Densities and Viscosities of Binary and Ternary Mixtures of Ethanol, 2-Butanone, and 2,2,4-Trimethylpentane at T = (298.15, 308.15, and 318.15) K

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Densities and viscosities of the ternary mixture ethanol + 2-butanone + 2,2,4-trimethylpentane and the binary mixtures ethanol + 2-butanone, ethanol + 2,2,4-trimethylpentane, and 2-butanone + 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 Ubbelohde capillary viscometer. Excess molar volumes V^E and deviations in viscosity $\Delta\eta$ for the mixtures were derived from experimental data. The binary data were correlated with liquid composition 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 are commonly methanol, ethanol, propanol, and butanols as well as methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), and *tert*-amyl methyl ether (TAME). These oxygenated compounds are added to improve the octane rating and pollution-reducing capability of gasoline. MTBE, the primary oxygenated compound currently used in reformulated gasoline, is being phased out because of groundwater pollution problems. Thus, it is important to investigate the possible use of other oxygenates to comply with environmental regulations. In this sense, there has been increasing interest in the thermodynamic behavior of liquid mixtures of oxygenated compounds in hydrocarbon mixtures.[1−6]

For these reasons, we measured the densities and viscosities of the ternary mixture ethanol + 2-butanone + 2,2,4-trimethylpentane (isooctane) and the binary mixtures ethanol + 2-butanone, ethanol + 2,2,4-trimethylpentane, and 2-butanone + 2,2,4-trimethylpentane at atmospheric pressure. The experimental data are used to calculate excess molar volumes and viscosity deviations from the mole fraction average. The excess quantities of binary mixtures have been fit to a Redlich−Kister equation to estimate the coefficients. For the ternary data, several polynomial equations have been tested to minimize the set of parameters needed to correlate adequately. As far as we know, no such ternary data are available for the mixtures in the open literature.

Experimental Section

Materials. The chemicals used were of analytical grade and were obtained from Showa, Tedia, and Merck. All chemicals were used without further purification. The purity of all of the chemicals was checked by gas chromatography. The gas chromatographic analyses of pure components showed that the major peak areas exceeding 99.8% were used for the experimental investigations. The purity of the solvents was further ascertained by comparing their densities, viscosities, and refractive indices at 298.15 K, which agreed well with the corresponding literature values as shown in Table 1. Densities and viscosities were determined with the apparatus used in this study. Refractive indices, n_D, were measured with an automatic Anton Paar RXA-156 refractometer, which works with the wavelength corresponding to the D-ray of sodium (589 nm). The temperature range of this refractometer is from 283.15 K to 343.15 K with an accuracy of ±0.03 K. The accuracy of the refractive index measurement is ±0.00002 units in the range of (1.32 to 1.56) units.

Table 1. Comparison of Measured Densities, Viscosities, and Refractive Indices of 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	0.78514	0.78493[a]	1.088	1.0826[a]	1.35949	1.35941[a]
		0.7854[b]		1.099[b]		1.3605[b]
2-butanone	0.79968	0.7997[a]	0.378	0.378[a]	1.37623	1.37685[a]
2,2,4-trimethylpentane	0.68776	0.68781[a]	0.473		1.38902	1.38898[a]

[a] Riddick et al.,1986.[7] [b] Aralaguppi et al., 1999.[8]

Apparatus and Procedure. Liquids 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 ±3 × 10^{-5} g. Densities were measured with an Anton Paar DMA-5000 vibrating-tube densimeter (Anton-Paar, Graz, Austria) with an accuracy of ±5 × 10^{-6} g·cm^{-3} in the range of (0 to 3) g·cm^{-3}. The temperature range of this densimeter is from 273.15 K to 363.15 K with an accuracy of ±0.01 K. Calibration was performed periodically under atmospheric pressure, in accordance with specifications, using deionized water and dry air. Precautions were taken to avoid evaporation losses and air dissolved during the experiment.

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Table 2. Experimental Densities (ρ), Viscosities (η), and Excess Molar Volumes (V^E) for Ethanol (1) + 2-Butanone (2)

x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}
			$T = 298.15$ K				
0.0000	0.7997	0.378	0.000	0.5500	0.7940	0.512	−0.070
0.0500	0.7993	0.380	−0.009	0.6000	0.7933	0.539	−0.073
0.1000	0.7989	0.386	−0.020	0.6500	0.7926	0.576	−0.078
0.1500	0.7984	0.393	−0.022	0.7000	0.7918	0.618	−0.078
0.2000	0.7979	0.400	−0.026	0.7500	0.7909	0.673	−0.072
0.2500	0.7974	0.409	−0.031	0.8000	0.7900	0.734	−0.070
0.3000	0.7969	0.420	−0.039	0.8500	0.7889	0.799	−0.055
0.3500	0.7964	0.431	−0.049	0.9000	0.7878	0.869	−0.045
0.4000	0.7958	0.446	−0.050	0.9500	0.7866	0.961	−0.031
0.4500	0.7952	0.469	−0.055	1.0000	0.7851	1.088	0.000
0.5000	0.7946	0.490	−0.061				
			$T = 308.15$ K				
0.0000	0.7892	0.341	0.000	0.5500	0.7840	0.443	−0.039
0.0500	0.7888	0.345	−0.002	0.6000	0.7834	0.467	−0.043
0.1000	0.7883	0.349	0.005	0.6500	0.7828	0.493	−0.049
0.1500	0.7879	0.353	−0.001	0.7000	0.7821	0.526	−0.049
0.2000	0.7874	0.359	0.003	0.7500	0.7814	0.560	−0.051
0.2500	0.7870	0.366	−0.006	0.8000	0.7806	0.601	−0.048
0.3000	0.7865	0.376	−0.007	0.8500	0.7797	0.654	−0.040
0.3500	0.7861	0.387	−0.019	0.9000	0.7787	0.722	−0.028
0.4000	0.7856	0.397	−0.024	0.9500	0.7777	0.803	−0.019
0.4500	0.7851	0.412	−0.030	1.0000	0.7765	0.904	0.000
0.5000	0.7846	0.426	−0.038				
			$T = 318.15$ K				
0.0000	0.7784	0.307	0.000	0.5500	0.7738	0.398	−0.012
0.0500	0.7780	0.313	0.005	0.6000	0.7733	0.412	−0.016
0.1000	0.7776	0.316	0.009	0.6500	0.7728	0.434	−0.023
0.1500	0.7772	0.320	0.012	0.7000	0.7722	0.456	−0.022
0.2000	0.7768	0.324	0.012	0.7500	0.7716	0.482	−0.023
0.2500	0.7764	0.330	0.011	0.8000	0.7710	0.519	−0.028
0.3000	0.7760	0.337	0.008	0.8500	0.7703	0.560	−0.026
0.3500	0.7756	0.345	0.003	0.9000	0.7695	0.613	−0.019
0.4000	0.7752	0.355	−0.003	0.9500	0.7686	0.676	−0.008
0.4500	0.7747	0.365	−0.001	1.0000	0.7677	0.763	0.000
0.5000	0.7743	0.381	−0.010				

Table 3. Experimental Densities (ρ), Viscosities (η), and Excess Molar Volumes (V^E) for Ethanol (1) + 2,2,4-Trimethylpentane (2)

x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}
			$T = 298.15$ K				
0.0000	0.6878	0.474	0.000	0.5500	0.7145	0.613	0.396
0.0500	0.6888	0.476	0.181	0.6000	0.7188	0.643	0.382
0.1000	0.6903	0.478	0.265	0.6500	0.7236	0.678	0.366
0.1500	0.6921	0.480	0.306	0.7000	0.7291	0.718	0.333
0.2000	0.6940	0.484	0.354	0.7500	0.7354	0.760	0.287
0.2500	0.6962	0.494	0.370	0.8000	0.7423	0.806	0.268
0.3000	0.6985	0.507	0.402	0.8500	0.7505	0.861	0.218
0.3500	0.7011	0.521	0.413	0.9000	0.7601	0.929	0.157
0.4000	0.7040	0.540	0.411	0.9500	0.7715	0.999	0.082
0.4500	0.7071	0.561	0.420	1.0000	0.7851	1.088	0.000
0.5000	0.7106	0.586	0.412				
			$T = 308.15$ K				
0.0000	0.6795	0.422	0.000	0.5500	0.7057	0.527	0.465
0.0500	0.6804	0.424	0.208	0.6000	0.7100	0.550	0.446
0.1000	0.6818	0.426	0.314	0.6500	0.7149	0.576	0.409
0.1500	0.6835	0.429	0.375	0.7000	0.7203	0.606	0.384
0.2000	0.6854	0.433	0.419	0.7500	0.7266	0.641	0.332
0.2500	0.6875	0.439	0.453	0.8000	0.7336	0.677	0.296
0.3000	0.6898	0.450	0.480	0.8500	0.7417	0.720	0.251
0.3500	0.6924	0.462	0.486	0.9000	0.7514	0.768	0.175
0.4000	0.6952	0.474	0.497	0.9500	0.7628	0.829	0.094
0.4500	0.6983	0.487	0.501	1.0000	0.7765	0.904	0.000
0.5000	0.7018	0.506	0.487				
			$T = 318.15$ K				
0.0000	0.6710	0.382	0.000	0.5500	0.6966	0.463	0.553
0.0500	0.6717	0.384	0.260	0.6000	0.7009	0.480	0.527
0.1000	0.6730	0.385	0.389	0.6500	0.7058	0.500	0.483
0.1500	0.6747	0.389	0.447	0.7000	0.7113	0.524	0.437
0.2000	0.6765	0.391	0.511	0.7500	0.7176	0.550	0.379
0.2500	0.6786	0.397	0.540	0.8000	0.7247	0.580	0.326
0.3000	0.6809	0.404	0.562	0.8500	0.7329	0.616	0.265
0.3500	0.6834	0.412	0.583	0.9000	0.7425	0.657	0.194
0.4000	0.6862	0.422	0.588	0.9500	0.7539	0.702	0.108
0.4500	0.6893	0.433	0.586	1.0000	0.7677	0.763	0.000
0.5000	0.6928	0.446	0.566				

Table 4. Experimental Densities (ρ), Viscosities (η), and Excess Molar Volumes (V^E) for 2-Butanone (1) + 2,2,4-Trimethylpentane (2)

x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}
			T = 298.15 K				
0.0000	0.6878	0.474	0.000	0.5500	0.7288	0.398	0.620
0.0500	0.6901	0.461	0.190	0.6000	0.7345	0.394	0.579
0.1000	0.6927	0.451	0.335	0.6500	0.7406	0.390	0.533
0.1500	0.6956	0.443	0.441	0.7000	0.7472	0.387	0.474
0.2000	0.6987	0.436	0.534	0.7500	0.7542	0.384	0.424
0.2500	0.7022	0.429	0.576	0.8000	0.7619	0.381	0.348
0.3000	0.7059	0.423	0.614	0.8500	0.7704	0.379	0.244
0.3500	0.7099	0.417	0.631	0.9000	0.7793	0.377	0.174
0.4000	0.7141	0.412	0.653	0.9500	0.7892	0.377	0.073
0.4500	0.7187	0.407	0.646	1.0000	0.7997	0.378	0.000
0.5000	0.7236	0.402	0.633				
			T = 308.15 K				
0.0000	0.6795	0.426	0.000	0.5500	0.7194	0.360	0.680
0.0500	0.6817	0.416	0.205	0.6000	0.7249	0.356	0.651
0.1000	0.6842	0.408	0.363	0.6500	0.7310	0.353	0.583
0.1500	0.6870	0.400	0.479	0.7000	0.7374	0.350	0.533
0.2000	0.6901	0.394	0.558	0.7500	0.7443	0.347	0.475
0.2500	0.6934	0.388	0.628	0.8000	0.7519	0.345	0.389
0.3000	0.6970	0.382	0.671	0.8500	0.7602	0.343	0.286
0.3500	0.7009	0.377	0.692	0.9000	0.7690	0.342	0.203
0.4000	0.7051	0.372	0.697	0.9500	0.7788	0.341	0.087
0.4500	0.7095	0.368	0.709	1.0000	0.7892	0.341	0.000
0.5000	0.7143	0.363	0.695				
			T = 318.15 K				
0.0000	0.6710	0.382	0.000	0.5500	0.7098	0.325	0.736
0.0500	0.6731	0.374	0.220	0.6000	0.7153	0.322	0.686
0.1000	0.6754	0.367	0.415	0.6500	0.7212	0.320	0.628
0.1500	0.6782	0.360	0.517	0.7000	0.7275	0.317	0.571
0.2000	0.6811	0.354	0.627	0.7500	0.7343	0.315	0.504
0.2500	0.6843	0.349	0.703	0.8000	0.7417	0.313	0.421
0.3000	0.6878	0.344	0.750	0.8500	0.7499	0.311	0.306
0.3500	0.6916	0.339	0.773	0.9000	0.7586	0.309	0.210
0.4000	0.6957	0.335	0.778	0.9500	0.7682	0.308	0.091
0.4500	0.7001	0.331	0.770	1.0000	0.7784	0.307	0.000
0.5000	0.7048	0.328	0.755				

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}.

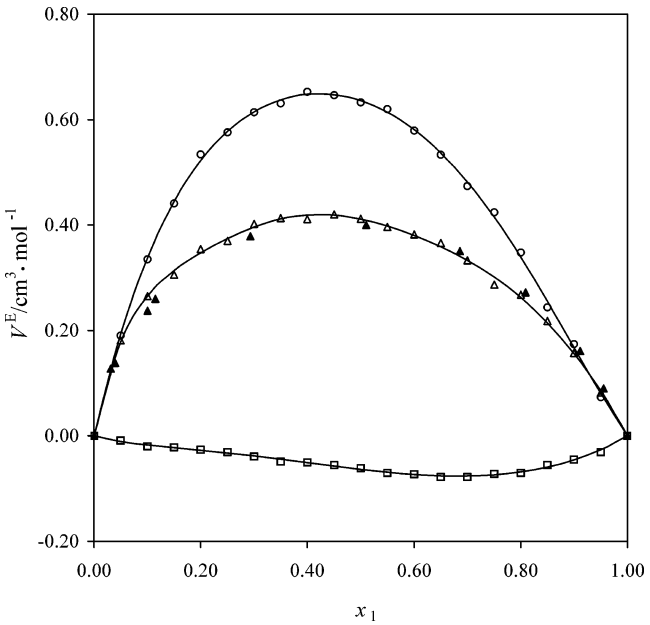

Figure 1. Excess volume variation with mole fraction at 298.15 K: □, ethanol (1) + 2-butanone (2); Δ, ethanol (1) + 2,2,4-trimethylpentane (2); ○, 2-butanone (1) + 2,2,4-trimethylpentane (2); ▲, ethanol (1) + 2,2,4-trimethylpentane (2) from Kretschmer et al. Solid curves were calculated from the Redlich−Kister equation.

The kinematic viscosities were determined with commercial Ubbelohde capillary viscometers (Cannon Instrument Co., State College, PA) of (0.36, 0.47, 0.53, and 0.63)-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

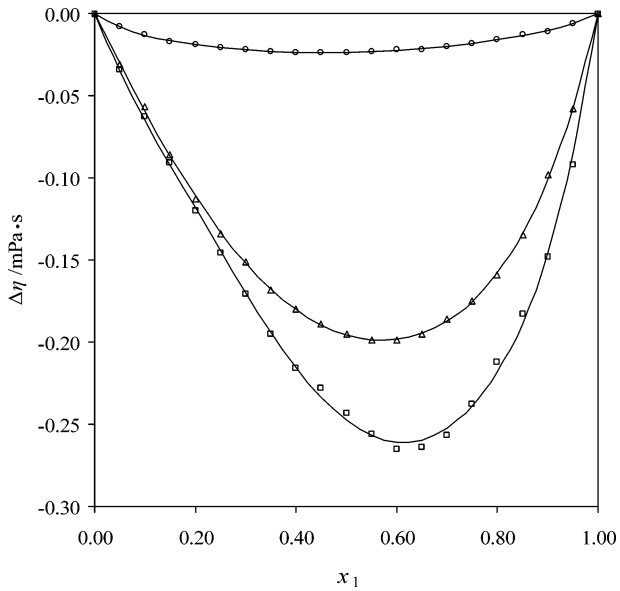

Figure 2. Viscosity deviation variation with mole fraction at 298.15 K: □, ethanol (1) + 2-butanone (2); Δ, ethanol (1) + 2,2,4-trimethylpentane (2); ○, 2-butanone (1) + 2,2,4-trimethylpentane (2). Solid curves were calculated from the Redlich−Kister equation.

Table 5. Coefficients of the Redlich−Kister Equation and Standard Deviations for V^E and $\Delta\eta$

Y^E	T/K	a_0	a_1	a_2	a_3	a_4	a_5	a_6	$\sigma \times 10^2$
				Ethanol (1) + 2-Butanone (2)					
V^E/cm^3·mol^{-1}	298.15	−0.2491	0.2538	−0.2803	−0.1958	0.7433	0.1752	−0.8486	0.22
	308.15	−0.1422	0.2060	−0.0327	0.2334	0.1696	−0.3203	−0.2474	0.23
	318.15	−0.3379	0.1505	−0.0330	0.2545	0.0083	−0.2931		0.18
$\Delta\eta$/mPa·s	298.15	−0.9786	0.5447	−0.4005	−0.4146	1.1840	0.7312	−1.5506	0.16
	308.15	−0.7855	0.4431	−0.1448	0.0985	−0.5550	0.0945	0.4882	0.13
	318.15	−0.6178	0.3353	−0.2641	0.2287				0.12
				Ethanol (1) + 2,2,4-Trimethylpentane (3)					
V^E/cm^3·mol^{-1}	298.15	1.6445	0.4222	0.5137	−0.5552	0.1596	1.6873	1.1466	0.63
	308.15	1.9484	0.6281	0.2622	−0.6117	1.5150	1.7602		0.45
	318.15	2.2897	0.6982	0.5378	0.1371	0.0728	1.3794	2.1052	0.48
$\Delta\eta$/mPa·s	298.15	−0.7819	0.1828	−0.1641	0.1661				0.12
	308.15	−0.6360	0.2048	−0.0701	−0.0051	−0.1899	0.1453		0.11
	318.15	−0.5041	0.1929	−0.0669	0.0131	−0.1151	0.1157		0.05
				2-Butanone (2) + 2,2,4-Trimethylpentane (3)					
V^E/cm^3·mol^{-1}	298.15	2.5434	0.6659	0.4117	0.8042				0.66
	308.15	2.7879	0.6292	0.4835	0.8322				0.65
	318.15	3.0230	1.0034	0.8313	−0.0123	−0.4904	0.8726		0.76
$\Delta\eta$/mPa·s	298.15	−0.0954	−0.0121	−0.0202	−0.0113	−0.0560			0.03
	308.15	−0.0795	−0.0145	−0.0214	0.0261	−0.0091	−0.0484		0.03
	318.15	−0.0656	−0.0238	−0.0089	0.0081				0.03

		C_0	C_1	C_2	σ
V^E/cm^3·mol^{-1}	298.15	11.0194	−18.1656	−16.5782	0.050
	308.15	12.3316	−22.2788	−16.8291	0.062
	318.15	13.9429	−22.3579	−17.9743	0.075
$\Delta\eta$/mPa·s	298.15	3.0680	−9.4126	2.3081	0.026
	308.15	2.6926	−9.7076	3.2818	0.026
	318.15	1.7904	−7.2431	3.2119	0.022

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

	three-body			four-body			
T/K	ν_{12}	ν_{21}	$\sigma/10^{-6}$ m^2·s^{-1}	ν_{1112}	ν_{1122}	ν_{2221}	$\sigma/10^{-6}$ m^2·s^{-1}
			Ethanol (1) + 2-Butanone (2)				
298.15	0.44294	0.62263	0.0082	0.44509	0.85775	0.43961	0.0085
308.15	0.52537	0.47670	0.0035	0.62052	0.52632	0.45074	0.0017
318.15	0.46462	0.44202	0.0047	0.53859	0.48491	0.41244	0.0026
			Ethanol (1) + 2,2,4-Trimethylpentane (2)				
298.15	0.98645	0.67031	0.0042	0.10593	0.80438	0.67187	0.0044
308.15	0.82608	0.61253	0.0038	0.87221	0.72643	0.60265	0.0030
318.15	0.71165	0.57523	0.0014	0.76080	0.63629	0.56962	0.0014
			2-Butanone (1) + 2,2,4-Trimethylpentane (2)				
298.15	0.52833	0.58383	0.0018	0.50198	0.57423	0.59515	0.0007
308.15	0.48554	0.53561	0.0009	0.46560	0.51753	0.55084	0.0006
318.15	0.45057	0.48528	0.0005	0.43278	0.47003	0.50204	0.0004

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 160 s to 750 s. The kinematic viscosity, ν, was then obtained from the following relationship

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

where t is the flow time, η is the absolute viscosity, and k and θ are respectively the viscometer constant and the Hagenbach correction. The k values for several viscometers were provided by the manufacturer and checked by measuring the viscosities of pure water, ethanol, and heptane; the results at $T = 298.15$ K were $\eta(H_2O) = 0.892$ [0.89025] mPa·s, $\eta(C_2H_5OH) = 1.088$ [1.0826] mPa·s, and $\eta(C_7H_{16}) = 0.394$ [0.3967] mPa·s. Literature values[7] are in brackets. 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 within ±0.03%. The uncertainty of the viscosity measurement was estimated to be less than ±0.8%.

The densities and viscosities of the binary systems ethanol + 2-butanone, ethanol + 2,2,4-trimethylpentane, and 2-butanone + 2,2,4-trimethylpentane were measured at temperatures of 298.15 K, 308.15 K, and 318.15 K and atmospheric pressure (100.8 ± 0.2 kPa). A set with compositions varying from 0.05 to 0.95 mole fraction was prepared for each binary system. A total of 55 compositions were measured for the ternary system ethanol + 2-butanone + 2,2,4-trimethylpentane at each temperature (298.15 K, 308.15 K, and 318.15 K). 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

The experimental densities, viscosities, and excess molar volumes of three binary mixtures ethanol + 2-butanone, ethanol + 2,2,4-trimethylpentane, and 2-butanone + 2,2,4-

Table 7. Experimental Densities (ρ), Viscosities (η), and Excess Molar Volumes (V^E) for Ethanol (1) + 2-Butanone (2) + 2,2,4-Trimethylpentane (3) at 298.15 K

x_1	x_2	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	x_1	x_2	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}
0.0500	0.9000	0.7882	0.392	0.115	0.2999	0.5501	0.7647	0.430	0.234
0.0501	0.7999	0.7690	0.401	0.311	0.3000	0.4500	0.7479	0.438	0.349
0.0501	0.6999	0.7530	0.407	0.445	0.2999	0.3500	0.7338	0.451	0.420
0.0500	0.6001	0.7394	0.407	0.538	0.3001	0.2499	0.7216	0.466	0.488
0.0500	0.4999	0.7276	0.412	0.610	0.3000	0.1500	0.7112	0.482	0.506
0.0500	0.4000	0.7175	0.416	0.627	0.2999	0.0500	0.7025	0.499	0.434
0.0500	0.3001	0.7087	0.427	0.608	0.4000	0.5500	0.7838	0.448	0.028
0.0501	0.2000	0.7010	0.447	0.547	0.4000	0.4500	0.7626	0.462	0.223
0.0500	0.1001	0.6945	0.456	0.388	0.4000	0.3500	0.7453	0.476	0.353
0.0500	0.0501	0.6917	0.462	0.259	0.4000	0.2499	0.7310	0.495	0.419
0.1000	0.8500	0.7878	0.383	0.084	0.3999	0.1500	0.7189	0.506	0.447
0.1000	0.7501	0.7684	0.388	0.270	0.3999	0.0500	0.7087	0.528	0.415
0.1000	0.6500	0.7521	0.397	0.417	0.5001	0.4499	0.7820	0.488	0.034
0.1000	0.5500	0.7383	0.404	0.521	0.5001	0.3499	0.7604	0.499	0.205
0.1000	0.4500	0.7265	0.414	0.580	0.4999	0.2500	0.7428	0.522	0.322
0.1000	0.3499	0.7163	0.433	0.603	0.5000	0.1500	0.7282	0.560	0.395
0.1001	0.2499	0.7075	0.456	0.575	0.5000	0.0500	0.7162	0.582	0.385
0.1000	0.1500	0.6999	0.468	0.490	0.6000	0.3500	0.7803	0.549	0.017
0.1001	0.0500	0.6933	0.483	0.350	0.6001	0.2500	0.7583	0.566	0.160
0.2000	0.7500	0.7868	0.400	0.038	0.5999	0.1500	0.7402	0.593	0.282
0.1999	0.6501	0.7667	0.410	0.241	0.6000	0.0500	0.7256	0.626	0.319
0.2001	0.5499	0.7500	0.420	0.391	0.7001	0.2499	0.7784	0.622	0.004
0.2000	0.4500	0.7362	0.431	0.457	0.7000	0.1500	0.7554	0.688	0.178
0.2001	0.3499	0.7241	0.440	0.537	0.7000	0.0500	0.7372	0.728	0.268
0.1999	0.2500	0.7139	0.450	0.539	0.8000	0.1500	0.7761	0.771	0.011
0.2000	0.1500	0.7050	0.459	0.516	0.8000	0.0500	0.7525	0.813	0.174
0.2001	0.0500	0.6975	0.475	0.403	0.9000	0.0500	0.7730	0.914	0.067
0.3001	0.6499	0.7854	0.424	0.028					

Table 8. Experimental Densities (ρ), Viscosities (η), and Excess Molar Volumes (V^E) for Ethanol (1) + 2-Butanone (2) + 2,2,4-Trimethylpentane (3) at 308.15 K

x_1	x_2	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	x_1	x_2	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}
0.0500	0.9000	0.7780	0.353	0.114	0.2999	0.5501	0.7547	0.382	0.299
0.0501	0.7999	0.7592	0.361	0.309	0.3000	0.4500	0.7381	0.391	0.436
0.0501	0.6999	0.7432	0.368	0.490	0.2999	0.3500	0.7242	0.401	0.523
0.0500	0.6001	0.7298	0.376	0.598	0.3001	0.2499	0.7124	0.411	0.570
0.0500	0.4999	0.7183	0.381	0.662	0.3000	0.1500	0.7023	0.425	0.574
0.0500	0.4000	0.7083	0.386	0.700	0.2999	0.0500	0.6938	0.441	0.497
0.0500	0.3001	0.6997	0.397	0.679	0.4000	0.5500	0.7737	0.397	0.069
0.0501	0.2000	0.6922	0.406	0.610	0.4000	0.4500	0.7530	0.407	0.256
0.0500	0.1001	0.6858	0.414	0.459	0.4000	0.3500	0.7359	0.416	0.404
0.0500	0.0501	0.6830	0.424	0.343	0.4000	0.2499	0.7221	0.431	0.438
0.1000	0.8500	0.7774	0.361	0.114	0.3999	0.1500	0.7103	0.445	0.453
0.1000	0.7501	0.7584	0.366	0.302	0.3999	0.0500	0.6999	0.461	0.484
0.1000	0.6500	0.7423	0.370	0.470	0.5001	0.4499	0.7721	0.427	0.071
0.1000	0.5500	0.7287	0.378	0.589	0.5001	0.3499	0.7508	0.440	0.256
0.1000	0.4500	0.7171	0.384	0.658	0.4999	0.2500	0.7335	0.454	0.378
0.1000	0.3499	0.7071	0.392	0.685	0.5000	0.1500	0.7191	0.471	0.463
0.1001	0.2499	0.6985	0.403	0.656	0.5000	0.0500	0.7073	0.492	0.458
0.1000	0.1500	0.6911	0.411	0.563	0.6000	0.3500	0.7706	0.471	0.051
0.1001	0.0500	0.6847	0.428	0.409	0.6001	0.2500	0.7486	0.485	0.239
0.2000	0.7500	0.7764	0.377	0.081	0.5999	0.1500	0.7313	0.506	0.307
0.1999	0.6501	0.7567	0.377	0.289	0.6000	0.0500	0.7167	0.531	0.378
0.2001	0.5499	0.7402	0.378	0.461	0.7001	0.2499	0.7688	0.529	0.046
0.2000	0.4500	0.7265	0.380	0.558	0.7000	0.1500	0.7462	0.552	0.221
0.2001	0.3499	0.7148	0.388	0.616	0.7000	0.0500	0.7283	0.589	0.314
0.1999	0.2500	0.7048	0.399	0.623	0.8000	0.1500	0.7667	0.619	0.053
0.2000	0.1500	0.6962	0.410	0.578	0.8000	0.0500	0.7434	0.653	0.227
0.2001	0.0500	0.6888	0.422	0.476	0.9000	0.0500	0.7642	0.748	0.077
0.3001	0.6499	0.7749	0.376	0.097					

trimethylpentane are listed in Tables 2 to 4, respectively. The excess molar volumes, V^E, were calculated from density data according to the following equation

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

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

In the systems studied, excess molar volumes are positive for the binary mixtures ethanol + 2,2,4-trimethylpentane and 2-butanone + 2,2,4-trimethylpentane over the whole composition range. The values of V^E are negative over the whole composition range except for mixtures in the low mole fraction region of ethanol for the binary mixture ethanol + 2-butanone. The values of V^E increase systematically from 298.15 K to 318.15 K over the whole range of mole fractions and lead to maxima showing little variation with temperature. The excess molar volume $V^E(x = 0.5)$ increases in the sequence 2-butanone + 2,2,4-

Table 9. Experimental Densities (ρ), Viscosities (η), and Excess Molar Volumes (V^E) for Ethanol (1) + 2-Butanone (2) + 2,2,4-Trimethylpentane (3) at 318.15 K

x_1	x_2	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	x_1	x_2	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}
0.0500	0.9000	0.7672	0.320	0.152	0.2999	0.5501	0.7447	0.342	0.334
0.0501	0.7999	0.7487	0.319	0.366	0.3000	0.4500	0.7283	0.349	0.493
0.0501	0.6999	0.7331	0.323	0.544	0.2999	0.3500	0.7147	0.358	0.581
0.0500	0.6001	0.7199	0.328	0.670	0.3001	0.2499	0.7030	0.366	0.653
0.0500	0.4999	0.7086	0.333	0.747	0.3000	0.1500	0.6931	0.377	0.662
0.0500	0.4000	0.6989	0.338	0.773	0.2999	0.0500	0.6848	0.389	0.581
0.0500	0.3001	0.6905	0.346	0.750	0.4000	0.5500	0.7634	0.361	0.106
0.0501	0.2000	0.6832	0.356	0.674	0.4000	0.4500	0.7430	0.367	0.309
0.0500	0.1001	0.6770	0.364	0.508	0.4000	0.3500	0.7261	0.375	0.480
0.0500	0.0501	0.6743	0.371	0.383	0.4000	0.2499	0.7123	0.388	0.560
0.1000	0.8500	0.7669	0.327	0.123	0.3999	0.1500	0.7007	0.399	0.588
0.1000	0.7501	0.7480	0.330	0.354	0.3999	0.0500	0.6908	0.411	0.575
0.1000	0.6500	0.7322	0.341	0.533	0.5001	0.4499	0.7621	0.385	0.094
0.1000	0.5500	0.7189	0.345	0.655	0.5001	0.3499	0.7410	0.392	0.305
0.1000	0.4500	0.7075	0.352	0.735	0.4999	0.2500	0.7240	0.403	0.435
0.1000	0.3499	0.6977	0.356	0.768	0.5000	0.1500	0.7098	0.419	0.533
0.1001	0.2499	0.6893	0.358	0.738	0.5000	0.0500	0.6983	0.440	0.519
0.1000	0.1500	0.6821	0.368	0.638	0.6000	0.3500	0.7607	0.422	0.082
0.1001	0.0500	0.6759	0.377	0.469	0.6001	0.2500	0.7390	0.433	0.285
0.2000	0.7500	0.7656	0.338	0.142	0.5999	0.1500	0.7220	0.449	0.357
0.1999	0.6501	0.7464	0.337	0.345	0.6000	0.0500	0.7077	0.466	0.425
0.2001	0.5499	0.7304	0.342	0.499	0.7001	0.2499	0.7589	0.468	0.096
0.2000	0.4500	0.7170	0.341	0.595	0.7000	0.1500	0.7366	0.484	0.287
0.2001	0.3499	0.7054	0.348	0.679	0.7000	0.0500	0.7190	0.506	0.386
0.1999	0.2500	0.6955	0.355	0.707	0.8000	0.1500	0.7572	0.534	0.086
0.2000	0.1500	0.6871	0.366	0.661	0.8000	0.0500	0.7341	0.559	0.281
0.2001	0.0500	0.6799	0.379	0.551	0.9000	0.0500	0.7549	0.632	0.114
0.3001	0.6499	0.7646	0.339	0.117					

trimethylpentane > ethanol + 2,2,4-trimethylpentane > ethanol + 2-butanone, and the same sequence is valid for the maximum values of V^E. The values of $V^E(x = 0.5)$ vary from −0.010 cm^3·mol^{-1} to 0.755 cm^3·mol^{-1}. Figure 1 shows the excess molar volumes with liquid composition for the three binary systems at $T = 298.15$ K. In the literature, the system ethanol + 2,2,4-trimethylpentane has been measured at 298.15 K,[9] and our results are in good agreement with their measurements (Figure 1).

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). In the present investigation, ethanol is strongly self-associated through hydrogen bonding, but 2,2,4-trimethylpentane and 2-butanone do not exhibit this property. The interactions of ethanol and 2-butanone against 2,2,4-trimethylpentane molecules involve mainly dispersion forces, giving a positive contribution to V^E. The interactions between ethanol and 2-butanone molecules lead to hydrogen bond effects and/or weak dispersion-type effects, giving a negative contribution to V^E.

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

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

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 $\Delta\eta$ follow the order 2-butanone + 2,2,4-trimethylpentane > ethanol + 2,2,4-trimethylpentane > 2-butanone + ethanol. The value of $\Delta\eta(x = 0.5)$ varies from −0.0160 mPa·s to −0.243 mPa·s. Figure 2 illustrates the results of $\Delta\eta$ for the three binary mixtures at 298.15 K.

The excess molar volumes and deviations in the viscosity for the binary mixtures were correlated with the Redlich−Kister equation[10]

$$\Delta Q_{ij} = x_i x_j \sum_{k=0}^{m} a_k (x_i - x_j)^k \tag{4}$$

where ΔQ_{ij} refers to V^E/cm^3·mol^{-1} or $\Delta\eta$/mPa·s 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

$$\sigma = \left[\sum_{i=1}^{n} \frac{(\Delta Q_i^{\text{exptl}} - \Delta Q_i^{\text{calcd}})^2}{n - p} \right]^{1/2} \tag{5}$$

where n is the number of experimental points and p is the number of adjustable parameters. The σ values lie between 0.0018 cm^3·mol^{-1} and 0.0076 cm^3·mol^{-1} for V^E and between 0.0003 mPa·s and 0.0016 mPa·s for $\Delta\eta$, respectively. The largest σ value corresponds to the 2-butanol + 2,2,4-trimethylpentane system at 318.15 K for V^E and the ethanol + 2-butanone system at 298.15 K for $\Delta\eta$, respectively.

McAllister's multibody interaction model[11] is widely used to correlate the kinematic viscosity of binary mixtures with mole fraction. The three-body model is defined as

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln \nu_{12} + 3x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln(x_1 + x_2 M_2/M_1) + 3x_1^2 x_2 \ln\left(\frac{2 + M_2/M_1}{3}\right) + 3x_1 x_2^2 \ln\left(\frac{1 + 2M_2/M_1}{3}\right) + x_2^3 \ln(M_2/M_1) \tag{6}$$

and the four-body model is given by

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3 x_2 \ln \nu_{1112} + 6x_1^2 x_2^2 \ln \nu_{1122} + 4x_1 x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \ln(x_1 + x_2 M_2/M_1) + 4x_1^3 x_2 \ln\left(\frac{3 + M_2/M_1}{4}\right) + 6x_1^2 x_2^2 \ln\left(\frac{1 + M_2/M_1}{2}\right) + 4x_1 x_2^3 \ln\left(\frac{1 + 3M_2/M_1}{4}\right) + x_2^4 \ln(M_2/M_1) \quad (7)$$

where ν, ν_1, and ν_2 are the kinematic viscosities of the mixture and the viscosities of pure components 1 and 2, respectively. 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 in eq 6. It is shown that the McAllister interaction models are adequate for those three systems. The $\sigma/10^{-6}$ m^2·s^{-1} values lie between 0.0004 and 0.0085, and the largest σ value corresponds to the ethanol + 2-butanone system at 298.15 K.

The experimental densities, viscosities, and excess molar volumes of the ternary mixture ethanol (1) + 2-butanone (2) + 2,2,4-trimethylpentane (3) at temperatures of 298.15 K, 308.15 K, and 318.15 K are listed in Tables 7 to 9, respectively. The derived properties V^E/cm^3·mol^{-1} and $\Delta\eta$/mPa·s of the ternary system at each temperature were correlated respectively using the equation

$$\Delta Q_{123} = \Delta Q_{12} + \Delta Q_{13} + \Delta Q_{23} + x_1 x_2 x_3 \Delta_{123} \quad (8)$$

where ΔQ_{123} refers to V^E or $\Delta\eta$ for the ternary mixture $x_3 = 1 - x_1 - x_2$, and ΔQ_{ij} represents the binary contribution of each i–j pair to the V^E or $\Delta\eta$ given by eq 4 with the parameters shown in Table 5. The ternary contribution term Δ_{123} was correlated using the expression suggested by Cibulka[12]

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

and the one proposed by Nagata–Tamura[13]

$$\Delta_{123} = D_0 + D_1 x_1 + D_2 x_2 + D_3 x_1^2 + D_4 x_2^2 + D_5 x_1 x_2 + D_6 x_1^3 + D_7 x_2^3 + D_8 x_1^2 x_2 \quad (10)$$

Ternary excess properties have also been correlated using the following expression introduced by Piñeiro et al.:[14]

$$\Delta Q_{123} = E_1 x_1 x_2 + E_2 x_2 x_3 + E_3 x_3 x_1 + E_4 x_1^2 x_2 + E_5 x_2^2 x_3 + E_6 x_3^2 x_1 \quad (11)$$

$$\Delta Q_{123} = F_1 x_1 x_2 + F_2 x_2 x_3 + F_3 x_3 x_1 + F_4 x_1^2 x_2 + F_5 x_2^2 x_3 + F_6 x_3^2 x_1 + F_7 x_1^3 x_2 + F_8 x_2^3 x_3 + F_9 x_3^3 x_1 \quad (12)$$

The ternary parameters C_i, D_i, E_i, and F_i were determined with the optimization algorithm similar to that for the binary parameters. Table 10 presents a comparison among the standard deviations for ternary data obtained with the different correlation equations applied. Among them, eq 12 yields the smallest standard deviations of both V^E and $\Delta\eta$ for each temperature investigated. The parameters C_i of the Cibulka equation and the corresponding standard deviations are also given in Table 5. The isoclines calculated from eq 12 for the excess molar volume and deviations in the viscosity at 298.15 K were plotted in Figures 3 and 4, respectively. As can be expected, the ternary system shows positive values of V^E at almost all compositions (Figure 3), except at compositions close to those of the binary system ethanol + 2-butanone where a change in

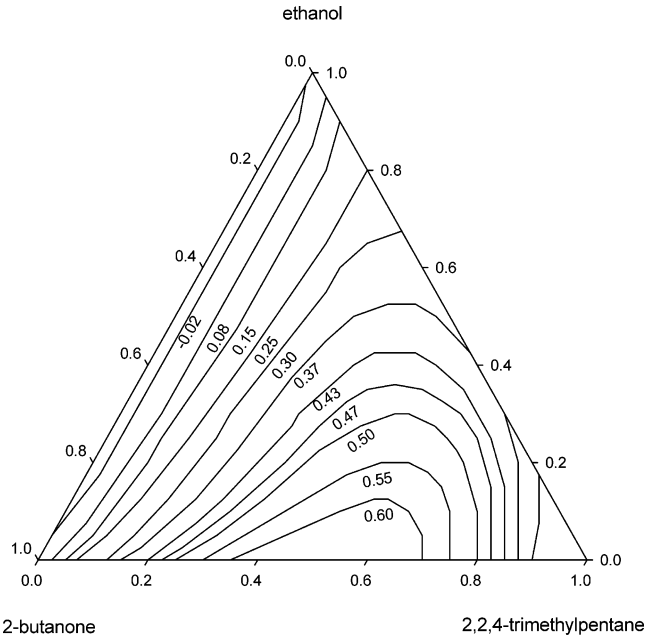

Figure 3. Isoclines of V^E for the ternary system ethanol (1) + 2-butanone (2) + 2,2,4-trimethylpentane (3) at 298.15 K using eq 12.

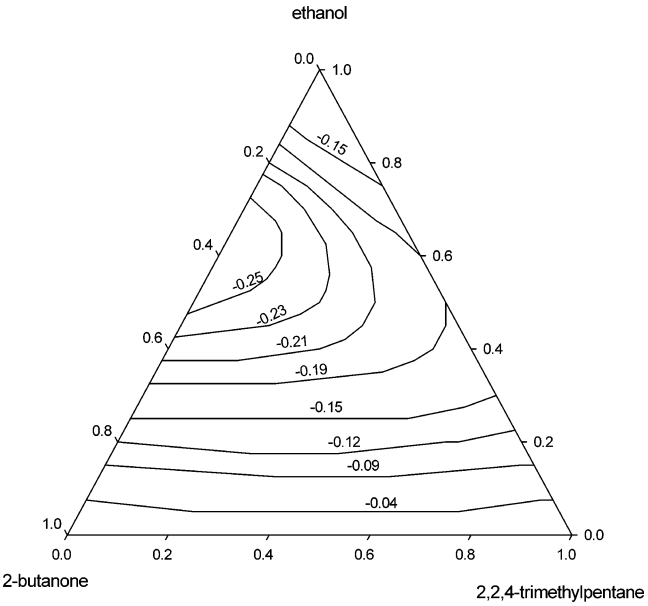

Figure 4. Isoclines of $\Delta\eta$ for the ternary system ethanol (1) + 2-butanone (2) + 2,2,4-trimethylpentane (3) at 298.15 K using eq 12.

Table 10. Comparison of Standard Deviations of V^E and $\Delta\eta$ Obtained with the Correlation Equations Applied for Ternary Mixtures

	T/K	eq 9	eq 10	eq 11	eq 12
V^E/cm^3·mol^{-1}	298.15	0.050	0.026	0.021	0.011
	308.15	0.062	0.035	0.019	0.016
	318.15	0.075	0.038	0.030	0.014
$\Delta\eta$/mPa·s	298.15	0.026	0.014	0.008	0.008
	308.15	0.026	0.013	0.004	0.003
	318.15	0.022	0.012	0.005	0.006

sign occurs. The maximum V^E value is found in the binary system 2-butanone + 2,2,4-trimethylpentane. Figure 4 shows a negative values for ternary $\Delta\eta$, with a minimum value for the binary system ethanol + 2-butanol.

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