Densities, Viscosities, and Refractive Indices for Binary and Ternary Mixtures of Diisopropyl Ether, Ethanol, and Methylcyclohexane

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Densities, viscosities, and refractive indices of the ternary system diisopropyl ether + ethanol + methylcyclohexane at $T = 298.15$ K and the binary systems diisopropyl ether + ethanol, diisopropyl ether + methylcyclohexane, and ethanol + methylcyclohexane 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 Ubbelholde capillary viscometer. Refractive indices were measured using a digital Abbe-type refractometer. Excess molar volumes V^E, deviations in the viscosity $\Delta\eta$, and deviations in the refractive index Δn_D for the mixtures were derived from experimental data. The binary data of V^E, $\Delta\eta$, and Δn_D were correlated as a function of the mole fraction by using the Redlich−Kister equation. For the ternary data, several polynomial equations have been tested to minimize the set of parameters for adequate correlation.

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 part of the project to investigate the thermodynamic behavior of liquid mixtures of the oxygenated compounds included in a hydrocarbon mixture.[1−4] The objective of the present paper is to determine the densities, viscosities, and refractive indices of binary and ternary systems formed from two oxygenated compounds, such as diisopropyl ether and ethanol, as well as methylcyclohexane.

The experimental results are used to calculate excess molar volumes, viscosity deviations, and refractive index deviations from the mole fraction average. The excess quantities of binary mixtures have been fitted to a Redlich−Kister equation to determine the coefficients. For the ternary data, several polynomial equations have been tested to minimize the set of parameters to correlate adequately. A thorough review of thermophysical property measurements on mixtures containing ethers with nonpolar solvents has been conducted by Marsh et al.[5] As far as we know, no binary and ternary data on densities, viscosities, and refractive indices for mixtures containing diisopropyl ether or ethanol with methylcyclohexane are available 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, and methylcyclohexane (>99.5%) was obtained from Tedia. 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 methylcyclohexane, respectively. The purity of the solvents was further ascertained by comparing their densities, viscosities, and refractive indices at a temperature of 298.15 K, and the results agreed generally well with the corresponding values reported in the literature as shown in Table 1.

Apparatus and Procedure. Liquids diisopropyl ether and ethanol were dried over activated molecular sieves, type 0.3 nm, from Aldrich. All of 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 joint stopper using a Precisa 262SMA balance with an accuracy 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 an accuracy of $\pm 5 \times 10^{-6}$ g·cm^{-3} in the range of (0 to 3) g·cm^{-3}, which was thermostatically controlled to within ±0.01 K in the range of (273.15 to 363.15) K. Calibration was performed periodically under atmospheric pressure, in accordance with specifications, using deionized water and dry air. Precautions were taken to prevent evaporation losses and dissolved air during the experiment. The uncertainty of the density measurements was estimated to be less than $\pm 1 \times 10^{-4}$ 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}.

The kinematic viscosities were determined with commercial Ubbelholde 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 was varied from 360 s to 750 s. The kinematic viscosity (ν) was then obtained from the following relationship

$$\nu \equiv \frac{\eta}{\rho} = k(t - \theta) \quad (1)$$

where t is the flow time, η is the absolute viscosity, and k

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

	ρ/g·cm^{-3}		η/mPa·s		n_D	
compound	this work	lit.	this work	lit.	this work	lit.
diisopropyl ether	0.7186	0.71854[a]	0.313	0.379[a]	1.36537	1.3655[a]
		0.71838[b]				
		0.71856[c]				1.3651[c]
ethanol	0.7852	0.78493[a]	1.085	1.0826[a]	1.35935	1.35941[a]
		0.78502[d]				1.35922[d]
methylcyclohexane	0.7650	0.76506[a]	0.685	0.685[a]	1.42053	1.42058[a]

[a] Riddick et al., 1986.[6] [b] Ouyang et al., 2004.[7] [c] Resa et al., 1996.[8] [d] Rodriguez et al., 1996.[9]

Table 2. Experimental Densities (ρ), Viscosities (η), Refractive Indices (n_D), and Excess Molar Volumes (V^E) at 288.15 K

x_1	ρ / g·cm^{-3}	η / mPa·s	n_D	V^E / cm^3·mol^{-1}	x_1	ρ / g·cm^{-3}	η / mPa·s	n_D	V^E / cm^3·mol^{-1}
Diisopropyl Ether (1) + Ethanol (2)									
0.0000	0.7936	1.310	1.36351	0.000	0.5500	0.7510	0.494	1.37175	−0.778
0.0500	0.7883	1.176	1.36570	−0.156	0.6000	0.7483	0.467	1.37190	−0.763
0.1000	0.7834	1.047	1.36697	−0.293	0.6500	0.7457	0.445	1.37197	−0.735
0.1500	0.7788	0.946	1.36800	−0.407	0.7000	0.7432	0.424	1.37196	−0.690
0.2000	0.7747	0.851	1.36883	−0.521	0.7500	0.7407	0.407	1.37192	−0.625
0.2500	0.7707	0.772	1.36952	−0.601	0.8000	0.7383	0.393	1.37188	−0.543
0.3000	0.7669	0.705	1.37013	−0.663	0.8500	0.7358	0.379	1.37178	−0.417
0.3500	0.7633	0.649	1.37062	−0.709	0.9000	0.7335	0.367	1.37162	−0.298
0.4000	0.7600	0.600	1.37102	−0.745	0.9500	0.7311	0.367	1.37141	−0.134
0.4500	0.7569	0.559	1.37134	−0.771	1.0000	0.7290	0.347	1.37126	0.000
0.5000	0.7538	0.523	1.37158	−0.778					
Diisopropyl Ether (1) + Methylcyclohexane (2)									
0.0000	0.7734	0.784	1.42578	0.000	0.5500	0.7484	0.466	1.39450	0.080
0.0502	0.7713	0.744	1.42321	0.013	0.6000	0.7462	0.447	1.39180	0.078
0.1000	0.7689	0.697	1.42014	0.027	0.6500	0.7439	0.431	1.38914	0.074
0.1500	0.7666	0.660	1.41715	0.042	0.7000	0.7417	0.415	1.38652	0.070
0.2000	0.7643	0.627	1.41419	0.051	0.7500	0.7396	0.403	1.38392	0.063
0.2500	0.7619	0.595	1.41129	0.061	0.8000	0.7374	0.389	1.38136	0.053
0.3000	0.7596	0.568	1.40842	0.069	0.8500	0.7353	0.379	1.37883	0.042
0.3500	0.7574	0.543	1.40558	0.074	0.9000	0.7331	0.368	1.37629	0.028
0.4000	0.7551	0.522	1.40277	0.078	0.9500	0.7310	0.358	1.37377	0.011
0.4500	0.7528	0.503	1.39999	0.081	1.0000	0.7290	0.347	1.37126	0.000
0.5000	0.7506	0.484	1.39721	0.081					
Ethanol (1) + Methylcyclohexane (2)									
0.0000	0.7734	0.784	1.42578	0.000	0.5500	0.7778	0.928	1.40150	0.331
0.0499	0.7734	0.771	1.42405	0.076	0.6000	0.7787	0.955	1.39844	0.327
0.1000	0.7734	0.769	1.42223	0.143	0.6500	0.7796	0.983	1.39516	0.321
0.1500	0.7737	0.770	1.42037	0.186	0.7000	0.7808	1.012	1.39166	0.307
0.2000	0.7740	0.779	1.41843	0.221	0.7500	0.7821	1.043	1.38785	0.290
0.2500	0.7743	0.793	1.41639	0.251	0.8000	0.7836	1.077	1.38377	0.260
0.3000	0.7747	0.811	1.41426	0.276	0.8500	0.7854	1.114	1.37933	0.224
0.3500	0.7751	0.831	1.41199	0.298	0.9000	0.7877	1.164	1.37449	0.167
0.4000	0.7757	0.853	1.40960	0.312	0.9500	0.7904	1.225	1.36921	0.091
0.4500	0.7763	0.877	1.40706	0.322	1.0000	0.7936	1.310	1.36351	0.000
0.5000	0.7770	0.902	1.40437	0.329					

and θ are respectively the viscometer constant and the Hagenbach correction. The k values were 0.000906 ± 0.000001 and 0.002913 ± 0.000002 for the capillary viscometers that were 0.36 mm and 0.47 mm in diameter, respectively. The value θ, which is dependent on the flow time and the size of the capillary, was taken from the tables supplied by the manufacturer. Triplicate measurements of flow times were reproducible to within ±0.02%. The uncertainty of the viscosity measurement was estimated to be less than ±0.5%.

Refractive indices, n_D, were measured with an automatic Anton-Paar RXA-156 refractometer, which works with the wavelength (589 nm) corresponding to the D line of sodium. The temperature range of this refractometer is from $T = 283.15$ K to $T = 343.15$ K with an uncertainty of 0.03 K. Calibration was performed periodically under atmospheric pressure, in accordance with specifications, using deionized water and dry air. The uncertainty of the refractive index measurement is 0.00002 units in the range of (1.32 to 1.56) units.

The densities, viscosities, and refractive indices of the binary systems diisopropyl ether + ethanol, diisopropyl ether + methylcyclohexane, and ethanol + methylcyclohexane were measured at temperatures of 288.15 K, 298.15 K, and 308.15 K and atmospheric pressure of (100.8 ± 0.2) kPa. A set with the compositions varying from 0.05 to 0.95 mole fraction was prepared for each binary system. A total of 55 compositions were measured at $T = 298.15$ K for the ternary system diisopropyl ether + ethanol + methylcyclohexane. An average of at least three measurements was taken for each composition. The uncertainties in the liquid composition and the investigated temperature were estimated to be $\pm 1 \times 10^{-4}$ and ±0.01 K, respectively.

Results and Discussion

Tables 2 to 4 list the experimental densities, viscosities, refractive indices, and excess molar volumes of three binary

Table 3. Experimental Densities (ρ), Viscosities (η), Refractive Indices (n_D), and Excess Molar Volumes (V^E) at 298.15 K

x_1	ρ / g·cm^{-3}	η / mPa·s	n_D	V^E / cm^3·mol^{-1}	x_1	ρ / g·cm^{-3}	η / mPa·s	n_D	V^E / cm^3·mol^{-1}
Diisopropyl Ether (1) + Ethanol (2)									
0.0000	0.7852	1.085	1.35935	0.000	0.5500	0.7412	0.432	1.36644	−0.810
0.0500	0.7798	0.976	1.36097	−0.172	0.6000	0.7384	0.413	1.36651	−0.800
0.1000	0.7748	0.876	1.36212	−0.319	0.6500	0.7358	0.393	1.36652	−0.774
0.1500	0.7700	0.793	1.36316	−0.441	0.7000	0.7332	0.378	1.36651	−0.733
0.2000	0.7657	0.718	1.36395	−0.551	0.7500	0.7307	0.363	1.36645	−0.672
0.2500	0.7614	0.655	1.36457	−0.626	0.8000	0.7283	0.349	1.36635	−0.589
0.3000	0.7575	0.605	1.36509	−0.691	0.8500	0.7258	0.338	1.36621	−0.478
0.3500	0.7539	0.559	1.36550	−0.744	0.9000	0.7234	0.330	1.36597	−0.343
0.4000	0.7504	0.519	1.36587	−0.779	0.9500	0.7209	0.319	1.36566	−0.178
0.4500	0.7471	0.487	1.36612	−0.797	1.0000	0.7186	0.313	1.36537	0.000
0.5000	0.7441	0.457	1.36632	−0.809					
Diisopropyl Ether (1) + Methylcyclohexane (2)									
0.0000	0.7650	0.685	1.42053	0.000	0.5500	0.7388	0.415	1.38878	0.058
0.0502	0.7625	0.653	1.41757	0.009	0.6000	0.7365	0.399	1.38610	0.055
0.1000	0.7601	0.612	1.41460	0.017	0.6500	0.7342	0.385	1.38347	0.052
0.1500	0.7577	0.579	1.41158	0.025	0.7000	0.7319	0.372	1.38082	0.048
0.2000	0.7553	0.551	1.40859	0.034	0.7500	0.7296	0.361	1.37823	0.042
0.2500	0.7529	0.524	1.40565	0.042	0.8000	0.7273	0.349	1.37565	0.033
0.3000	0.7505	0.502	1.40277	0.047	0.8500	0.7251	0.341	1.37309	0.024
0.3500	0.7481	0.481	1.39990	0.051	0.9000	0.7229	0.331	1.37053	0.014
0.4000	0.7458	0.464	1.39707	0.055	0.9500	0.7206	0.321	1.36799	0.006
0.4500	0.7434	0.447	1.39428	0.058	1.0000	0.7186	0.313	1.36537	0.000
0.5000	0.7411	0.431	1.39150	0.060					
Ethanol (1) + Methylcyclohexane (2)									
0.0000	0.7650	0.685	1.42053	0.000	0.5500	0.7689	0.778	1.39644	0.386
0.0499	0.7646	0.674	1.41871	0.139	0.6000	0.7698	0.799	1.39343	0.379
0.1000	0.7647	0.670	1.41690	0.205	0.6500	0.7708	0.820	1.39020	0.367
0.1500	0.7648	0.667	1.41505	0.256	0.7000	0.7720	0.843	1.38674	0.347
0.2000	0.7651	0.673	1.41313	0.294	0.7500	0.7734	0.867	1.38298	0.321
0.2500	0.7654	0.681	1.41112	0.323	0.8000	0.7749	0.894	1.37896	0.287
0.3000	0.7658	0.694	1.40902	0.350	0.8500	0.7767	0.926	1.37459	0.245
0.3500	0.7662	0.707	1.40679	0.368	0.9000	0.7790	0.971	1.36985	0.183
0.4000	0.7668	0.722	1.40442	0.380	0.9500	0.7818	1.021	1.36474	0.099
0.4500	0.7674	0.739	1.40192	0.386	1.0000	0.7852	1.085	1.35935	0.000
0.5000	0.7681	0.757	1.39927	0.390					

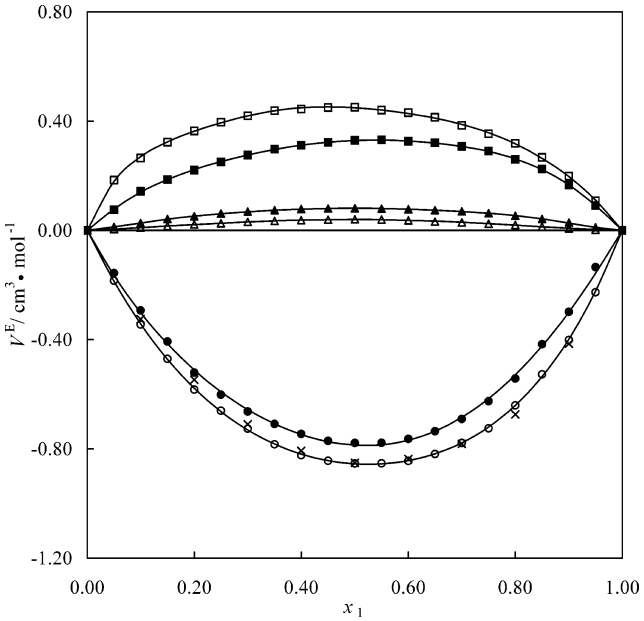

Figure 1. Variation of excess molar volume V^E with mole fraction x_1 for the following systems. Diisopropyl ether + ethanol: ●, 288.15 K; ○, 308.15 K; diisopropyl ether + ethanol from Rezanova et al.:[10] ×, 298.15 K; diisopropyl ether + methylcyclohexane: ▲, 288.15 K; △, 308.15 K, and ethanol + methylcyclohexane: ■, 288.15 K; □, 308.15 K. Solid curves were calculated from Redlich−Kister equation.

systems diisopropyl ether + ethanol, diisopropyl ether + methylcyclohexane, and ethanol + methylcyclohexane at temperatures of 288.15 K, 298.15 K, and 308.15 K. The molar excess volumes, V^E, were calculated from density data according to the equation

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

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 + methylcyclohexane and ethanol + methylcyclohexane and negative for the mixture diisopropyl ether + ethanol over the whole composition range. The values of V^E decrease for the systems diisopropyl ether + ethanol and diisopropyl ether + methylcyclohexane but increase for the system ethanol + methylcyclohexane from $T = 288.15$ K to $T = 308.15$ K over the whole range of mole fraction. The excess molar volume $V^E(x = 0.5)$ increases in the sequence ethanol + methylcyclohexane > diisopropyl ether + methylcyclohexane > diisopropyl ether + ethanol. The values of $V^E(x = 0.5)$ vary from −0.854 cm^3·mol^{-1} to 0.451 cm^3·mol^{-1}. In the literature, the system diisopropyl ether + ethanol had been measured at $T = 298.15$ K.[10] Figure 1 shows the excess molar volumes for the three binary systems investigated at $T = 288.15$ K and $T = 308.15$ K together with the literature values at 298.15 K.

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 and dispersive interactions between unlike molecules) and negative contributions (intermolecular dipolar interactions and geometrical fitting between components).

Table 4. Experimental Densities (ρ), Viscosities (η), Refractive Indices (n_D), and Excess Molar Volumes (V^E) at 308.15 K

x_1	ρ / g·cm^{-3}	η / mPa·s	n_D	V^E / cm^3·mol^{-1}	x_1	ρ / g·cm^{-3}	η / mPa·s	n_D	V^E / cm^3·mol^{-1}
Diisopropyl Ether (1) + Ethanol (2)									
0.0000	0.7765	0.906	1.35504	0.000	0.5500	0.7311	0.382	1.36119	−0.853
0.0500	0.7710	0.815	1.35649	−0.184	0.6000	0.7283	0.364	1.36118	−0.844
0.1000	0.7658	0.737	1.35757	−0.345	0.6500	0.7256	0.349	1.36116	−0.818
0.1500	0.7609	0.671	1.35852	−0.470	0.7000	0.7230	0.335	1.36112	−0.778
0.2000	0.7564	0.613	1.35926	−0.583	0.7500	0.7205	0.325	1.36103	−0.725
0.2500	0.7520	0.562	1.35980	−0.660	0.8000	0.7180	0.315	1.36089	−0.641
0.3000	0.7479	0.520	1.36021	−0.726	0.8500	0.7155	0.306	1.36071	−0.527
0.3500	0.7442	0.484	1.36057	−0.783	0.9000	0.7131	0.298	1.36042	−0.401
0.4000	0.7407	0.452	1.36083	−0.823	0.9500	0.7106	0.290	1.36000	−0.226
0.4500	0.7373	0.427	1.36102	−0.843	1.0000	0.7079	0.283	1.35954	0.000
0.5000	0.7341	0.403	1.36113	−0.854					
Diisopropyl Ether (1) + Methylcyclohexane (2)									
0.0000	0.7563	0.600	1.41537	0.000	0.5500	0.7292	0.373	1.38356	0.040
0.0502	0.7538	0.575	1.41250	0.005	0.6000	0.7268	0.360	1.38083	0.037
0.1000	0.7513	0.542	1.40957	0.010	0.6500	0.7244	0.347	1.37818	0.033
0.1500	0.7488	0.514	1.40663	0.016	0.7000	0.7220	0.335	1.37552	0.029
0.2000	0.7463	0.489	1.40365	0.022	0.7500	0.7196	0.325	1.37286	0.025
0.2500	0.7438	0.467	1.40068	0.026	0.8000	0.7173	0.316	1.37025	0.020
0.3000	0.7413	0.448	1.39775	0.031	0.8500	0.7149	0.308	1.36765	0.014
0.3500	0.7389	0.430	1.39484	0.035	0.9000	0.7126	0.299	1.36503	0.007
0.4000	0.7364	0.415	1.39197	0.038	0.9500	0.7103	0.291	1.36243	0.002
0.4500	0.7340	0.401	1.38912	0.039	1.0000	0.7079	0.283	1.35954	0.000
0.5000	0.7316	0.387	1.38631	0.041					
Ethanol (1) + Methylcyclohexane (2)									
0.0000	0.7563	0.600	1.41537	0.000	0.5500	0.7599	0.666	1.39153	0.441
0.0499	0.7558	0.589	1.41358	0.184	0.6000	0.7608	0.683	1.38856	0.431
0.1000	0.7557	0.588	1.41176	0.265	0.6500	0.7618	0.700	1.38538	0.414
0.1500	0.7558	0.585	1.40993	0.323	0.7000	0.7631	0.720	1.38197	0.385
0.2000	0.7561	0.588	1.40802	0.364	0.7500	0.7645	0.740	1.37827	0.354
0.2500	0.7564	0.593	1.40603	0.396	0.8000	0.7660	0.762	1.37432	0.318
0.3000	0.7568	0.602	1.40396	0.420	0.8500	0.7679	0.790	1.37001	0.267
0.3500	0.7572	0.612	1.40175	0.439	0.9000	0.7702	0.828	1.36536	0.198
0.4000	0.7578	0.623	1.39942	0.444	0.9500	0.7730	0.867	1.36042	0.108
0.4500	0.7584	0.635	1.39695	0.450	1.0000	0.7765	0.906	1.35504	0.000
0.5000	0.7591	0.650	1.39433	0.451					

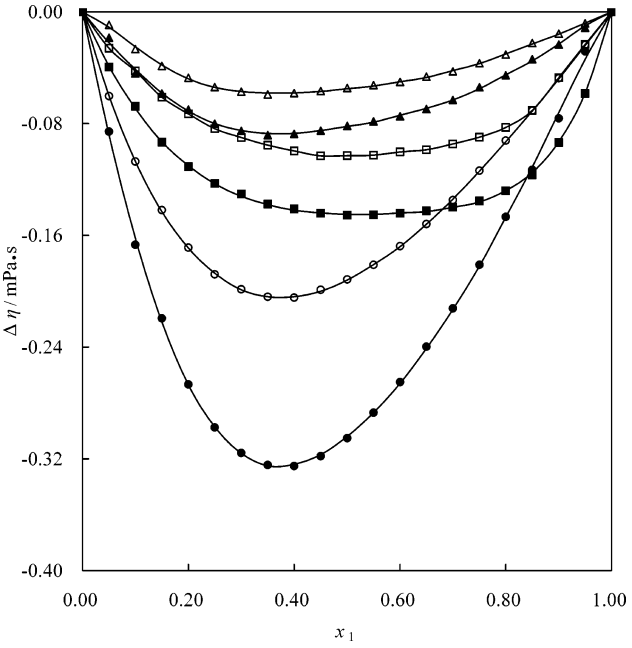

Figure 2. Variation of viscosity deviation $\Delta\eta$ with mole fraction x_1 for the following systems. Diisopropyl ether + ethanol: ●, 288.15 K; ○, 308.15 K; diisopropyl ether + methylcyclohexane: ▲, 288.15 K; △, 308.15 K; and ethanol + methylcyclohexane: ■, 288.15 K; □, 308.15 K. Solid curves were calculated from the Redlich−Kister equation.

In the present investigation, ethanol is strongly self-associated through hydrogen bonding, but diisopropyl ether and methylcyclohexane do not exhibit this property. The interactions of ethanol and diisopropyl ether against methylcyclohexane molecules involve mainly the 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 effects, giving a negative contribution to V^E.

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

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

where η is the absolute viscosity of the mixture and η_i is the absolute viscosity of pure component i. The $\Delta\eta$ values, which are negative over the entire range of composition, increase with increasing temperature. The values of $\Delta\eta(x = 0.5)$ follow the order diisopropyl ether + methylcyclohexane > ethanol + methylcyclohexane > diisopropyl ether + ethanol. The values of $\Delta\eta(x = 0.5)$ vary from −0.305 mPa·s to −0.055 mPa·s. Figure 2 plots the results of $\Delta\eta$ for the three binary systems at T = 288.15 K and T = 308.15 K.

The deviation in refractive index from the mole fraction average, Δn_D, is given by

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

where n_D and n_{D_i} are the refractive index of the mixture and the refractive index of pure component i, respectively. The Δn_D values are positive for the mixtures diisopropyl ether + methylcyclohexane and ethanol + methylcyclohexane and negative for the mixture diisopropyl ether + ethanol over the whole composition. The values of Δn_D

Table 5. Coefficients of Equation 5 and Standard Deviations (σ) of V^E, $\Delta\eta$, and Δn_D for the Binary Systems from T = 288.15 K to T = 308.15 K[a]

ΔQ_{ij}	T/K	$10a_0$	$10a_1$	$10a_2$	$10a_3$	$10a_4$	$10^4\sigma$
			Diisopropyl Ether (1) + Ethanol (2)				
V^E/cm^3·mol^{-1}	288.15	−31.451 ± 0.151	−2.295 ± 0.587	−2.923 ± 0.694	3.815 ± 1.510		93
	298.15	−32.397 ± 0.045	−2.637 ± 0.148	−10.838 ± 0.475	1.562 ± 0.382	6.458 ± 0.810	24
	308.15	−34.193 ± 0.057	−2.498 ± 0.223	−10.833 ± 0.263	−2.143 ± 0.573		35
$\Delta\eta$/mPa·s	288.15	−12.169 ± 0.048	6.125 ± 0.155	−3.112 ± 0.497	0.215 ± 0.399	2.727 ± 0.848	25
	298.15	−9.665 ± 0.034	4.977 ± 0.067	−1.743 ± 0.154			21
	308.15	−7.693 ± 0.010	3.780 ± 0.038	−1.396 ± 0.044	0.507 ± 0.097		5
Δn_D	288.15	−4.314 ± 0.024	−1.491 ± 0.092	−1.072 ± 0.109	0.065 ± 0.238		15
	298.15	−4.573 ± 0.018	−0.299 ± 0.036	−1.203 ± 0.082			11
	308.15	−4.766 ± 0.013	−0.121 ± 0.051	−1.493 ± 0.061	−0.831 ± 0.132		8
			Diisopropyl Ether (1) + Methylcyclohexane (3)				
V^E/cm^3·mol^{-1}	288.15	3.266 ± 0.024	0.042 ± 0.048	−0.117 ± 0.111			15
	298.15	2.366 ± 0.015	0.113 ± 0.057	−0.839 ± 0.068	−0.457 ± 0.147		9
	308.15	1.599 ± 0.012	−10.491 ± 0.025	−0.959 ± 0.057			8
$\Delta\eta$/mPa·s	288.15	−3.299 ± 0.021	1.346 ± 0.069	−1.649 ± 0.220	−0.049 ± 0.177	1.956 ± 0.376	11
	298.15	−2.722 ± 0.023	1.238 ± 0.075	−1.822 ± 0.241	−0.247 ± 0.193	2.296 ± 0.410	12
	308.15	−2.191 ± 0.022	0.986 ± 0.073	−1.505 ± 0.234	−0.422 ± 0.180	2.169 ± 0.400	12
Δn_D	288.15	3.368 ± 0.011	−0.255 ± 0.043	0.428 ± 0.051	−1.307 ± 0.111		7
	298.15	2.993 ± 0.015	−0.317 ± 0.029	−1.038 ± 0.067			9
	308.15	2.593 ± 0.012	−0.028 ± 0.023	−1.675 ± 0.053			7
			Ethanol (2) + Methylcyclohexane (3)				
V^E/cm^3 · mol^{-1}	288.15	13.072 ± 0.040	1.919 ± 0.081	5.829 ± 0.185			25
	298.15	15.624 ± 0.091	0.625 ± 0.297	4.230 ± 0.952	−3.611 ± 0.765	8.282 ± 1.625	47
	308.15	18.047 ± 0.123	−0.718 ± 0.401	4.828 ± 1.284	−6.330 ± 1.031	11.908 ± 2.191	64
$\Delta\eta$/mPa · s	288.15	−5.800 ± 0.021	−0.126 ± 0.069	−3.936 ± 0.221	−2.374 ± 0.178	−1.794 ± 0.377	11
	298.15	−5.072 ± 0.021	−0.344 ± 0.080	−3.557 ± 0.095	−1.662 ± 0.207		13
	308.15	−4.242 ± 0.029	−0.402 ± 0.096	−2.398 ± 0.307	−0.641 ± 0.247	0.462 ± 0.524	15
Δn_D	288.15	1.343 ± 0.009	−0.061 ± 0.034	0.491 ± 0.041	−0.117 ± 0.089		5
	298.15	1.524 ± 0.011	−0.029 ± 0.022	0.818 ± 0.052			7
	308.15	1.739 ± 0.010	0.016 ± 0.020	1.103 ± 0.047			6

[a] ±Standard deviation.

Table 6. Parameters of McAllister's Three-Body and Four-Body Interaction Models and Standard Deviations (σ) for Kinematic Viscosities[a]

	three-body			four-body			
T	$10\nu_{12}$	$10\nu_{12}$	$10^4\sigma$	$10\nu_{1112}$	$10\nu_{1122}$	$10\nu_{2221}$	$10^4\sigma$
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	5.518 ± 0.061	8.071 ± 0.089	79	5.566 ± 0.067	6.063 ± 0.114	10.037 ± 0.120	40
298.15	4.985 ± 0.027	7.027 ± 0.038	43	4.921 ± 0.028	5.615 ± 0.050	8.446 ± 0.047	24
308.15	4.563 ± 0.020	6.140 ± 0.026	24	4.497 ± 0.014	5.040 ± 0.025	7.301 ± 0.023	9
			Diisopropyl Ether (1) + Methylcyclohexane (2)				
288.15	5.6520.021	6.8850.026	23	5.363 ± 0.029	6.344 ± 0.055	7.513 ± 0.041	23
298.15	5.1390.024	6.1670.029	28	4.873 ± 0.034	5.747 ± 0.063	6.693 ± 0.047	27
308.15	4.7000.022	5.6370.026	26	4.487 ± 0.033	5.197 ± 0.060	6.105 ± 0.045	27
			Ethanol (1) + Methylcyclohexane (2)				
288.15	12.909 ± 0.208	9.917 ± 0.160	177	12.361 ± 0.047	13.313 ± 0.080	9.030 ± 0.034	28
298.15	10.755 ± 0.141	8.585 ± 0.113	121	10.499 ± 0.037	10.951 ± 0.061	7.999 ± 0.028	20
308.15	9.421 ± 0.071	7.505 ± 0.057	59	9.447 ± 0.045	8.990 ± 0.067	7.272 ± 0.034	27

[a] ±Standard deviation.

decrease for the systems diisopropyl ether + ethanol and diisopropyl ether + methylcyclohexane but increase for the system ethanol + methylcyclohexane with an increase in temperature over the whole range of mole fraction. The values of $\Delta n_D(x = 0.5)$ follow the order diisopropyl ether + methylcyclohexane > ethanol + methylcyclohexane > diisopropyl ether + ethanol. The values of $\Delta n_D(x = 0.5)$ vary from −0.1202 to 0.0853. Figure 3 shows the results of Δn_D for the three binary systems at T = 288.15 K and 308.15 K.

The mixing functions V^E, $\Delta\eta$, and Δn_D were represented mathematically by the Redlich−Kister equation[11] for correlating the experimental data

$$\Delta Q_{ij} = x_i x_j \sum_{k=0}^{m} a_k (x_i - x_j)^k \qquad (5)$$

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 represents 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 is defined by

$$\sigma = \left[\sum_{i=1}^{n} \frac{(\Delta Q_i^{\text{exptl}} - \Delta Q_i^{\text{calcd}})^2}{(n-p)}\right]^{1/2} \qquad (6)$$

where n is the number of experimental points and p is the number of adjustable parameters. The σ values lie between 0.0008 cm^3·mol^{-1} and 0.0093 cm^3·mol^{-1}, between 0.0005 mPa·s and 0.0025 mPa·s, and between 0.0005 and 0.0015 for V^E, $\Delta\eta$, and Δn_D, respectively.

McAllister's multibody interaction model[12] is widely used for correlating the kinematic viscosity of binary mixtures

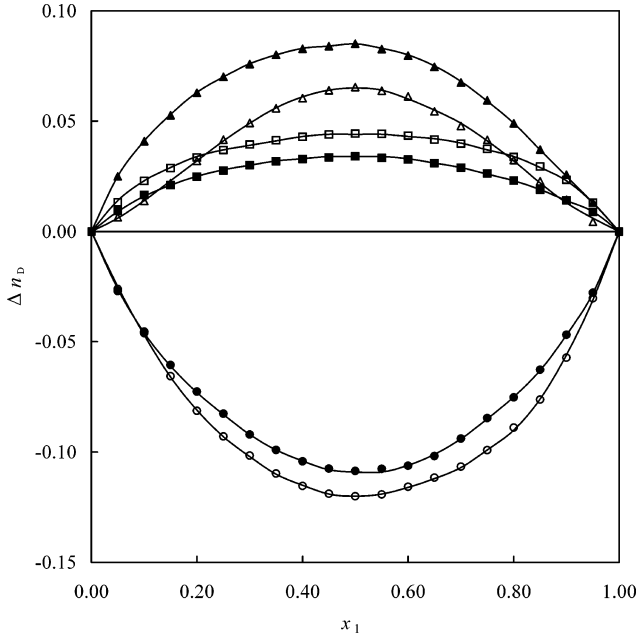

Figure 3. Variation of refractive index deviation Δn_D with mole fraction x_1 for the following systems. Diisopropyl ether + ethanol: ●, 288.15 K; ○, 308.15 K; diisopropyl ether + methylcyclohexane: ▲, 288.15 K; △, 308.15 K; and ethanol + methylcyclohexane: ■, 288.15 K; □, 308.15 K. Solid curves were calculated from the Redlich−Kister equation.

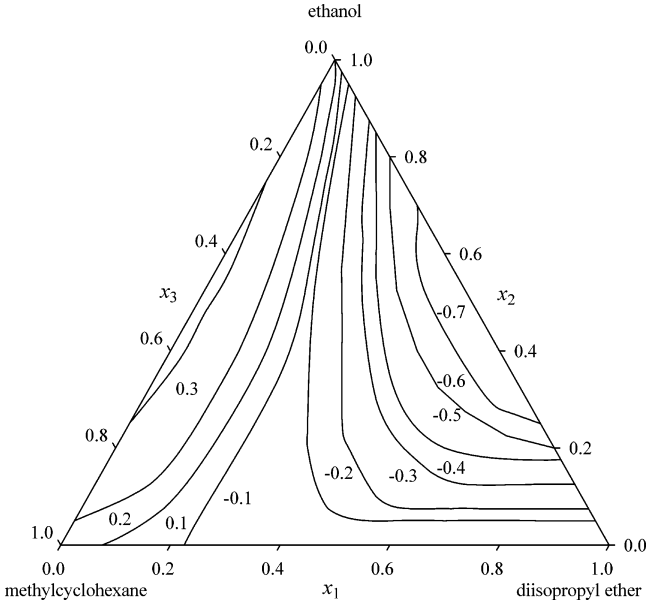

Figure 4. Curves of constant V^E/cm^3·mol^{-1} for the ternary system diisopropyl ether (1) + ethanol (2) + methylcyclohexane (3) at T = 298.15 K.

as function of mole fraction. The three-body model is

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln \nu_{12} + 3x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln\left(x_1 + \frac{x_2 M_2}{M_1}\right) + 3x_1^2 x_2 \ln\left[\frac{2 + (M_2/M_1)}{3}\right] + 3x_1 x_2^2 \ln\left[\frac{1 + (2M_2/M_1)}{3}\right] + x_2^3 \ln\left(\frac{M_2}{M_1}\right) \quad (7)$$

and the four-body model is

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3 x_2 \ln \nu_{1112} + 6x_1^2 x_2^2 \ln \nu_{1122} + 4x_1 x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \ln\left(x_1 + \frac{x_2 M_2}{M_1}\right) + 4x_1^3 x_2 \ln\left[\frac{3 + M_2/M_1}{4}\right] + 6x_1^2 x_2^2 \ln\left[\frac{1 + M_2/M_1}{2}\right] + 4x_1 x_2^3 \ln\left[\frac{1 + 3M_2/M_1}{4}\right] + x_2^4 \ln\left(\frac{M_2}{M_1}\right) \quad (8)$$

where ν, ν_1, and ν_2 are the kinematic viscosity of the mixture and the viscosities of pure components 1 and 2,

Table 7. Experimental Densities, Viscosities, Refractive Indices, and Excess Molar Volumes for the Diisopropyl Ether (1) + Ethanol (2) + Methylcyclohexane (3) System at T = 298.15 K

x_1	x_2	ρ / g·cm^{-3}	η / mPa·s	n_D	V^E / cm^3·mol^{-1}	x_1	x_2	ρ / g·cm^{-3}	η / mPa·s	n_D	V^E / cm^3·mol^{-1}
0.0500	0.9000	0.7769	0.914	1.36600	−0.071	0.3000	0.5500	0.7545	0.555	1.37604	−0.459
0.0500	0.8000	0.7727	0.843	1.37519	0.070	0.3000	0.4500	0.7532	0.541	1.38221	−0.350
0.0500	0.7000	0.7697	0.793	1.38316	0.157	0.3000	0.3500	0.7523	0.517	1.38787	−0.269
0.0500	0.6000	0.7675	0.746	1.39006	0.209	0.3000	0.2500	0.7516	0.508	1.39267	−0.203
0.0500	0.5000	0.7658	0.709	1.39601	0.235	0.3000	0.1500	0.7511	0.503	1.39721	−0.159
0.0500	0.4000	0.7646	0.682	1.40126	0.243	0.3000	0.0500	0.7508	0.502	1.40130	−0.129
0.0500	0.3000	0.7635	0.656	1.40597	0.235	0.4000	0.5500	0.7496	0.502	1.36947	−0.703
0.0500	0.2000	0.7628	0.643	1.41015	0.201	0.4000	0.4500	0.7484	0.484	1.37581	−0.552
0.0500	0.1000	0.7624	0.640	1.41389	0.134	0.4000	0.3500	0.7475	0.473	1.38156	−0.433
0.0500	0.0501	0.7623	0.639	1.41572	0.079	0.4000	0.2599	0.7469	0.467	1.38669	−0.337
0.1000	0.8500	0.7723	0.831	1.36686	−0.219	0.4000	0.1500	0.7465	0.459	1.39130	−0.255
0.1000	0.7500	0.7687	0.772	1.37565	−0.081	0.4000	0.0500	0.7461	0.461	1.39537	−0.178
0.1000	0.6500	0.7661	0.725	1.38313	0.015	0.5000	0.4500	0.7435	0.443	1.36968	−0.738
0.1000	0.5500	0.7642	0.689	1.38970	0.076	0.5000	0.3500	0.7427	0.434	1.37545	−0.584
0.1000	0.4500	0.7628	0.654	1.39540	0.111	0.5000	0.2500	0.7423	0.427	1.38082	−0.460
0.1000	0.3500	0.7617	0.630	1.40043	0.126	0.5000	0.1500	0.7419	0.426	1.38552	−0.336
0.1000	0.2500	0.7609	0.612	1.40497	0.122	0.5000	0.0500	0.7415	0.425	1.38980	−0.207
0.1000	0.1500	0.7603	0.605	1.40910	0.093	0.6000	0.3500	0.7380	0.404	1.36951	−0.717
0.1000	0.0500	0.7601	0.609	1.41273	0.023	0.6000	0.2500	0.7376	0.399	1.37499	−0.559
0.2000	0.7500	0.7638	0.687	1.36825	−0.455	0.6000	0.1501	0.7372	0.397	1.38001	−0.396
0.2000	0.6500	0.7613	0.644	1.37597	−0.312	0.5999	0.0501	0.7368	0.397	1.38431	−0.229
0.2000	0.5500	0.7594	0.613	1.38282	−0.200	0.7000	0.2500	0.7329	0.372	1.36926	−0.648
0.2000	0.4500	0.7580	0.593	1.38887	−0.126	0.7000	0.1500	0.7326	0.371	1.37437	−0.449
0.2000	0.3500	0.7570	0.572	1.39409	−0.080	0.7004	0.0500	0.7323	0.370	1.37886	−0.243
0.2000	0.2500	0.7563	0.559	1.39881	−0.049	0.8000	0.1500	0.7280	0.347	1.36888	−0.494
0.2000	0.1500	0.7557	0.552	1.40309	−0.044	0.8000	0.0500	0.7277	0.348	1.37351	−0.248
0.2000	0.0500	0.7554	0.549	1.40691	−0.063	0.9000	0.0500	0.7232	0.326	1.36826	−0.231
0.3000	0.6500	0.7563	0.582	1.36899	−0.609						

Table 8. Coefficients A_i, B_i, and C_i of Equation 11 and Standard Deviations (σ) for the Diisopropyl Ether (1) + Ethanol (2) + Methylcyclohexane (3) System at $T = 298.15$ K[a]

ΔQ_{123}	$10A_1$	$10B_1$	$10C_1$	$10A_2$	$10B_2$	$10C_2$	$10^4\sigma$
V^E/cm^3·mol^{-1}	−1.710 ± 0.646	−3.498 ± 0.596	−13.046 ± 0.643	1.880 ± 1.348	5.436 ± 1.241	9.252 ± 1.336	134
$\Delta\eta$/mPa·s	0.198 ± 0.055	0.046 ± 0.050	0.369 ± 0.055				33
Δn_D	−5.522 ± 0.162	−0.212 ± 0.065	−2.960 ± 0.062	1.182 ± 0.327			36

[a] ±Standard deviation.

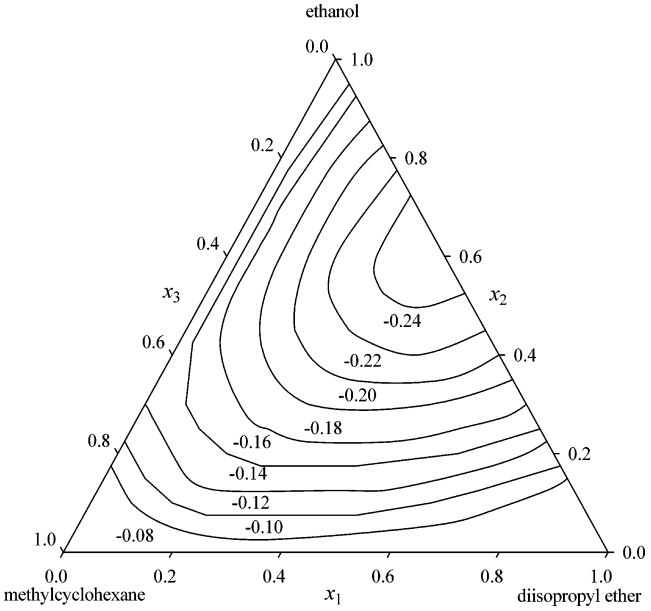

Figure 5. Curves of constant $\Delta\eta$ for the ternary system diisopropyl ether (1) + ethanol (2) + methylcyclohexane (3) at T = 298.15 K.

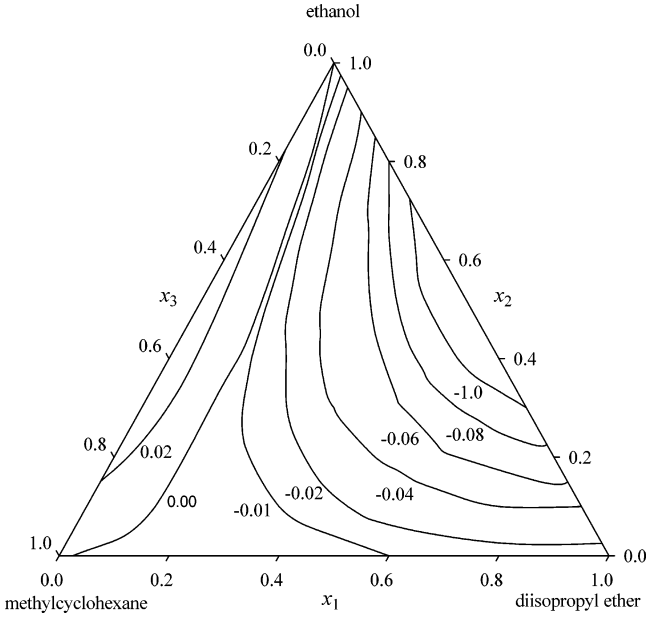

Figure 6. Curves of constant Δn_D for the ternary system diisopropyl ether (1) + ethanol (2) + methylcyclohexane (3) at T = 298.15 K.

respectively. The terms 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 6. It is shown that the McAllister four-body interaction model gave a better result for those three systems. The σ/mm^2·s^{-1} values for this model lie between 0.0009 and 0.0040, and the largest σ value corresponds to the diisopropyl ether + ethanol system at T = 288.15 K.

The experimental densities, viscosities, and excess molar volumes of the ternary system diisopropyl ether (1) + ethanol (2) + methylcyclohexane (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 of the ternary system were correlated using the equations

$$\Delta Q_{123} = \Delta Q_{bin} + \Delta_{123} \tag{9}$$

and

$$\Delta Q_{bin} = \Delta Q_{12} + \Delta Q_{13} + \Delta Q_{23} \tag{10}$$

where ΔQ_{123} refers to V^E, $\Delta\eta$, or Δn_D for the ternary mixture $x_3 = 1 - x_1 - x_2$ and ΔQ_{ij} is the binary contribution of each $i-j$ pair to the V^E, $\Delta\eta$, or Δn_D given by eq 5 with the parameters shown in Table 5. The ternary contribution term Δ_{123} was correlated using an expression of the form

$$\Delta_{123} = \sum_{i=1}^{m} (A_i x_1^i x_2 + B_i x_2^i x_3 + C_i x_3^i x_1) \tag{11}$$

The ternary parameters A_i, B_i, and C_i were determined with the optimization algorithm similar to that for the binary parameters. The parameters A_i, B_i, and C_i and the corresponding standard deviations are given in Table 8.

The curves of constant excess molar volume, deviations the viscosity, and deviations in refractive index at T = 298.15 K were calculated from eqs 9 to 11 and were plotted in Figures 4 to 6, respectively. As can be expected, the ternary system shows positive values of V^E at almost all compositions (Figure 4), except at compositions close to that of the binary system ethanol + methylcyclohexane where a change in sign occurs. The maximum V^E value was found in the system ethanol + methylcyclohexane near $x_1 = 0.5$. Figure 5 shows negative values for ternary $\Delta\eta$, with a minimum value near $x_1 = 0.4$ for the system diisopropyl ether + ethanol. A similar phenomenon to that of ternary V^E was observed for ternary Δn_D as shown in Figure 6.

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