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

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Densities, viscosities, and refractive indices of the ternary system ethanol + 2-methylpropan-2-ol + 2,2,4-trimethylpentane at $T = 298.15$ K and the binary systems ethanol + 2-methylpropan-2-ol, ethanol + 2,2,4-trimethylpentane, and 2-methylpropan-2-ol + 2,2,4-trimethylpentane were measured at $T = (298.15, 308.15,$ and $318.15)$ K and atmospheric pressure over the whole composition range. Densities were determined using a vibrating-tube densimeter. Viscosities were measured with an automatic microviscometer based on the rolling ball principle. Refractive indices were measured using a digital Abbe-type refractometer. Excess molar volumes (V^E), deviations in the viscosity ($\Delta\eta$) from the mole fraction average, and deviations in the refractive index (Δn_D) from the volume fraction average for the mixtures were derived from experimental data. The binary and ternary data of V^E, $\Delta\eta$, and Δn_D were correlated as a function of the mole fraction 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.[1−5]

The objective of the present paper is to determine the densities, viscosities, and refractive indices for the binary and ternary systems formed by two oxygenated compounds, such as ethanol and 2-methylpropan-2-ol, as well as 2,2,4-trimethylpentane. This hydrocarbon liquid is the component that generally appears in gasoline. The experimental results are used to calculate excess molar volumes, viscosity deviations from the mole fraction average, and refractive index deviations from the volume fraction average. The excess quantities of binary mixtures have been fitted to the Redlich−Kister equation to determine the coefficients. For correlating the ternary data, the Cibulka equation was used. As far as we know, no ternary data are available for the mixtures investigated in the open literature.

Experimental Section

Materials. The chemicals used were of analytical grade. Ethanol (>99.8 %) and 2-methylpropan-2-ol (>99.5 %) were obtained from Merck (Germany), and 2,2,4-trimethylpentane (99.7 %) was obtained from Tedia (USA). All chemicals were used without further purification. The purity of these chemicals was analyzed by gas chromatography (Perkin-Elmer Autosystem) using a flame ionization detector with a 60 m × 0.53 mm capillary column packed by Stabilwax. Gas chromatographic analysis showed that the major peak areas are 99.9 %, 99.8 %, and 99.8 % for ethanol, 2-methylpropan-2-ol, 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, and the results are generally in agreement with the corresponding values reported in the literature as shown in Table 1.

Apparatus and Procedures. Liquid 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 joint stopper, using a Precisa 262SMA balance with accuracy of $\pm 3 \times 10^{-5}$ g. The uncertainty in the liquid composition was believed to be less than $\pm 1 \times 10^{-4}$.

Densities were measured with an Anton Paar DMA-5000 vibrating-tube densimeter (Anton-Paar, Graz, Austria) with an accuracy of $\pm 5 \times 10^{-6}$ g·cm^{-3} in the range (0 to 3) g·cm^{-3}, thermostatically controlled to within ± 0.01 K in the range (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 in order to prevent evaporation losses or dissolved air during the experiment. The uncertainty of the density measurements was estimated to be less than $\pm 3 \times 10^{-5}$ 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}.

The viscosities were determined with an Anton Paar automated microviscometer (AMVn). The AMVn uses the rolling ball principle, where a steel ball rolls down inside an inclined, sample-filled glass capillary with an inner diameter of 1.6 mm. The viscosity of the test fluid was determined by measuring the rolling time of the steel ball with a diameter of 1.5 mm. The accuracy of the flow time measurement in the range (0 to 250) s is less than 0.002 s. The range of the flow time for the liquids investigated is varied from 20 s to 80 s. The temperature was maintained by the Peltier effect with accuracy of less than 0.05 K in the range (283.15 to 373.15) K. Calibration was performed periodically under atmospheric pressure, in accordance with specifications, using deionized water. Triplicate mea-

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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.
ethanol	0.78510	0.78493[a] 0.78502[b]	1.085	1.0826[a]	1.35932	1.35941[a] 1.35922[b]
2-methylpropan-2-ol	0.78099	0.7812[a]	4.430	4.438[a]	1.38481	1.3852[a]
2,2,4-trimethylpentane	0.68789	0.68781[a]	0.475	0.4802[c]	1.38898	1.38898[a]

[a] From ref 6. [b] From ref 7. [c] From ref 8.

Table 2. Experimental Densities (ρ), Viscosities (η), Refractive Indices (n_D), Excess Molar Volumes (V^E), Deviations in Viscosity ($\Delta\eta$), and Deviations in 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
Ethanol (1) + 2-Methylpropan-2-ol (2)						
0.0000	0.78099	4.430	1.38481	0.000	0.000	0.00000
0.0500	0.78227	4.295	1.38427	−0.137	0.032	0.00026
0.1000	0.78282	4.135	1.38367	−0.183	0.040	0.00050
0.1500	0.78319	3.949	1.38294	−0.205	0.021	0.00064
0.2000	0.78347	3.752	1.38213	−0.216	−0.009	0.00073
0.2500	0.78365	3.552	1.38123	−0.214	−0.042	0.00078
0.3000	0.78381	3.348	1.38027	−0.210	−0.078	0.00080
0.3500	0.78394	3.134	1.37923	−0.202	−0.125	0.00079
0.4000	0.78403	2.905	1.37813	−0.189	−0.187	0.00076
0.4500	0.78411	2.668	1.37698	−0.174	−0.257	0.00073
0.5000	0.78418	2.462	1.37576	−0.159	−0.296	0.00069
0.5500	0.78429	2.272	1.37449	−0.146	−0.318	0.00065
0.6000	0.78432	2.097	1.37312	−0.126	−0.326	0.00058
0.6500	0.78440	1.934	1.37171	−0.110	−0.322	0.00052
0.7000	0.78442	1.782	1.37018	−0.089	−0.307	0.00042
0.7500	0.78449	1.644	1.36859	−0.072	−0.277	0.00034
0.8000	0.78462	1.518	1.36690	−0.059	−0.236	0.00024
0.8500	0.78475	1.400	1.36515	−0.046	−0.187	0.00017
0.9000	0.78486	1.285	1.36332	−0.031	−0.135	0.00012
0.9500	0.78502	1.188	1.36137	−0.019	−0.064	0.00005
1.0000	0.78510	1.085	1.35932	0.000	0.000	0.00000
Ethanol (1) + 2,2,4-Trimethylpentane (2)						
0.0000	0.68789	0.474	1.38898	0.000	0.000	0.00000
0.0500	0.68894	0.472	1.38825	0.171	−0.033	−0.00019
0.1000	0.69043	0.470	1.38749	0.255	−0.065	−0.00037
0.1500	0.69216	0.476	1.38668	0.311	−0.090	−0.00056
0.2000	0.69408	0.485	1.38586	0.354	−0.111	−0.00071
0.2500	0.69622	0.494	1.38499	0.383	−0.133	−0.00086
0.3000	0.69858	0.506	1.38408	0.401	−0.151	−0.00100
0.3500	0.70119	0.520	1.38311	0.411	−0.168	−0.00113
0.4000	0.70404	0.538	1.38208	0.417	−0.180	−0.00125
0.4500	0.70719	0.558	1.38098	0.417	−0.191	−0.00135
0.5000	0.71069	0.583	1.37980	0.408	−0.197	−0.00144
0.5500	0.71459	0.611	1.37853	0.393	−0.199	−0.00150
0.6000	0.71895	0.642	1.37716	0.370	−0.199	−0.00154
0.6500	0.72382	0.675	1.37567	0.344	−0.196	−0.00156
0.7000	0.72934	0.710	1.37403	0.309	−0.192	−0.00155
0.7500	0.73556	0.750	1.37223	0.274	−0.182	−0.00149
0.8000	0.74267	0.797	1.37023	0.232	−0.166	−0.00138
0.8500	0.75087	0.853	1.36799	0.185	−0.140	−0.00121
0.9000	0.76047	0.916	1.36547	0.126	−0.108	−0.00095
0.9500	0.77178	0.989	1.36261	0.059	−0.065	−0.00055
1.0000	0.78510	1.085	1.35932	0.000	0.000	0.00000
2-Methylpropan-2-ol (1) + 2,2,4-Trimethylpentane (2)						
0.0000	0.68789	0.475	1.38898	0.000	0.000	0.00000
0.0500	0.68977	0.483	1.38834	0.198	−0.190	−0.00052
0.1000	0.69189	0.509	1.38784	0.358	−0.362	−0.00089
0.1500	0.69445	0.515	1.38735	0.441	−0.553	−0.00125
0.2000	0.69714	0.553	1.38693	0.520	−0.713	−0.00153
0.2500	0.70002	0.564	1.38650	0.586	−0.900	−0.00181
0.3000	0.70312	0.598	1.38612	0.635	−1.064	−0.00204
0.3500	0.70640	0.614	1.38573	0.679	−1.245	−0.00227
0.4000	0.70987	0.665	1.38537	0.718	−1.392	−0.00246
0.4500	0.71352	0.698	1.38505	0.758	−1.557	−0.00260
0.5000	0.71743	0.765	1.38473	0.785	−1.688	−0.00273
0.5500	0.72162	0.805	1.38445	0.802	−1.845	−0.00282
0.6000	0.72619	0.912	1.38420	0.794	−1.936	−0.00286
0.6500	0.73111	0.984	1.38398	0.773	−2.062	−0.00285
0.7000	0.73655	1.107	1.38381	0.717	−2.137	−0.00279
0.7500	0.74244	1.297	1.38371	0.646	−2.144	−0.00264
0.8000	0.74888	1.557	1.38368	0.551	−2.082	−0.00240
0.8500	0.75587	1.895	1.38381	0.441	−1.942	−0.00198
0.9000	0.76354	2.426	1.38405	0.307	−1.609	−0.00144
0.9500	0.77190	3.172	1.38436	0.158	−1.060	−0.00080
1.0000	0.78099	4.430	1.38481	0.000	0.000	0.00000

Table 3. Experimental Densities (ρ), Viscosities (η), Refractive Indices (n_D), Excess Molar Volumes (V^E), Deviations in Viscosity ($\Delta\eta$), and Deviations in 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
Ethanol (1) + 2-Methylpropan-2-ol (2)						
0.0000	0.77070	2.622	1.37960	0.000	0.000	0.00000
0.0500	0.77223	2.587	1.37911	−0.165	0.051	0.00028
0.1000	0.77295	2.536	1.37861	−0.225	0.086	0.00058
0.1500	0.77360	2.463	1.37797	−0.274	0.098	0.00078
0.2000	0.77403	2.374	1.37726	−0.294	0.095	0.00094
0.2500	0.77434	2.277	1.37648	−0.299	0.084	0.00106
0.3000	0.77462	2.180	1.37558	−0.299	0.073	0.00111
0.3500	0.77487	2.082	1.37463	−0.295	0.061	0.00114
0.4000	0.77507	1.978	1.37360	−0.284	0.042	0.00114
0.4500	0.77529	1.877	1.37253	−0.274	0.027	0.00115
0.5000	0.77545	1.772	1.37136	−0.257	0.008	0.00111
0.5500	0.77561	1.675	1.37013	−0.239	−0.003	0.00107
0.6000	0.77568	1.575	1.36883	−0.213	−0.017	0.00101
0.6500	0.77577	1.475	1.36741	−0.187	−0.032	0.00090
0.7000	0.77585	1.380	1.36593	−0.160	−0.041	0.00079
0.7500	0.77593	1.291	1.36438	−0.133	−0.044	0.00069
0.8000	0.77607	1.206	1.36271	−0.111	−0.043	0.00055
0.8500	0.77618	1.126	1.36096	−0.086	−0.037	0.00042
0.9000	0.77628	1.048	1.35914	−0.059	−0.030	0.00031
0.9500	0.77640	0.976	1.35720	−0.033	−0.016	0.00018
1.0000	0.77643	0.906	1.35509	0.000	0.000	0.00000
Ethanol (1) + 2,2,4-Trimethylpentane (2)						
0.0000	0.67955	0.425	1.38398	0.000	0.000	0.00000
0.0500	0.68044	0.421	1.38325	0.211	−0.028	−0.00020
0.1000	0.68185	0.419	1.38247	0.313	−0.054	−0.00042
0.1500	0.68355	0.423	1.38169	0.373	−0.074	−0.00060
0.2000	0.68546	0.428	1.38087	0.415	−0.093	−0.00077
0.2500	0.68759	0.435	1.38002	0.443	−0.110	−0.00092
0.3000	0.68991	0.443	1.37913	0.465	−0.126	−0.00105
0.3500	0.69248	0.453	1.37819	0.478	−0.140	−0.00118
0.4000	0.69533	0.469	1.37719	0.480	−0.148	−0.00129
0.4500	0.69847	0.487	1.37612	0.476	−0.154	−0.00139
0.5000	0.70195	0.507	1.37497	0.466	−0.159	−0.00147
0.5500	0.70581	0.530	1.37373	0.451	−0.160	−0.00154
0.6000	0.71014	0.555	1.37239	0.427	−0.159	−0.00159
0.6500	0.71499	0.583	1.37093	0.398	−0.155	−0.00161
0.7000	0.72046	0.614	1.36933	0.363	−0.148	−0.00160
0.7500	0.72664	0.647	1.36757	0.326	−0.139	−0.00155
0.8000	0.73371	0.685	1.36562	0.282	−0.125	−0.00145
0.8500	0.74188	0.731	1.36345	0.231	−0.103	−0.00127
0.9000	0.75145	0.784	1.36102	0.167	−0.074	−0.00099
0.9500	0.76283	0.843	1.35826	0.087	−0.039	−0.00058
1.0000	0.77643	0.906	1.35509	0.000	0.000	0.00000
2-Methylpropan-2-ol (1) + 2,2,4-Trimethylpentane (2)						
0.0000	0.67955	0.425	1.38398	0.000	0.000	0.00000
0.0500	0.68115	0.425	1.38325	0.257	−0.110	−0.00060
0.1000	0.68325	0.449	1.38271	0.412	−0.196	−0.00101
0.1500	0.68562	0.447	1.38219	0.525	−0.308	−0.00139
0.2000	0.68828	0.478	1.38177	0.598	−0.386	−0.00166
0.2500	0.69111	0.480	1.38135	0.660	−0.494	−0.00193
0.3000	0.69414	0.522	1.38095	0.709	−0.562	−0.00217
0.3500	0.69738	0.523	1.38055	0.745	−0.671	−0.00240
0.4000	0.70080	0.564	1.38021	0.779	−0.740	−0.00256
0.4500	0.70442	0.590	1.37986	0.808	−0.824	−0.00272
0.5000	0.70824	0.633	1.37955	0.836	−0.891	−0.00284
0.5500	0.71237	0.672	1.37926	0.846	−0.961	−0.00292
0.6000	0.71685	0.726	1.37903	0.836	−1.017	−0.00293
0.6500	0.72169	0.786	1.37881	0.810	−1.067	−0.00291
0.7000	0.72703	0.866	1.37862	0.750	−1.097	−0.00286
0.7500	0.73281	0.994	1.37850	0.675	−1.079	−0.00271
0.8000	0.73910	1.140	1.37847	0.581	−1.043	−0.00246
0.8500	0.74589	1.332	1.37858	0.477	−0.960	−0.00205
0.9000	0.75343	1.622	1.37879	0.336	−0.780	−0.00152
0.9500	0.76162	2.020	1.37914	0.184	−0.492	−0.00083
1.0000	0.77070	2.622	1.37960	0.000	0.000	0.00000

surements 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 with the wavelength (589 nm) corresponding to the D-line of sodium. The temperature range of this refractometer is from 283.15 K to 343.15 K with 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 less than ± 0.00002 units.

The densities, viscosities, and refractive indices of the binary systems ethanol + 2-methylpropan-2-ol, ethanol + 2,2,4-trimethylpentane, and 2-methylpropan-2-ol + 2,2,4-trimethylpentane were measured at temperatures of 298.15 K, 308.15 K, and 318.15 K and atmospheric pressure of (100.8±0.2) kPa. A set with the compositions varying from 0.05 to 0.95 mol fractions was prepared for each binary system. A total of 55 compositions was measured at 298.15 K for the ternary system ethanol + 2-methylpropan-2-ol + 2,2,4-trimethylpentane. An average of at least three measurements was taken for each composition.

Results and Discussion

Tables 2 to 4 list the experimental densities, viscosities, refractive indices, excess molar volumes, deviations in viscosity from mole fraction average, and deviations in refractive index from volume fraction average for three binary systems ethanol + 2-methylpropan-2-ol, ethanol + 2,2,4-trimethylpentane, and 2-methylpropan-2-ol + 2,2,4-trimethylpentane at temperatures of 298.15 K, 308.15 K, and 318.15 K. The molar excess volumes (V^E) were calculated from density data according to

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

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

In the system studied, excess molar volumes are positive for the systems ethanol + 2,2,4-trimethylpentane and 2-methylpropan-2-ol + 2,2,4-trimethylpentane and are negative for the system ethanol + 2-methylpropan-2-ol over the whole composition range. The values of V^E increase systematically from 298.15 K to 318.15 K except for those of the system ethanol + 2-methylpropan-2-ol, which decrease with the increase of temperature. The excess molar volume V^E ($x = 0.5$) increases in the sequence: 2-methylpropan-2-ol + 2,2,4-trimethylpentane > ethanol + 2,2,4-trimethylpentane > ethanol + 2-methylpropan-2-ol. The values of V^E ($x = 0.5$) vary from −0.348 $cm^3 \cdot mol^{-1}$ to 0.906 $cm^3 \cdot mol^{-1}$. In the literature, V^E of the binary system ethanol + 2,2,4-trimethylpentane had been measured at 298.15 K.[9,10] Figure 1 shows the excess molar volumes for the three binary systems at $T = 298.15$ K together with the literature values. Our results were found to be in agreement with their measurements.

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, alcohols are strongly self-associated through hydrogen bonding with degrees of association depending on such variables as chain length, the position of the -OH group, temperature, and dilution by other substances. With higher alcohols, structure contribution is negligible and association decreases with an increase in the chain length of alcohols. The 2,2,4-trimethylpentane molecules do not exhibit this property because they have no groups having that ability. The interactions of ethanol or 2-methylpropan-2-ol against 2,2,4-trimethylpentane molecules involve mainly dispersion force giving a positive

Table 4. Experimental Densities (ρ), Viscosities (η), Refractive Indices (n_D), Excess Molar Volumes (V^E), Deviations in Viscosity ($\Delta\eta$), and Deviations in Refractive Index (Δn_D) for the Binary Systems at 318.15 K

x_1	ρ / g·cm^{-3}	η / mPa·s	n_D	V^E / cm^3·mol^{-1}	$\Delta\eta$ / mPa·s	Δn_D
Ethanol (1) + 2-Methylpropan-2-ol (2)						
0.0000	0.76005	1.708	1.37416	0.000	0.000	0.00000
0.0500	0.76194	1.730	1.37378	−0.207	0.070	0.00035
0.1000	0.76282	1.719	1.37336	−0.281	0.106	0.00068
0.1500	0.76353	1.698	1.37284	−0.330	0.133	0.00095
0.2000	0.76414	1.662	1.37224	−0.363	0.144	0.00117
0.2500	0.76459	1.618	1.37150	−0.375	0.148	0.00128
0.3000	0.76501	1.568	1.37072	−0.381	0.146	0.00139
0.3500	0.76541	1.515	1.36984	−0.384	0.140	0.00144
0.4000	0.76574	1.456	1.36891	−0.376	0.129	0.00149
0.4500	0.76604	1.395	1.36791	−0.364	0.115	0.00151
0.5000	0.76631	1.332	1.36682	−0.347	0.100	0.00148
0.5500	0.76658	1.272	1.36567	−0.329	0.088	0.00145
0.6000	0.76672	1.213	1.36442	−0.298	0.076	0.00138
0.6500	0.76687	1.153	1.36304	−0.266	0.064	0.00123
0.7000	0.76701	1.092	1.36162	−0.233	0.050	0.00111
0.7500	0.76715	1.032	1.36007	−0.199	0.038	0.00093
0.8000	0.76727	0.974	1.35848	−0.162	0.028	0.00079
0.8500	0.76741	0.919	1.35677	−0.127	0.020	0.00061
0.9000	0.76751	0.862	1.35498	−0.088	0.011	0.00044
0.9500	0.76760	0.805	1.35308	−0.047	0.001	0.00026
1.0000	0.76761	0.756	1.35100	0.000	0.000	0.00000
Ethanol (1) + 2,2,4-Trimethylpentane (2)						
0.0000	0.67110	0.380	1.37898	0.000	0.000	0.00000
0.0500	0.67189	0.376	1.37815	0.239	−0.023	−0.00032
0.1000	0.67320	0.377	1.37738	0.364	−0.041	−0.00054
0.1500	0.67481	0.378	1.37662	0.442	−0.058	−0.00072
0.2000	0.67667	0.381	1.37584	0.492	−0.074	−0.00087
0.2500	0.67874	0.387	1.37503	0.528	−0.087	−0.00100
0.3000	0.68105	0.392	1.37417	0.547	−0.101	−0.00113
0.3500	0.68360	0.401	1.37326	0.559	−0.111	−0.00125
0.4000	0.68641	0.413	1.37229	0.562	−0.117	−0.00136
0.4500	0.68953	0.426	1.37125	0.556	−0.123	−0.00145
0.5000	0.69300	0.443	1.37013	0.541	−0.125	−0.00154
0.5500	0.69687	0.461	1.36892	0.519	−0.126	−0.00162
0.6000	0.70118	0.483	1.36762	0.491	−0.123	−0.00166
0.6500	0.70600	0.505	1.36621	0.459	−0.119	−0.00168
0.7000	0.71143	0.528	1.36466	0.423	−0.115	−0.00167
0.7500	0.71760	0.557	1.36295	0.380	−0.105	−0.00162
0.8000	0.72466	0.589	1.36106	0.329	−0.092	−0.00152
0.8500	0.73281	0.626	1.35896	0.273	−0.074	−0.00134
0.9000	0.74233	0.668	1.35660	0.206	−0.050	−0.00107
0.9500	0.75376	0.712	1.35396	0.114	−0.025	−0.00063
1.0000	0.76761	0.756	1.35095	0.000	0.000	0.00000
2-Methylpropan-2-ol (1) + 2,2,4-Trimethylpentane (2)						
0.0000	0.67110	0.380	1.37898	0.000	0.000	0.00000
0.0500	0.67212	0.377	1.37818	0.393	−0.069	−0.00066
0.1000	0.67411	0.400	1.37755	0.559	−0.113	−0.00114
0.1500	0.67656	0.394	1.37703	0.638	−0.185	−0.00151
0.2000	0.67920	0.413	1.37655	0.698	−0.233	−0.00183
0.2500	0.68196	0.420	1.37611	0.759	−0.292	−0.00210
0.3000	0.68492	0.449	1.37570	0.805	−0.329	−0.00233
0.3500	0.68811	0.450	1.37528	0.834	−0.395	−0.00256
0.4000	0.69143	0.480	1.37491	0.869	−0.431	−0.00274
0.4500	0.69499	0.504	1.37458	0.890	−0.474	−0.00286
0.5000	0.69877	0.542	1.37427	0.906	−0.502	−0.00295
0.5500	0.70281	0.564	1.37397	0.913	−0.546	−0.00302
0.6000	0.70721	0.614	1.37371	0.895	−0.563	−0.00304
0.6500	0.71198	0.649	1.37348	0.859	−0.594	−0.00302
0.7000	0.71721	0.706	1.37331	0.795	−0.604	−0.00291
0.7500	0.72288	0.798	1.37317	0.713	−0.578	−0.00276
0.8000	0.72903	0.889	1.37313	0.615	−0.553	−0.00249
0.8500	0.73565	1.028	1.37323	0.509	−0.481	−0.00207
0.9000	0.74304	1.164	1.37339	0.361	−0.411	−0.00155
0.9500	0.75107	1.398	1.37372	0.202	−0.244	−0.00085
1.0000	0.76005	1.708	1.37416	0.000	0.000	0.00000

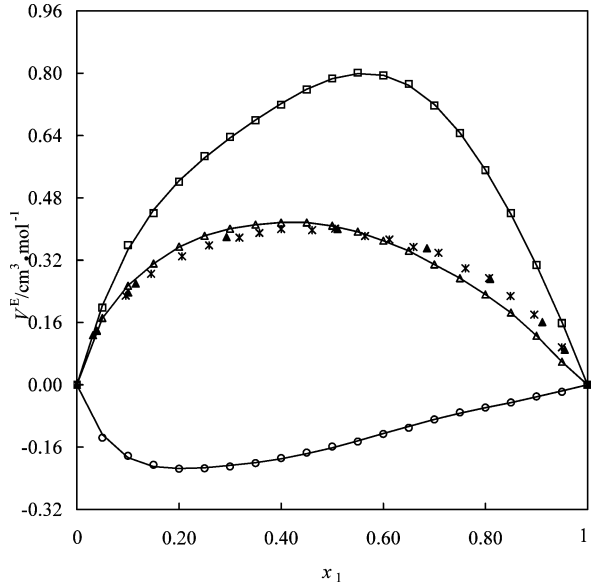

Figure 1. Change of excess molar volume V^E with mole fraction x_1 at $T = 298.15$ K: ○, ethanol + 2-methylpropan-2-ol; △, ethanol + 2,2,4-trimethylpentane; ▲, ethanol + 2,2,4-trimethylpentane from Kretschmer et al.;[9] ∗, ethanol + 2,2,4-trimethylpentane from Blanco et al.;[10] □, 2-methylpropan-2-ol + 2,2,4-trimethylpentane. Solid curves were calculated from the Redlich−Kister equation.

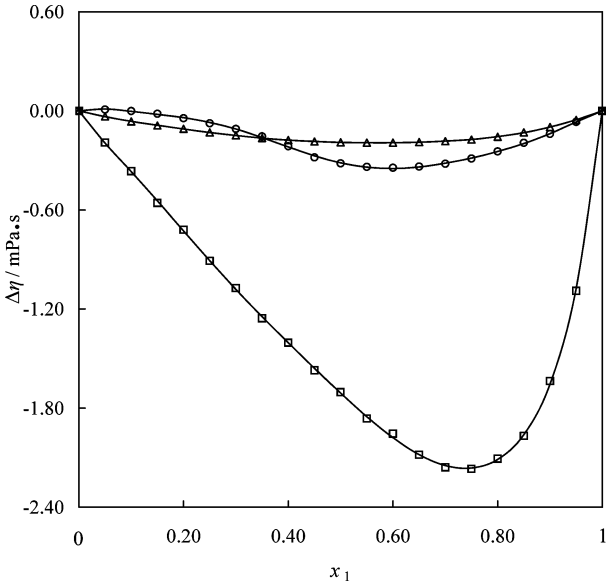

Figure 2. Change of viscosity deviation $\Delta\eta$ with mole fraction x_1 at $T = 298.15$ K: ○, ethanol + 2-methylpropan-2-ol; △, ethanol + 2,2,4-trimethylpentane; □, 2-methylpropan-2-ol + 2,2,4-trimethylpentane. Solid curves were calculated from the Redlich−Kister equation.

contribution to V^E. The interactions between ethanol and 2-methylpropan-2-ol 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

$$\Delta\eta = \eta - \sum_{i=1}^{N} x_i \eta_i \qquad (2)$$

where η is the absolute viscosities of the mixtures and η_i is the absolute viscosities of pure component i. In the system studied, $\Delta\eta$ values increase with a rise in temperature for all of the mixtures. The $\Delta\eta$ values are also graphically represented as a function of mole fraction at 298.15 K in Figure 2. It is observed that the $\Delta\eta$ values are negative for the systems ethanol + 2,2,4-trimethylpentane and 2-methylpropan-2-ol + 2,2,4-trimethylpentane over the whole composition range. For the system of ethanol + 2-methylpropan-2-ol, positive values of $\Delta\eta$ were observed in the region of x_1 below 0.35 while negative values of $\Delta\eta$ were found for the other composition range. A sigmoid shape observed may be attributed to the hydrogen bond effect occurred between ethanol and 2-methylpropan-2-ol molecules. The values of $\Delta\eta$ ($x = 0.5$) show the order as ethanol + 2,2,4-trimethylpentane > ethanol + 2-methylpropan-2-ol > 2-methylpropan-2-ol + 2,2,4-trimethylpentane. The values of $\Delta\eta$ ($x = 0.5$) vary from −1.704 mPa·s to 0.100 mPa·s.

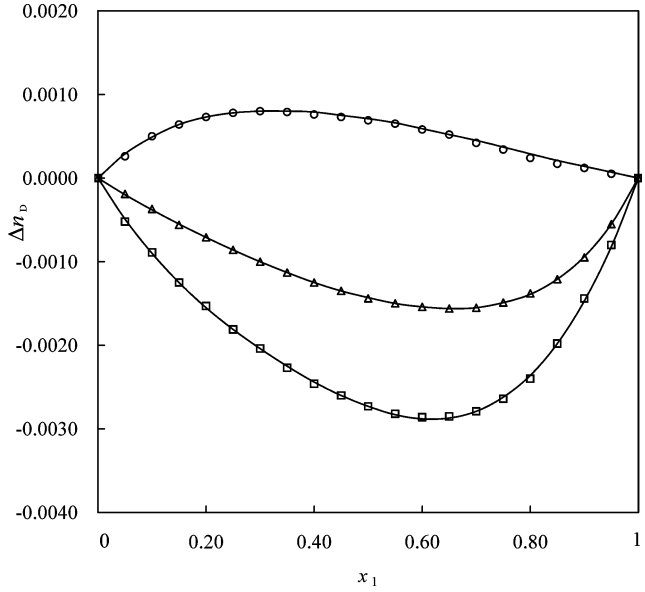

Figure 3. Change of refractive indices Δn_D with mole fraction x_1 at $T = 298.15$ K: ○, ethanol + 2-methylpropan-2-ol; △, ethanol + 2,2,4-trimethylpentane; □, 2-methylpropan-2-ol + 2,2,4-trimethylpentane. Solid curves were calculated from the Redlich−Kister equation.

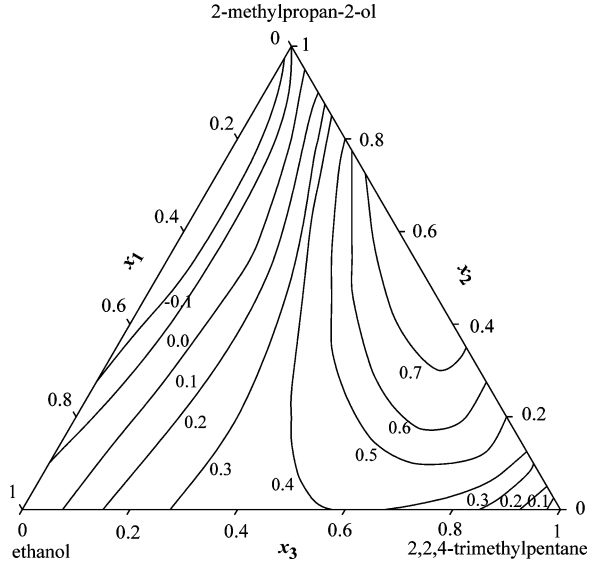

Figure 4. Curves of constant V^E/cm^3·mol^{-1} for the ternary system ethanol (1) + 2-methylpropan-2-ol (2) + 2,2,4-trimethylpentane (3) at $T = 298.15$ K.

Table 5. Binary Coefficients of the Redlich−Kister Equation from T = 298.15 K to T = 318.15 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
			Ethanol (1) + 2-Methylpropan-2-ol (2)				
V^E/cm^3·mol^{-1}	298.15	−0.6493	0.5765	−0.1679	0.7519	−1.1356	4.7×10^{-3}
	308.15	−1.0313	0.6865	−0.1827	0.8022	−1.2063	4.7×10^{-3}
	318.15	−1.4008	0.6976	−0.0822	1.0502	−1.5868	7.1×10^{-3}
$\Delta\eta$/mPa·s	298.15	−1.1248	−1.3950	1.0256	0.4062		9.1×10^{-3}
	308.15	−0.0312	−0.6356	0.3863	−0.2359		2.9×10^{-3}
	318.15	0.4072	−0.5278	0.3818	−0.2372		1.9×10^{-3}
Δn_D	298.15	0.0028	−0.0022	0.0010			1.9×10^{-5}
	308.15	0.0045	−0.0019	0.0006			1.7×10^{-5}
	318.15	0.0059	−0.0017	0.0004			2.2×10^{-5}
			Ethanol (1) + 2,2,4-Trimethylpentane (2)				
V^E/cm^3·mol^{-1}	298.15	1.6318	−0.3895	0.2407	−0.7980	0.8458	5.4×10^{-3}
	308.15	1.8728	−0.4321	0.3559	−0.8910	1.4005	6.3×10^{-3}
	318.15	2.1778	−0.6268	0.5190	−0.7391	1.6192	5.7×10^{-3}
$\Delta\eta$/mPa·s	298.15	−0.7803	−0.2071	−0.2555	−0.1747		1.7×10^{-3}
	308.15	−0.6352	−0.1453	−0.1173			1.6×10^{-3}
	318.15	−0.5031	−0.0805	−0.0276			1.6×10^{-3}
Δn_D	298.15	−0.0057	−0.0035	−0.0024			2.3×10^{-3}
	308.15	−0.0059	−0.0035	−0.0029			2.2×10^{-5}
	318.15	−0.0061	−0.0034	−0.0041			2.1×10^{-5}
			2-Methylpropan-2-ol (1) + 2,2,4-Trimethylpentane (2)				
V^E/cm^3·mol^{-1}	298.15	3.1423	0.7887	0.4055	−1.6974	0.5544	4.8×10^{-3}
	308.15	3.3358	0.5543	0.6170	−1.7292	1.1293	4.7×10^{-3}
	318.15	3.6586	0.4773	0.1388	−2.8049	3.4162	1.2×10^{-2}
$\Delta\eta$/mPa·s	298.15	−6.8118	−5.4318	−4.1213	−5.0710	−3.9856	1.8×10^{-2}
	308.15	−3.5877	−2.7326	−2.0241	−1.9834	−1.4857	8.4×10^{-3}
	318.15	−2.0277	−1.3818	−1.2753	−0.8229		9.3×10^{-3}
Δn_D	298.15	−0.0109	−0.0043	−0.0035			2.4×10^{-5}
	308.15	−0.0113	−0.0040	−0.0044			2.6×10^{-5}
	318.15	−0.0118	−0.0033	−0.0047			2.4×10^{-5}

ΔQ_{123}	C_0	C_1	C_2	σ
V^E/cm^3·mol^{-1}	3.0964	−6.2941	−7.8323	2.3×10^{-2}
$\Delta\eta$/mPa·s	5.1868	−2.6619	−22.439	2.7×10^{-2}
Δn_D	−0.0093	0.0226	−0.0031	3.3×10^{-4}

The deviation in the refractive index (Δn_D) was calculated from the volume fraction average as suggested by Brocos et al.[11] and is given by

$$\Delta n_D = n_D - \sum_{i=1}^{N} \phi_i n_{D_i} \tag{3}$$

and

$$\phi_i = \frac{x_i V}{\sum_{i=1}^{N} x_i V_i} \tag{4}$$

where n_D, n_{D_i}, and ϕ_i are the refractive index of the mixture, the refractive index of pure component i, and the volume fraction of pure component i, respectively. V and V_i are the molar volume of the mixture and the molar volume of pure component i, respectively. For the whole composition range, the Δn_D values are negative for the mixtures ethanol + 2,2,4-trimethylpentane and 2-methylpropan-2-ol + 2,2,4-trimethylpentane, while the positive values were found for the system ethanol + 2-methylprop-2-ol. The values of Δn_D decrease systematically from 298.15 K to 318.15 K except for those of the system ethanol + 2-methylpropan-2-ol, which increase with the increase of temperature. The values of Δn_D (x = 0.5) follow the order ethanol + 2-methylpropan-2-ol > ethanol + 2,2,4-trimethylpentane > 2-methylpropan-2-ol + 2,2,4-trimethylpentane. The values of Δn_D (x = 0.5) vary from −0.00295 to 0.00148. Figure 3 shows the results of Δn_D for the three binary mixtures at T = 298.15 K.

The mixing functions V^E, $\Delta\eta$, and Δn_D were represented mathematically by the Redlich−Kister equation for correlating the experimental data:[12]

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

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 values 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 the fitted values of the respective functions in Table 5. The standard deviation is defined by

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

where n is the number of experimental points and p is the number of adjustable parameters. The σ values lie between 0.0047 cm^3·mol^{-1} and 0.012 cm^3·mol^{-1}, between 0.0015 mPa·s and 0.018 mPa·s, and between 0.000017 and 0.000026 for V^E, $\Delta\eta$, and Δn_D, respectively.

The experimental densities, viscosities, excess molar volumes, deviations in the viscosity from mole fraction average, and deviations in the refractive index from volume fraction average of ternary mixtures ethanol (1) + 2-methylpropan-2-ol (2) + 2,2,4-trimethylpentane (3) at T = 298.15 K are listed in Table 6. The derived data, V^E/cm^3·mol^{-1}, $\Delta\eta$/mPa·s, and Δn_D as defined in eqs 1−3 for the

Table 6. Experimental Densities (ρ), Viscosities (η), Refractive Indices (n_D), Excess Molar Volumes (V^E), Deviations in Viscosity ($\Delta\eta$), and Deviations in Refractive Index (Δn_D) for the Ternary System Ethanol (1) + 2-Methylpropan-2-ol (2) + 2,2,4-Trimethylpentane (3) at 298.15 K

		ρ	η		V^E	$\Delta\eta$	
x_1	x_2	g·cm^{-3}	mPa·s	n_D	cm^3·mol^{-1}	mPa·s	Δn_D
0.0500	0.9000	0.77297	3.302	1.38394	0.018	−0.791	−0.00047
0.0500	0.8000	0.75639	2.019	1.38352	0.325	−1.676	−0.00159
0.0500	0.7000	0.74249	1.342	1.38342	0.560	−1.954	−0.00229
0.0502	0.5999	0.73081	0.989	1.38359	0.714	−1.908	−0.00279
0.0500	0.5000	0.72105	0.817	1.38405	0.769	−1.682	−0.00280
0.0500	0.4001	0.71270	0.695	1.38469	0.756	−1.405	−0.00244
0.0500	0.3000	0.70545	0.648	1.38538	0.697	−1.053	−0.00227
0.0500	0.2001	0.69908	0.611	1.38621	0.591	−0.692	−0.00150
0.0500	0.1000	0.69360	0.572	1.38706	0.421	−0.332	−0.00110
0.0500	0.0501	0.69079	0.537	1.38748	0.393	−0.168	−0.00082
0.1000	0.8500	0.77343	3.173	1.38334	−0.041	−0.752	−0.00028
0.1000	0.7500	0.75661	1.928	1.38316	0.252	−1.598	−0.00135
0.1000	0.6500	0.74249	1.275	1.38305	0.483	−1.853	−0.00199
0.1000	0.5500	0.73070	0.967	1.38329	0.624	−1.762	−0.00233
0.1000	0.4500	0.72074	0.789	1.38378	0.688	−1.541	−0.00249
0.1000	0.3500	0.71217	0.677	1.38442	0.697	−1.255	−0.00217
0.1000	0.2500	0.70485	0.632	1.38505	0.634	−0.901	−0.00195
0.1000	0.1500	0.69836	0.607	1.38585	0.546	−0.527	−0.00152
0.1002	0.0500	0.69287	0.540	1.38677	0.370	−0.195	−0.00093
0.2000	0.7500	0.77377	2.932	1.38196	−0.086	−0.656	0.00003
0.2000	0.6500	0.75663	1.814	1.38191	0.165	−1.376	−0.00106
0.2000	0.5500	0.74222	1.213	1.38208	0.366	−1.578	−0.00155
0.2000	0.4500	0.73016	0.930	1.38242	0.491	−1.462	−0.00189
0.2001	0.3500	0.71988	0.755	1.38294	0.562	−1.238	−0.00198
0.2000	0.2500	0.71105	0.676	1.38361	0.581	−0.919	−0.00185
0.2001	0.1500	0.70344	0.638	1.38433	0.546	−0.558	−0.00161
0.1999	0.0501	0.69699	0.559	1.38514	0.429	−0.238	−0.00123
0.3000	0.6500	0.77383	2.635	1.38020	−0.095	−0.617	−0.00004
0.3000	0.5500	0.75632	1.666	1.38042	0.119	−1.187	−0.00076
0.3000	0.4500	0.74163	1.160	1.38077	0.290	−1.294	−0.00134
0.3000	0.3500	0.72922	0.883	1.38155	0.413	−1.172	−0.00137
0.3000	0.2500	0.71870	0.760	1.38212	0.479	−0.897	−0.00151
0.3000	0.1500	0.70969	0.684	1.38280	0.495	−0.574	−0.00146
0.3000	0.0500	0.70203	0.586	1.38362	0.443	−0.273	−0.00120
0.4000	0.5500	0.77378	2.304	1.37835	−0.092	−0.611	0.00038
0.4000	0.4500	0.75570	1.502	1.37879	0.107	−1.014	−0.00060
0.4000	0.3500	0.74063	1.088	1.37932	0.263	−1.029	−0.00117
0.4000	0.2599	0.72796	0.877	1.38011	0.372	−0.842	−0.00132
0.4000	0.1499	0.71721	0.752	1.38082	0.433	−0.568	−0.00158
0.4001	0.0499	0.70811	0.625	1.38165	0.432	−0.296	−0.00134
0.5000	0.4501	0.77343	1.994	1.37595	−0.058	−0.584	0.00001
0.5000	0.3501	0.75472	1.355	1.37675	0.132	−0.824	−0.00071
0.4999	0.2501	0.73931	1.020	1.37742	0.267	−0.761	−0.00118
0.5000	0.1500	0.72643	0.826	1.37828	0.355	−0.556	−0.00156
0.5000	0.0499	0.71549	0.680	1.37923	0.406	−0.303	−0.00157
0.6000	0.3500	0.77298	1.719	1.37354	−0.018	−0.522	−0.00017
0.6000	0.2500	0.75365	1.218	1.37435	0.157	−0.624	−0.00100
0.6000	0.1501	0.73780	0.951	1.37540	0.282	−0.493	−0.00145
0.5999	0.0501	0.72469	0.747	1.37652	0.352	−0.298	−0.00161
0.7000	0.2500	0.77251	1.503	1.37081	0.020	−0.401	−0.00016
0.7000	0.1500	0.75245	1.094	1.37193	0.185	−0.412	−0.00099
0.7004	0.0500	0.73625	0.835	1.37327	0.287	−0.272	−0.00140
0.8000	0.1500	0.77210	1.307	1.36775	0.049	−0.261	−0.00034
0.8000	0.0500	0.75137	0.954	1.36923	0.190	−0.215	−0.00131
0.9000	0.0500	0.77182	1.126	1.36433	0.062	−0.105	−0.00057

ternary system were correlated respectively using the equation:

$$\Delta Q_{123} = \Delta Q_{bin} + x_1 x_2 x_3 \Delta_{123} \quad (7)$$

and

$$\Delta Q_{bin} = \sum_{i=1}^{3}\sum_{j>i}^{3} \Delta Q_{ij} \quad (8)$$

where ΔQ_{123} refers to V^E, $\Delta\eta$, or Δn_D for the ternary system ethanol (1) + 2-methylpropan-2-ol (2) + 2,2,4-trimethylpentane (3) and $x_3 = 1 - x_1 - x_2$. ΔQ_{ij} in eq 8 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

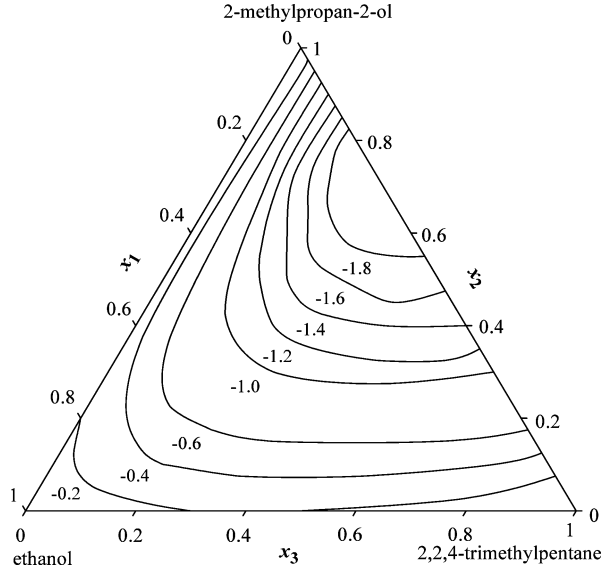

Figure 5. Curves of constant $\Delta\eta$ for the ternary system ethanol (1) + 2-methylpropan-2-ol (2) + 2,2,4-trimethylpentane (3) at T = 298.15 K.

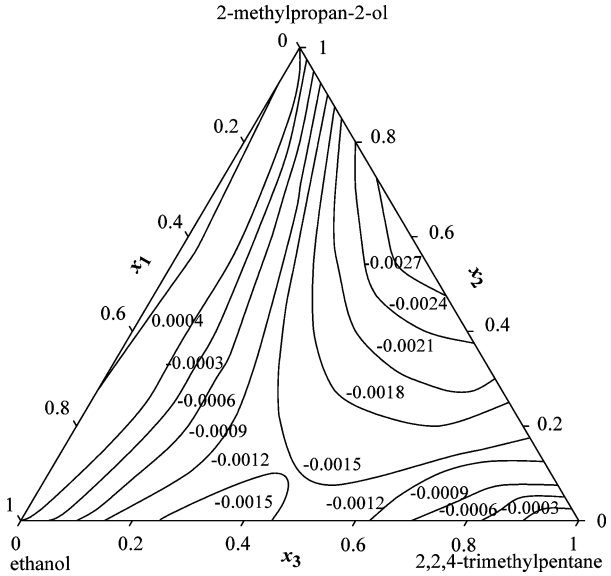

Figure 6. Curves of constant Δn_D for the ternary system ethanol (1) + 2-methylpropan-2-ol (2) + 2,2,4-trimethylpentane (3) at T = 298.15 K.

the expression suggested by Cibulka:[13]

$$\Delta_{123} = C_0 + C_1 x_1 + C_2 x_2 \quad (9)$$

The ternary parameters C_0, C_1, and C_2 were determined with the optimization algorithm similar to that for the binary parameters. The fitting parameters and the corresponding standard deviations are given in Table 5. The σ values are 0.023 cm^3·mol^{-1}, 0.027 mPa·s, and 0.00033 for V^E, $\Delta\eta$, and Δn_D, respectively. The curves of constant V^E, $\Delta\eta$, and Δn_D calculated from eqs 7 to 9 at T = 298.15 K 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 the binary system ethanol + 2-methylpropan-2-ol where a change in sign occurs. The maximum V^E value was found in the binary system 2-methylpropan-2-ol + 2,2,4-trimethylpentane near x_1 = 0.6. Figure 5 shows negative values of ternary $\Delta\eta$ with a minimum value near

$x_1 = 0.7$ of the binary system 2-methylpropan-2-ol + 2,2,4-trimethylpentane. Figure 6 shows the negative values for ternary Δn_D at almost all compositions, except at compositions close to the binary system ethanol + 2-methylpropan-2-ol where a change in sign occurs. The minimum Δn_D value was found near $x_1 = 0.6$ in the binary system 2-methylpropan-2-ol + 2,2,4-trimethylpentane.

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