K, and 308.15 K. The other binary mixture ethanol + 2,2,4-trimethylpentane was studied in a previous paper.[8]

The experimental results are used to calculate excess molar volumes, deviations in the viscosity from mole fraction average, and deviations in the refractive index from volume fraction average. The calculated binary data have been fitted to the Redlich−Kister equation to determine the coefficients. For correlating the ternary data, the Cibulka equation was used. A thorough review for thermophysical property measurements on mixtures containing ethers with nonpolar solvents has been conducted by Marsh et al.[9] In the literature, excess molar volumes of the binary mixtures diisopropyl ether + ethanol and diisopropyl ether + 2,2,4-trimethylpentane had been measured at 298.15 K.[10,11] As far as we know, no other data are available for the mixtures investigated here in the open literature.

Experimental Section

Materials. The chemicals used were of analytical grade. Diisopropyl ether (>99 %) and ethanol (>99.8 %) were obtained from Merck (Germany), and 2,2,4-trimethylpentane (>99.5 %) was obtained from Tedia (U.S.A.). All chemicals were used without further purification. The purity of all chemicals was checked by gas chromatography. Gas chromatographic analysis showed that the major peak areas are 99.7 %, 99.9 %, and 99.8 % for diisopropyl ether, ethanol, and 2,2,4-trimethylpentane, respectively. The purity of solvents was further ascertained by comparing their densities, viscosities, and refractive indices at a temperature of 298.15 K. The results are generally in agreement with the corresponding values reported in the literature as shown in Table 1.

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

	ρ/g·cm^{-3}		η/mPa·s		n_D	
	this work	lit	this work	lit	this work	lit
ethanol	0.78517	0.78493[a]	1.084	1.0826[a]	1.35924	1.35941[a]
		0.78502[b]				1.35922[b]
		0.78515[c]				1.3593[c]
diisopropyl ether	0.71870	0.71854[a]	0.313		1.36524	1.3655[a]
2,2,4-trimethyl-entane	0.68774	0.68781[a]	0.480	0.4802[d]	1.38900	1.38898[a]

[a] Riddick et al.[12] [b] Rodriguez et al.[13] [c] Segade et al.[14] [d] Bouzas et al.[15]

Apparatus and Procedure. Liquids were dried over activated molecular sieves, type 0.3 nm, from Aldrich. All the dried liquids were shaken in an ultrasonic oscillator to remove dissolved air. Samples were prepared by mass in a 50 cm^3 Erlenmeyer flask provided with a ground glass joint stopper, using a Precisa 262SMA balance with uncertainty of $\pm 3 \times 10^{-5}$ g. Densities were measured with an Anton Paar DMA-5000 vibrating-tube density meter (Anton-Paar, Graz, Austria) with a stated accuracy of 5×10^{-6} g·cm^{-3} in the range (0 to 3) g·cm^{-3}, thermostatically controlled to within $\pm$ 0.01 K in the temperature range (273.15 to 363.15) K. Calibration was performed periodically under atmospheric pressure, in accordance with specifications, using deionized water and dry air. The uncertainty of the density measurements was estimated to be $\pm 3 \times 10^{-5}$ g·cm^{-3}. The excess molar volumes were calculated from density data, and the uncertainties were estimated to be within $\pm 5 \times 10^{-3}$ cm^3·mol^{-1}.

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Table 2. Experimental Densities (ρ), Viscosities (η), Refractive Indices (n_D), Excess Molar Volumes (V^E), Deviations in the Viscosity ($\Delta\eta$), and Deviations in the Refractive Index (Δn_D) for the Binary Systems at 288.15 K

x_1	ρ / g·cm^{-3}	η / mPa·s	n_D	V^E / cm^3·mol^{-1}	$\Delta\eta$ / mPa·s	Δn_D
Diisopropyl Ether (1) + Ethanol (2)						
0.0000	0.79374	1.309	1.36342	0.000	0.000	0.00000
0.0500	0.78865	1.176	1.36501	−0.173	−0.085	0.00074
0.1000	0.78360	1.046	1.36653	−0.299	−0.167	0.00152
0.1500	0.77902	0.946	1.36768	−0.415	−0.219	0.00202
0.2000	0.77489	0.850	1.36860	−0.527	−0.267	0.00235
0.2500	0.77069	0.771	1.36935	−0.589	−0.298	0.00258
0.3000	0.76692	0.705	1.36998	−0.653	−0.316	0.00274
0.3500	0.76336	0.648	1.37047	−0.700	−0.325	0.00281
0.4000	0.76002	0.599	1.37086	−0.736	−0.326	0.00281
0.4500	0.75693	0.558	1.37117	−0.767	−0.319	0.00276
0.5000	0.75387	0.523	1.37140	−0.768	−0.306	0.00267
0.5500	0.75098	0.493	1.37159	−0.759	−0.287	0.00256
0.6000	0.74829	0.468	1.37172	−0.747	−0.264	0.00241
0.6500	0.74573	0.444	1.37181	−0.725	−0.240	0.00225
0.7000	0.74319	0.423	1.37185	−0.677	−0.213	0.00205
0.7499	0.74073	0.407	1.37185	−0.613	−0.181	0.00183
0.8000	0.73840	0.392	1.37178	−0.543	−0.148	0.00155
0.8500	0.73594	0.378	1.37167	−0.425	−0.114	0.00125
0.9000	0.73360	0.367	1.37147	−0.300	−0.077	0.00087
0.9500	0.73115	0.357	1.37120	−0.127	−0.039	0.00043
1.0000	0.72909	0.348	1.37093	0.000	0.000	0.00000
Diisopropyl Ether (1) + 2,2,4-Trimethylpentane (2)						
0.0000	0.69595	0.537	1.39404	0.000	0.000	0.00000
0.0500	0.69720	0.523	1.39293	0.041	−0.005	−0.00012
0.1000	0.69846	0.511	1.39183	0.084	−0.007	−0.00021
0.1500	0.69973	0.498	1.39072	0.128	−0.011	−0.00029
0.2000	0.70106	0.486	1.38960	0.163	−0.013	−0.00037
0.2500	0.70244	0.474	1.38846	0.192	−0.016	−0.00046
0.3000	0.70386	0.463	1.38733	0.216	−0.017	−0.00052
0.3500	0.70533	0.452	1.38619	0.233	−0.019	−0.00057
0.4000	0.70684	0.442	1.38504	0.247	−0.019	−0.00062
0.4500	0.70837	0.432	1.38390	0.262	−0.020	−0.00064
0.5000	0.70997	0.423	1.38274	0.266	−0.020	−0.00066
0.5500	0.71164	0.414	1.38158	0.262	−0.019	−0.00066
0.6000	0.71336	0.405	1.38042	0.252	−0.019	−0.00064
0.6500	0.71515	0.397	1.37926	0.233	−0.017	−0.00061
0.7000	0.71697	0.389	1.37809	0.215	−0.016	−0.00056
0.7500	0.71885	0.382	1.37691	0.190	−0.013	−0.00051
0.8000	0.72080	0.375	1.37573	0.158	−0.011	−0.00043
0.8500	0.72280	0.368	1.37456	0.122	−0.008	−0.00033
0.9000	0.72490	0.361	1.37337	0.074	−0.006	−0.00022
0.9499	0.72700	0.354	1.37217	0.031	−0.003	−0.00010
1.0000	0.72909	0.348	1.37093	0.000	0.000	0.00000

Table 3. Experimental Densities (ρ), Viscosities (η), Refractive Indices (n_D), Excess Molar Volumes (V^E), Deviations in the Viscosity ($\Delta\eta$), and Deviations in the Refractive Index (Δn_D) for the Binary Systems at 298.15 K

x_1	ρ / g·cm^{-3}	η / mPa·s	n_D	V^E / cm^3·mol^{-1}	$\Delta\eta$ / mPa·s	Δn_D
Diisopropyl Ether (1) + Ethanol (2)						
0.0000	0.78517	1.084	1.35924	0.000	0.000	0.00000
0.0500	0.77996	0.975	1.36077	−0.186	−0.070	0.00085
0.1000	0.77478	0.875	1.36210	−0.321	−0.132	0.00159
0.1500	0.77005	0.793	1.36310	−0.443	−0.175	0.00206
0.2000	0.76579	0.719	1.36392	−0.561	−0.211	0.00242
0.2500	0.76145	0.656	1.36456	−0.624	−0.235	0.00264
0.3000	0.75763	0.603	1.36510	−0.698	−0.250	0.00280
0.3500	0.75393	0.558	1.36550	−0.745	−0.256	0.00286
0.4000	0.75047	0.519	1.36582	−0.779	−0.257	0.00287
0.4500	0.74728	0.486	1.36608	−0.810	−0.251	0.00285
0.5000	0.74413	0.458	1.36630	−0.811	−0.241	0.00281
0.5500	0.74118	0.432	1.36642	−0.804	−0.228	0.00269
0.6000	0.73839	0.412	1.36648	−0.788	−0.209	0.00253
0.6500	0.73573	0.392	1.36649	−0.759	−0.191	0.00234
0.7000	0.73310	0.376	1.36646	−0.704	−0.168	0.00212
0.7499	0.73059	0.362	1.36638	−0.639	−0.144	0.00187
0.8000	0.72819	0.350	1.36627	−0.564	−0.117	0.00159
0.8500	0.72576	0.339	1.36611	−0.455	−0.090	0.00128
0.9000	0.72336	0.329	1.36588	−0.323	−0.061	0.00090
0.9500	0.72098	0.320	1.36558	−0.166	−0.032	0.00047
1.0000	0.71870	0.313	1.36524	0.000	0.000	0.00000
Diisopropyl Ether (1) + 2,2,4-Trimethylpentane (2)						
0.0000	0.68774	0.480	1.38900	0.000	0.000	0.00000
0.0500	0.68886	0.468	1.38786	0.051	−0.004	−0.00012
0.1000	0.69003	0.456	1.38672	0.095	−0.007	−0.00022
0.1500	0.69123	0.445	1.38557	0.135	−0.010	−0.00031
0.2000	0.69245	0.435	1.38443	0.174	−0.012	−0.00038
0.2500	0.69375	0.425	1.38326	0.199	−0.013	−0.00047
0.3000	0.69508	0.415	1.38209	0.222	−0.015	−0.00053
0.3500	0.69643	0.406	1.38092	0.244	−0.016	−0.00058
0.4000	0.69784	0.397	1.37974	0.257	−0.016	−0.00063
0.4500	0.69926	0.388	1.37856	0.273	−0.017	−0.00065
0.5000	0.70076	0.380	1.37737	0.277	−0.017	−0.00067
0.5500	0.70232	0.372	1.37618	0.272	−0.016	−0.00067
0.6000	0.70394	0.364	1.37499	0.260	−0.016	−0.00065
0.6500	0.70561	0.357	1.37380	0.242	−0.014	−0.00062
0.7000	0.70732	0.350	1.37259	0.222	−0.013	−0.00058
0.7499	0.70908	0.343	1.37138	0.197	−0.012	−0.00052
0.8000	0.71090	0.337	1.37016	0.166	−0.009	−0.00045
0.8500	0.71278	0.330	1.36896	0.128	−0.008	−0.00034
0.9000	0.71475	0.325	1.36774	0.080	−0.005	−0.00023
0.9500	0.71673	0.319	1.36650	0.034	−0.002	−0.00012
1.0000	0.71870	0.313	1.36524	0.000	0.000	0.00000

The kinematic viscosities were determined with commercial Ubbelohde capillary viscometers (Cannon Instrument Co., State College, PA) of (0.36 and 0.47) mm diameter. The viscometer was kept in a Lauda D20 KP thermostat controlled to ± 0.01 K with a proportional-integral-differential regulator. A computer-controlled measuring system (Lauda, Lauda-Königshofen, Germany) with an uncertainty of ± 0.01 s was used for flow-time measurement. The range of the flow time for the liquids investigated varied from 360 s to 750 s. The kinematic viscosities (ν) were determined according to

$$\nu = k(t - \theta) \tag{1}$$

where k is the viscometer constant, t is the flow time, and θ is the Hagenbach correction. The absolute viscosity (η) was then calculated from the density by the relation $\eta = \nu\rho$. The values of k, which were determined by calibrating with pure water at working temperatures, are 0.001047 ± 0.000001 mm^2·s^{-2} and 0.002736 ± 0.000002 mm^2·s^{-2} for the capillary viscometers with 0.36 mm and 0.47 mm in diameter, respectively. The value θ, which is dependent on the flow time and the size of capillary, was taken from the tables supplied by the manufacturer. Triplicate measurements of flow times were reproducible within ± 0.02 s. The uncertainty of the viscosity measurement was estimated to be less than ± 0.006 mPa·s.

Refractive indices (n_D) were measured with an automatic Anton Paar RXA-156 refractometer, which works at the wavelength (589 nm) corresponding to the D-line of sodium. The measuring temperature range of this refractometer is from 283.15 K to 343.15 K with an accuracy of 0.03 K. Calibration was performed periodically under atmospheric pressure, in accordance with specifications, using double distilled water. The uncertainty of refractive index measurement was estimated to be within ± 0.00002.

The densities, viscosities, and refractive indices of the binary systems diisopropyl ether + ethanol and diisopropyl ether + 2,2,4-trimethylpentane were measured at temperatures of (288.15, 298.15, and 308.15) K. A set with the compositions varying from 0.05 to 0.95 mole fractions was prepared for each binary system. A total of 55 compositions were measured at 298.15 K for the ternary system diisopropyl ether + ethanol + 2,2,4-trimethylpentane. All measurements described above were performed at least three times at atmospheric pressure (100.5 ± 0.3) kPa, and an average of at least three measurements was calculated for each temperature.

Results and Discussion

Tables 2 to 4 list the experimental densities, viscosities, refractive indices, excess molar volumes, deviations in the viscosity from mole fraction average, and deviations in the refractive index from volume fraction average for two binary mixtures diisopropyl ether + ethanol and diisopropyl ether +

Table 4. Experimental Densities (ρ), Viscosities (η), Refractive Indices (n_D), Excess Molar Volumes (V^E), Deviations in the Viscosity ($\Delta\eta$), and Deviations in the Refractive Index (Δn_D) for the Binary Systems at 308.15 K

x_1	ρ / g·cm^{-3}	η / mPa·s	n_D	V^E / cm^3·mol^{-1}	$\Delta\eta$ / mPa·s	Δn_D
Diisopropyl Ether (1) + Ethanol (2)						
0.0000	0.77649	0.905	1.35502	0.000	0.000	0.00000
0.0500	0.77113	0.814	1.35646	−0.198	−0.060	0.00094
0.1000	0.76584	0.736	1.35763	−0.345	−0.107	0.00167
0.1500	0.76098	0.670	1.35850	−0.475	−0.142	0.00215
0.2000	0.75658	0.612	1.35923	−0.599	−0.169	0.00254
0.2500	0.75216	0.562	1.35977	−0.673	−0.188	0.00277
0.3000	0.74812	0.520	1.36021	−0.739	−0.198	0.00293
0.3500	0.74432	0.484	1.36052	−0.789	−0.203	0.00299
0.4000	0.74076	0.453	1.36077	−0.826	−0.203	0.00302
0.4500	0.73750	0.426	1.36093	−0.861	−0.199	0.00297
0.5000	0.73430	0.403	1.36107	−0.868	−0.191	0.00292
0.5500	0.73125	0.383	1.36113	−0.858	−0.180	0.00280
0.6000	0.72837	0.365	1.36113	−0.839	−0.167	0.00264
0.6500	0.72559	0.350	1.36108	−0.802	−0.151	0.00244
0.7000	0.72286	0.336	1.36098	−0.739	−0.134	0.00220
0.7499	0.72023	0.324	1.36085	−0.660	−0.115	0.00194
0.8000	0.71779	0.314	1.36068	−0.585	−0.093	0.00165
0.8500	0.71531	0.305	1.36044	−0.472	−0.071	0.00130
0.9000	0.71289	0.297	1.36019	−0.340	−0.048	0.00094
0.9500	0.71053	0.289	1.35986	−0.190	−0.025	0.00051
1.0000	0.70812	0.283	1.35944	0.000	0.000	0.00000
Diisopropyl Ether (1) + 2,2,4-Trimethylpentane (2)						
0.0000	0.67943	0.432	1.38395	0.000	0.000	0.00000
0.0500	0.68044	0.422	1.38277	0.052	−0.003	−0.00012
0.1000	0.68152	0.412	1.38159	0.095	−0.005	−0.00023
0.1500	0.68262	0.402	1.38042	0.136	−0.008	−0.00031
0.2000	0.68375	0.393	1.37924	0.175	−0.009	−0.00038
0.2500	0.68495	0.384	1.37803	0.200	−0.011	−0.00047
0.3000	0.68617	0.375	1.37682	0.225	−0.012	−0.00054
0.3500	0.68742	0.367	1.37561	0.247	−0.013	−0.00059
0.4000	0.68872	0.359	1.37440	0.262	−0.013	−0.00063
0.4500	0.69003	0.351	1.37317	0.279	−0.014	−0.00067
0.5000	0.69142	0.343	1.37195	0.282	−0.015	−0.00068
0.5500	0.69286	0.336	1.37072	0.279	−0.014	−0.00068
0.6000	0.69435	0.329	1.36949	0.270	−0.014	−0.00067
0.6500	0.69592	0.323	1.36826	0.248	−0.012	−0.00063
0.7000	0.69750	0.316	1.36703	0.230	−0.012	−0.00057
0.7500	0.69914	0.310	1.36578	0.204	−0.010	−0.00052
0.8000	0.70083	0.305	1.36452	0.173	−0.008	−0.00045
0.8500	0.70259	0.299	1.36327	0.133	−0.006	−0.00035
0.9000	0.70442	0.294	1.36201	0.085	−0.004	−0.00024
0.9499	0.70628	0.288	1.36073	0.037	−0.002	−0.00013
1.0000	0.70812	0.283	1.35944	0.000	0.000	0.00000

2,2,4-trimethylpentane at temperatures of (288.15, 298.15, and 308.15) K. The molar excess volumes (V^E) were calculated from density data according to

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

where x_i, M_i, and ρ_i, are the mole fraction, molar mass, and density of pure component i, respectively; ρ is the density of the mixture; and N is the number of components.

In the system studied, excess molar volumes are positive for the mixtures diisopropyl ether + 2,2,4-trimethylpentane and negative for the mixture diisopropyl ether + ethanol over the whole composition range. The values of V^E increase for the system the diisopropyl ether + 2,2,4-trimethylpentane and decrease for the system diisopropyl ether + ethanol from 288.15 K to 308.15 K. The excess molar volume V^E ($x = 0.5$) increases in the sequence: diisopropyl ether + 2,2,4-trimethylpentane > diisopropyl ether + ethanol. The values of V^E ($x = 0.5$) vary from −0.087 cm^3·mol^{-1} to 0.283 cm^3·mol^{-1}. In the literature, V^E of the two binary systems in this study had been measured

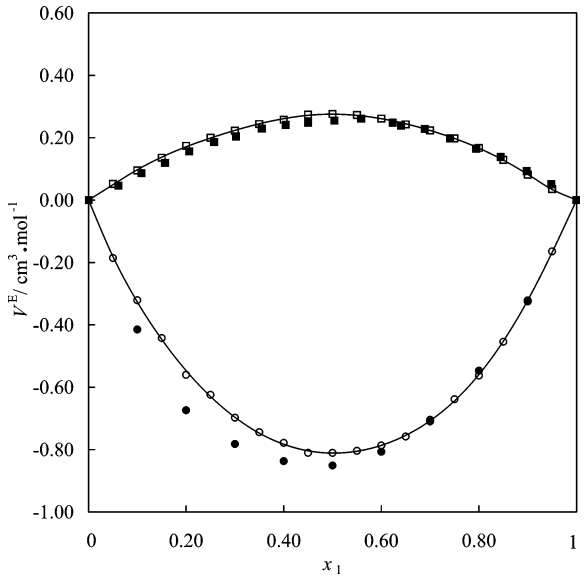

Figure 1. Variation of excess molar volume (V^E) with mole fraction (x_1) for the binary systems at $T = 298.15$ K: ○, diisopropyl ether + ethanol; ●, diisopropyl ether + ethanol from Rezanova et al.;[10] □, diisopropyl ether + 2,2,4-trimethylpentane; ■, diisopropyl ether + 2,2,4-trimethylpentane from from Blanco et al.[11] Solid curves were calculated from the Redlich−Kister equation.

at 298.15 K. Figure 1 shows the excess molar volumes for these two systems at $T = 298.15$ K together with the literature values. From this figure, it can be seen that our results are generally in agreement with the literature data for the system diisopropyl ether + 2,2,4-trimethylpentane.[10] However, in the high ethanol region, our data gave somewhat higher values than the literature data for the system diisopropyl ether + ethanol.[11]

The dependence of V^E on both composition and temperature for the present mixtures may be explained as a balance between positive contributions (hydrogen bond rupture, dispersive interactions between unlike molecules) and negative contributions (intermolecular dipolar interactions and geometrical fitting between components). In the present investigation, ethanol is strongly self-associated through hydrogen bonding, but diisopropyl ether and 2,2,4-trimethylpentane do not exhibit this property. The interactions of ethanol and diisopropyl ether against 2,2,4-trimethylpentane molecules involve mainly dispersion force giving a positive contribution to V^E. The interactions between ethanol and diisopropyl ether molecules lead to hydrogen bond effects and/or weak dispersion type, giving a negative contribution to V^E.

The deviation of the viscosity from the mole fraction average ($\Delta\eta$) is given by

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

where η is the absolute viscosities of the mixtures and η_i is the absolute viscosities of pure component i. The $\Delta\eta$ values, which are negative over the entire range of composition, increase as the increase of temperature. However, the $\Delta\eta$ values in the mixture diisopropyl ether + 2,2,4-trimethylpentane show little variation with temperature. The values of $\Delta\eta$ show the order as diisopropyl ether + 2,2,4-trimethylpentane > diisopropyl ether + ethanol. The values of $\Delta\eta$ ($x = 0.5$) vary from −0.305 mPa·s to −0.014 mPa·s. Figure 2 plots the results of $\Delta\eta$ for these two binary mixtures at 298.15 K.

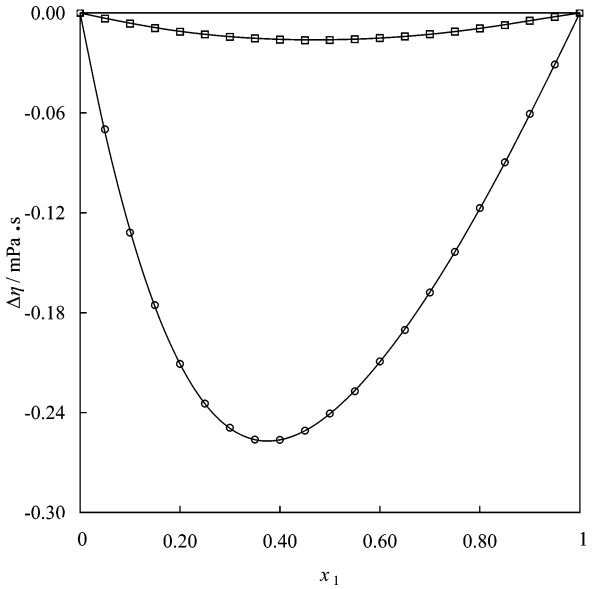

Figure 2. Variation of deviation in the viscosity ($\Delta\eta$) with mole fraction (x_1) for the binary systems at $T = 298.15$ K: ○, diisopropyl ether + ethanol; □, diisopropyl ether + 2,2,4-trimethylpentane, Solid curves were calculated from the Redlich−Kister equation.

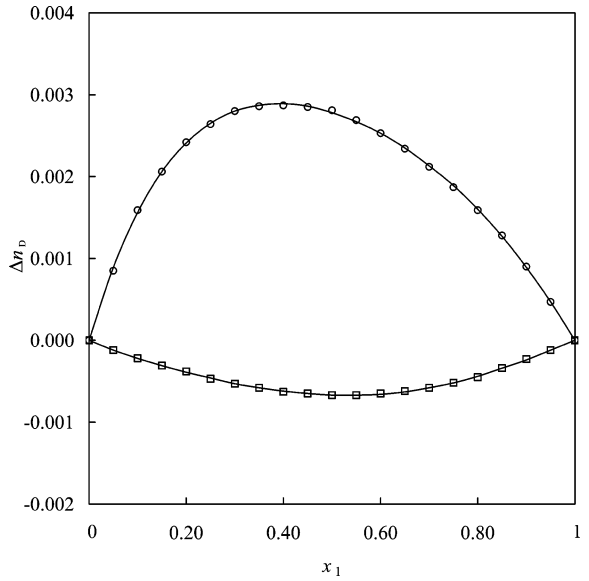

Figure 3. Variation of deviation in the refractive index (Δn_D) with mole fraction (x_1) for the binary systems at $T = 298.15$ K: ○, diisopropyl ether + ethanol; □, diisopropyl ether + 2,2,4-trimethylpentane. Solid curves were calculated from the Redlich−Kister equation.

The deviations in refractive index (Δn_D) were calculated from the volume fraction average as suggested by Brocos et al.[16] and are given by

$$\Delta n_D = n_D - \sum_{i=1}^{N} \phi_i n_{Di} \tag{4}$$

and

$$\phi_i = \frac{x_i V}{\sum_{i=1}^{N} x_i V_i} \tag{5}$$

where n_D, n_{Di}, and ϕ_i are the refractive index of the mixture, the refractive index of pure component i, and the volume fraction of component i, respectively. V and V_i are the molar volume of the mixture and the molar volume of component i, respectively. N is the number of components. The Δn_D values, which increase as the increase of temperature, are negative for the systems diisopropyl ether + 2,2,4-trimethylpentane and positive for the system diisopropyl ether + ethanol over the whole composition. The values of Δn_D ($x = 0.5$) follow the order: diisopropyl ether + ethanol > diisopropyl ether + 2,2,4-trimethylpentane. The values of Δn_D ($x = 0.5$) vary from −0.00066 to 0.00292. Figure 3 shows the results of Δn_D as a function of mole fraction for these two binary systems at $T = 298.15$ K.

The mixing functions V^E, $\Delta\eta$, and Δn_D were represented mathematically by the Redlich−Kister equation[17] for correlating the experimental data:

$$\Delta Q_{ij} = x_i x_j \sum_{k=0}^{m} a_k (x_i - x_j)^k \tag{6}$$

where ΔQ_{ij} refers to V^E/cm^3·mol^{-1}, $\Delta\eta$/mPa·s, or Δn_D for each $i-j$ binary pair, x_i is the mole fraction of component i, and a_k are the coefficients. The values of coefficients a_k were determined by a multiple regression analysis based on the least-squares method and are summarized along with the standard deviations between the experimental and fitted values of the respective functions in Table 5. The standard deviation (σ) is defined by

$$\sigma = \left[\sum_{i=1}^{n} \frac{(\Delta Q_i^{exptl} - \Delta Q_i^{calcd})^2}{n - p}\right]^{1/2} \tag{7}$$

where n is the number of experimental points and p is the number of adjustable parameters. The σ values lie between 0.0032 cm^3·mol^{-1} and 0.0090 cm^3·mol^{-1}, between 0.00045 mPa·s and 0.0017 mPa·s, and between 0.000006 and 0.000017 for V^E, $\Delta\eta$, and Δn_D, respectively.

McAllister's multibody interaction model[18] is widely used for correlating the kinematic viscosity of binary mixtures with mole fraction. The three-body model is defined as

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln \nu_{12} + 3x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln\left(x_1 + \frac{x_2 M_2}{M_1}\right) + 3x_1^2 x_2 \ln\left(\frac{2 + M_2/M_1}{3}\right) + 3x_1 x_2^2 \ln\left(\frac{1 + 2M_2/M_1}{3}\right) + x_2^3 \ln\left(\frac{M_2}{M_1}\right) \tag{8}$$

and the four-body model is given by

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3 x_2 \ln \nu_{1112} + 6x_1^2 x_2^2 \ln \nu_{1122} + 4x_1 x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \ln\left(x_1 + \frac{x_2 M_2}{M_1}\right) + 4x_1^3 x_2 \ln\left(\frac{3 + M_2/M_1}{4}\right) + 6x_1^2 x_2^2 \ln\left(\frac{1 + M_2/M_1}{2}\right) + 4x_1 x_2^3 \ln\left(\frac{1 + 3M_2/M_1}{4}\right) + x_2^4 \ln\left(\frac{M_2}{M_1}\right) \tag{9}$$

where ν, ν_1, and ν_2 are the kinematic viscosities of the mixture and the viscosities of pure components 1 and 2, respectively. The ν_{12}, ν_{21}, ν_{1112}, ν_{1122}, and ν_{2221} are the model parameters. Table 6 records the calculated results with the standard deviation defined as eq 7. It is shown that McAllister's four-body equation

Table 5. Binary Coefficients of the Redlich−Kister Equation from T = 288.15 K to T = 308.15 K and Ternary Coefficients of the Cibulka Equation at T = 298.15 K for V^E, $\Delta\eta$, and Δn_D

ΔQ_{ij}	T/K	a_0	a_1	a_2	a_3	a_4	σ
Diisopropyl Ether (1) + Ethanol (2)							
V^E/cm^3·mol^{-1}	288.15	−3.0617	−0.2260	−0.8975	0.4632	0.8091	0.0090
	298.15	−3.2489	−0.0397	−0.5768			0.0062
	308.15	−3.4501	0.0222	−0.5725			0.0068
$\Delta\eta$/mPa·s	288.15	−1.2210	0.6352	−0.2577	−0.0646	0.1357	0.0017
	298.15	−0.9649	0.4896	−0.1934	−0.0171	−0.0627	0.00089
	308.15	−0.7649	0.3761	−0.1531	0.0482		0.00045
Δn_D	288.15	0.0107	−0.0041	0.0053	−0.0003	−0.0027	0.000025
	298.15	0.0111	−0.0037	0.0039	−0.0014		0.000017
	308.15	0.0116	−0.0040	0.0033	−0.0016	0.0016	0.000011
Diisopropyl Ether (1) + 2,2,4-Trimethylpentane (2)							
V^E/cm^3·mol^{-1}	288.15	1.0578	−0.0231	−0.2124			0.00041
	298.15	1.0937	0.0324	−0.1589	−0.2045		0.00032
	308.15	1.1128	0.0534	−0.1340	−0.2344		0.00032
$\Delta\eta$/mPa·s	288.15	−0.0794	0.0120	0.0086			0.00045
	298.15	−0.0667	0.0118	−0.0008			0.00042
	308.15	−0.0572	0.0053	0.0079			0.00045
Δn_D	288.15	−0.0026	−0.0004	0.0004	0.0004		0.000007
	298.15	−0.0027	−0.0004	0.0002	0.0004		0.000006
	308.15	−0.0027	−0.0003	0.0003	0.0003		0.000007
Ethanol (1) + 2,2,4-Trimethylpentane (2)[a]							
V^E/cm^3·mol^{-1}	288.15	1.3418	−0.1575	0.7057	−0.3862		0.0051
	298.15	1.5723	−0.2110	0.4907	−0.5872	0.7893	0.0064
	308.15	1.8273	−0.3084	0.4987	−0.8404	1.1139	0.0078
$\Delta\eta$/mPa·s	288.15	−0.9616	−0.2386	−0.2272	−0.2452	0.2253	0.00054
	298.15	−0.7755	−0.1974	−0.1710	−0.1549	−0.1920	0.00077
	308.15	−0.6353	−0.1626	−0.1065	−0.1225	−0.2260	0.00070
Δn_D	288.15	−0.0050	−0.0023	−0.0026	−0.0010	−0.0025	0.000006
	298.15	−0.0056	−0.0019	−0.0030	−0.0017	−0.0031	0.000008
	308.15	−0.0064	−0.0020	−0.0032	−0.0011	−0.0036	0.000014

ΔQ_{123}	C_0	C_1	C_2	σ
V^E/cm^3·mol^{-1}	−5.2826	3.8397	7.3305	0.0097
$\Delta\eta$/mPa·s	0.5508	−0.1780	−0.2629	0.0032
Δn_D	0.0094	0.0068	−0.0189	0.00010

[a] Chen and Tu.[8]

Table 6. Parameters of McAllister's Three-Body and Four-Body Interaction Model and Standard Deviations for Kinematic Viscosities

	three-body			four-body			
T	ν_{12}	ν_{21}	$10^4\sigma$	ν_{1112}	ν_{1122}	ν_{2221}	$10^4\sigma$
K	mm^2·s^{-1}	mm^2·s^{-1}	mm^2·s^{-1}	mm^2·s^{-1}	mm^2·s^{-1}	mm^2·s^{-1}	mm^2·s^{-1}
Diisopropyl Ether (1) + Ethanol (2)							
288.15	0.5443	0.7928	47	0.5393	0.6202	0.9689	21
298.15	0.4946	0.6906	27	0.4866	0.5598	0.8289	10
308.15	0.4543	0.6098	14	0.4432	0.5116	0.7177	6
Diisopropyl Ether (1) + 2,2,4-Trimethylpentane (2)							
288.15	0.5485	0.6405	6	0.5327	0.5864	0.6748	2
298.15	0.4998	0.5829	2	0.4837	0.5374	0.6110	1
308.15	0.4580	0.5342	2	0.4434	0.4928	0.5591	2

gave a better result for those two systems. The σ/mm^2·s^{-1} values for this model lie between 0.0001 and 0.0021, and the largest σ value corresponds to diisopropyl ether + ethanol system at T = 288.15 K.

The experimental densities, viscosities, refractive indices, excess molar volumes, deviations in the viscosity from mole fraction average, and deviations in the refractive index from volume fraction average for the ternary system diisopropyl ether (1) + ethanol (2) + 2,2,4-trimethylpentane (3) at a temperature of 298.15 K are listed in Table 7. The derived properties (V^E/cm^3·mol^{-1}, $\Delta\eta$/mPa·s, and Δn_D) as defined in eqs 2 to 4 for the ternary system were correlated respectively using

$$\Delta Q_{123} = \Delta Q_{bin} + x_1 x_2 x_3 \Delta_{123} \quad (10)$$

and

$$\Delta Q_{bin} = \Delta Q_{12} + \Delta Q_{13} + \Delta Q_{23} \quad (11)$$

where ΔQ_{123} refers to V^E, $\Delta\eta$, or Δn_D for the ternary system diisopropyl ether (1) + ethanol (2) + 2,2,4-trimethylpentane (3), $x_3 = 1 - x_1 - x_2$ and ΔQ_{ij} is the binary contribution of each $i-j$ pair to the V^E, $\Delta\eta$, or Δn_D given by eq 6 with the parameters shown in Table 5. The ternary contribution term Δ_{123} was correlated using the expression suggested by Cibulka:[19]

$$\Delta_{123} = C_0 + C_1 x_1 + C_2 x_2 \quad (12)$$

Table 7. Experimental Densities (ρ), Viscosities (η), Refractive Indices (n_D), and Excess Molar Volumes (V^E), Deviations in the Viscosity ($\Delta\eta$), and Deviations in the Refractive Index (Δn_D) for the Ternary System Diisopropyl Ether (1) + Ethanol (2) + 2,2,4-Trimethylpentane (3) at 298.15 K

x_1	x_2	ρ g·cm^{-3}	η mPa·s	n_D	V^E cm^3·mol^{-1}	$\Delta\eta$ mPa·s	Δn_D
0.0500	0.9000	0.76721	0.879	1.36383	−0.074	−0.136	0.00034
0.0500	0.8000	0.74779	0.768	1.36881	0.069	−0.187	−0.00035
0.0500	0.7000	0.73346	0.682	1.37278	0.164	−0.212	−0.00071
0.0500	0.6000	0.72240	0.618	1.37605	0.233	−0.216	−0.00084
0.0500	0.5001	0.71368	0.565	1.37872	0.273	−0.209	−0.00089
0.0500	0.3999	0.70656	0.523	1.38101	0.299	−0.190	−0.00089
0.0500	0.3000	0.70073	0.494	1.38297	0.302	−0.159	−0.00128
0.0500	0.2000	0.69590	0.474	1.38474	0.277	−0.118	−0.00063
0.0501	0.0999	0.69193	0.464	1.38637	0.210	−0.068	−0.00041
0.0500	0.0500	0.69025	0.461	1.38719	0.153	−0.041	−0.00020
0.1000	0.8500	0.76330	0.800	1.36481	−0.224	−0.177	0.00098
0.1000	0.7500	0.74518	0.702	1.36938	−0.064	−0.214	0.00019
0.1000	0.6500	0.73166	0.631	1.37305	0.045	−0.225	−0.00026
0.1000	0.5500	0.72115	0.574	1.37609	0.124	−0.221	−0.00050
0.1000	0.4499	0.71268	0.533	1.37866	0.189	−0.202	−0.00060
0.1000	0.3500	0.70585	0.500	1.38083	0.223	−0.175	−0.00066
0.1000	0.2500	0.70020	0.475	1.38275	0.234	−0.140	−0.00061
0.1000	0.1501	0.69552	0.460	1.38446	0.216	−0.094	−0.00048
0.1000	0.0500	0.69166	0.453	1.38605	0.153	−0.040	−0.00028
0.2000	0.7500	0.75585	0.664	1.36628	−0.439	−0.236	0.00186
0.2000	0.6500	0.73999	0.596	1.37017	−0.249	−0.243	0.00096
0.2000	0.5500	0.72792	0.543	1.37338	−0.114	−0.236	0.00038
0.2000	0.4500	0.71837	0.504	1.37610	−0.010	−0.215	0.00004
0.2000	0.3501	0.71062	0.475	1.37842	0.072	−0.183	−0.00018
0.2000	0.2500	0.70424	0.453	1.38042	0.129	−0.145	−0.00031
0.2000	0.1501	0.69893	0.439	1.38221	0.162	−0.098	−0.00032
0.2000	0.0500	0.69447	0.432	1.38382	0.168	−0.045	−0.00029
0.3000	0.6500	0.74906	0.564	1.36720	−0.570	−0.259	0.00231
0.3000	0.5500	0.73520	0.515	1.37058	−0.372	−0.247	0.00135
0.3000	0.4500	0.72434	0.479	1.37345	−0.213	−0.223	0.00072
0.3000	0.3500	0.71559	0.452	1.37592	−0.081	−0.189	0.00031
0.3000	0.2501	0.70846	0.432	1.37804	0.020	−0.149	0.00002
0.3000	0.1500	0.70250	0.421	1.37991	0.100	−0.100	−0.00016
0.3000	0.0500	0.69740	0.414	1.38153	0.176	−0.046	−0.00030
0.4000	0.5500	0.74302	0.492	1.36775	−0.648	−0.253	0.00247
0.4000	0.4501	0.73069	0.456	1.37077	−0.428	−0.229	0.00152
0.4000	0.3501	0.72086	0.431	1.37335	−0.246	−0.194	0.00085
0.3999	0.2501	0.71286	0.414	1.37560	−0.094	−0.150	0.00039
0.4000	0.1500	0.70620	0.402	1.37756	0.037	−0.102	0.00006
0.3999	0.0501	0.70047	0.395	1.37923	0.175	−0.049	−0.00027
0.5000	0.4500	0.73749	0.436	1.36799	−0.664	−0.232	0.00240
0.5000	0.3500	0.72648	0.413	1.37073	−0.430	−0.195	0.00147
0.5000	0.2499	0.71754	0.398	1.37309	−0.228	−0.149	0.00080
0.5000	0.1501	0.71011	0.387	1.37513	−0.041	−0.100	0.00027
0.5000	0.0500	0.70369	0.379	1.37684	0.162	−0.048	−0.00022
0.6000	0.3500	0.73250	0.398	1.36803	−0.638	−0.193	0.00214
0.6000	0.2500	0.72251	0.382	1.37050	−0.376	−0.149	0.00122
0.5999	0.1502	0.71425	0.370	1.37262	−0.135	−0.101	0.00050
0.6000	0.0499	0.70712	0.363	1.37440	0.126	−0.047	−0.00016
0.7000	0.2500	0.72778	0.366	1.36790	−0.542	−0.148	0.00175
0.7000	0.1499	0.71863	0.355	1.37012	−0.247	−0.099	0.00083
0.6999	0.0500	0.71076	0.349	1.37197	0.074	−0.044	−0.00002
0.7999	0.1501	0.72330	0.343	1.36759	−0.378	−0.094	0.00125
0.7999	0.0500	0.71465	0.336	1.36951	−0.004	−0.041	0.00021
0.8999	0.0501	0.71876	0.324	1.36701	−0.097	−0.036	0.00048

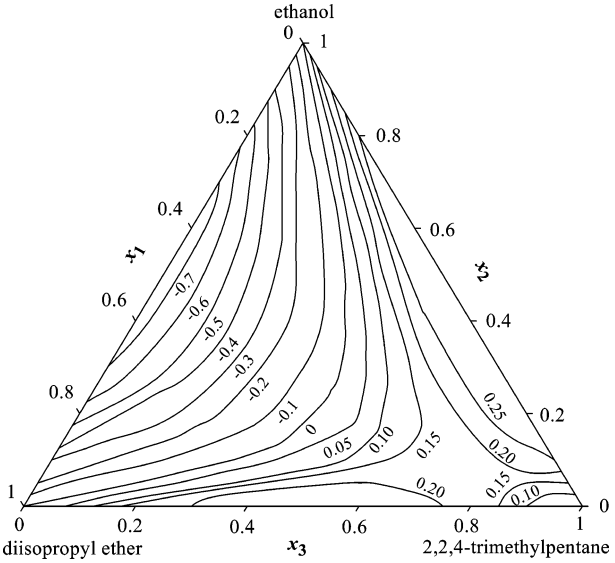

Figure 4. Curves of constant $V^E/cm^3 \cdot mol^{-1}$ for the ternary system diisopropyl ether (1) + ethanol (2) + 2,2,4-trimethylpentane (3) at 298.15 K.

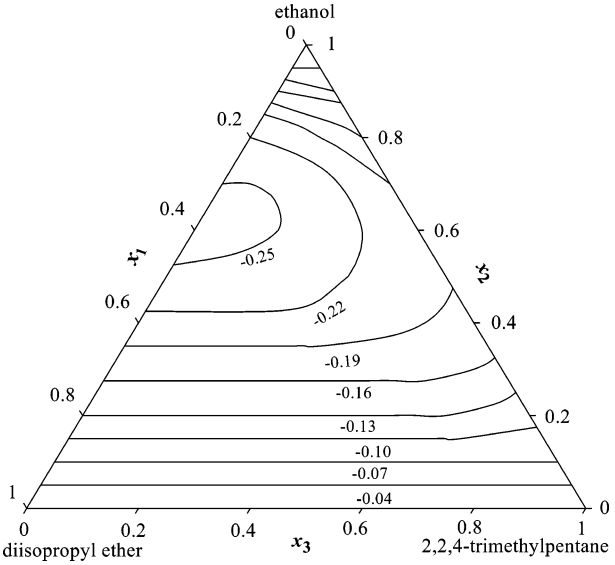

Figure 5. Curves of constant $\Delta\eta$ for the ternary system diisopropyl ether (1) + ethanol (2) + 2,2,4-trimethylpentane (3) at 298.15 K.

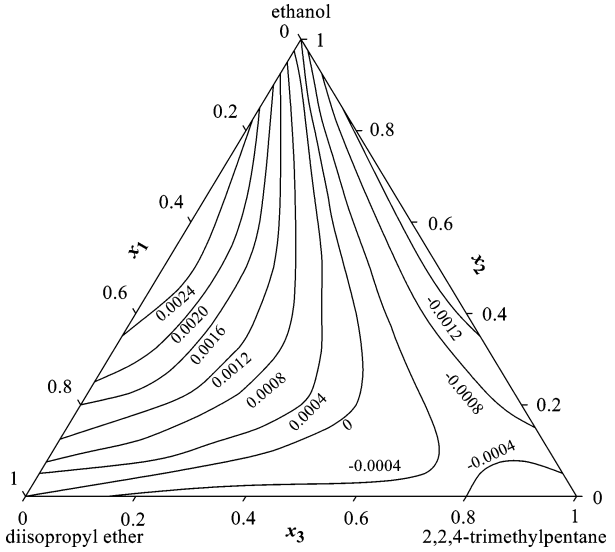

Figure 6. Curves of constant Δn_D for the ternary system diisopropyl ether (1) + ethanol (2) + 2,2,4-trimethylpentane (3) at 298.15 K.

The ternary parameters C_0, C_1, and C_2 were determined with the optimization algorithm similar to that for the binary parameters. The parameters C_0, C_1, and C_2 and the corresponding standard deviations are given in Table 5. The σ values are 0.0097 $cm^3 \cdot mol^{-1}$, 0.0032 mPa·s, and 0.00010 for V^E, $\Delta\eta$, and Δn_D, respectively. The curves of constant V^E, $\Delta\eta$, and Δn_D at 298.15 K were calculated from eqs 10 to12 and were plotted in Figures 4 to 6, respectively. As can be expected, the ternary system shows both positive and negative values of V^E (Figure 4). The minimum V^E value is found near $x_1 = 0.5$ of the binary system diisopropyl ether + ethanol. Figure 5 shows negative values for ternary $\Delta\eta$, with a minimum value near $x_1 = 0.4$ of the binary system diisopropyl ether + ethanol. Figure 6 shows the both positive and negative values for ternary Δn_D, with the maximum Δn_D value near $x_1 = 0.4$ of the binary system diisopropyl ether + ethanol.

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