Variation of Densities, Refractive Indices, and Speeds of Sound with Temperature of Methanol or Ethanol with Hexane, Heptane, and Octane

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In this work we present experimental values of the density, refractive index, and speed of sound of the binary mixtures methanol or ethanol plus hexane, heptane, and octane at the temperatures 303.15, 308.15, 313.15, and 318.15 K and at atmospheric pressure, as a function of mole fraction. The experimental results have been fitted as a funtion of composition. A comparison with other experimental data in the literature has been made.

1. Introduction

The thermodynamics of alcohol + alkane mixtures have been studied extensively in recent years, due to their application as additives to gasolines and alternative entrainers and coentrainers in modified rectification processes for binary azeotropes. As a continuation of our program on thermodynamic properties and phase equilibria of binary and ternary nonelectrolyte systems related to homogeneous and heterogeneous extractive distillation, we report experimental data on densities, refractive indices, and speeds of sound of the mixtures of methanol or ethanol with hexane, heptane, and octane, which were measured at 303.15, 308.15, 313.15, and 318.15 K and at atmospheric pressure, over the whole range of composition. From the experimental values, the corresponding derived properties were computed and correlated by means of the Redlich−Kister (Redlich and Kister, 1948) equation.

2. Experimental Section

The chemicals were supplied by Merck (Lichrosolv quality), recently acquired, and kept in an argon (N-55) atmosphere, as soon as the bottles were opened. They were degassed ultrasonically (at least 3 h) and dried over molecular sieves Type 4Å or 3Å, 1/16 in. (Aldrich cat. no. 20860-4 or 20858-2, respectively). Precautions were taken, such as cooling the chemicals before preparation of samples and reducing to a minimum the vapor space in the vessels, to avoid losses by evaporation during manipulation and possible errors in mole fraction calculations. Chromatographic (GLC) tests of the solvents showed purities better than 99.8 mass % for methanol and ethanol and better than 99.0 mass % for hexane, heptane, and octane, in accordance with vendor specifications and with maximum water contents of 1.5×10^{-2}, 2.2×10^{-2}, 7.8×10^{-4}, 8.1×10^{-4}, and 8.0×10^{-4} mass % (Metrohm 737 KF coulometer), respectively. The density and refractive index data of the pure components were in agreement with literature values, as shown in Table 1. Samples were prepared by mass using a Mettler AE-240 balance with an accuracy of $\pm 10^{-4}$ g.

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Table 1. Comparison of Measured Pure Component Properties Data with Literature Values at 298.15 K

	ρ/(g·cm^{-3})		n_D	
component	exptl	lit.[a]	exptl	lit.[a]
methanol	0.7865	0.786 64	1.326 45	1.326 52
ethanol	0.7852	0.785 09	1.359 22	1.359 41
hexane	0.6551	0.654 84	1.372 34	1.372 26
heptane	0.6794	0.679 46	1.385 12	1.385 11
octane	0.6985	0.698 62	1.395 14	1.395 12

[a] *TRC Thermodynamic Tables* (1994).

Density and speed of sound were measured with an Anton Paar DSA-48 density and sound analyzer, with a precision of $\pm 5 \times 10^{-5}$ g·cm^{-3} and $\pm 10^{-1}$ m·s^{-1}, respectively. The density of the sample was measured using an oscillating U-tube principle. The cell was made of glass (Duran 50) and inserted in a glass jacket with a gas of high thermal conductivity. The glass jacket was fully covered with a copper block, which ensures the proper heat transfer between the solid-state thermostat and the sample in the measuring cell. The sound velocity is measured by determining the propagation speed of ultrasonic pulses in a known within the sample. The sound velocity measuring cell is thermostated with the same solid-state thermostat as that used for the density cell. The cell consists of a cavity, which is laterally bordered by the receiver and transmitter for the ultrasonic pulses. The surfaces of the ultrasonic transmitter and receiver are made of stainless steel. A cuvette made of Teflon forms all other boundaries of the cavity. The solid-state thermostat ensures a temperature stability of 10^{-2} K. Refractive indices were measured with an automatic refractometer ABBEMAT-HP Dr. Kernchen with a precision of $\pm 10^{-5}$. The refractometer determines the refractive index of liquid substances by the critical angle method. The sample to be measured was placed on the polished surface of a prism made of synthetic sapphire. A cone-shaped yellow light beam of 589.3 nm sodium D wavelength iliminated the sample from its bottom side under different angles of reflection. The position of the bright/dark borderline was scanned by a linear photodiode array featuring 1024 photodiodes at intervals of 0.025 mm. A microprocessor averaged the results of 64 scans to calculate the refrac-

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Table 2. Refractive Indices, and Changes of Refractive Indices on Mixing of Binary Mixtures at Different Temperatures

x_1	n_D	δn_D	x_1	n_D	δn_D	x_1	n_D	δn_D	x_1	n_D	δn_D
$T = 303.15$ K						$T = 313.15$ K					
methanol (1) + hexane (2)			methanol (1) + heptane (2)			methanol (1) + hexane (2)			methanol (1) + heptane (2)		
0.0000	1.369 29	0.000 00	0.0000	1.382 48	0.000 00	0.0000	1.363 52	0.000 00	0.0000	1.376 55	0.000 00
0.0877	1.367 72	0.002 39	0.0321	1.381 83	0.001 22	0.0778	1.362 17	0.002 02	0.0831	1.375 56	0.003 69
0.1386	1.366 70	0.003 67	0.0559	1.381 21	0.001 99	0.2078	1.359 39	0.004 88	0.1337	1.374 63	0.005 62
0.1996	1.365 07	0.004 80	0.0875	1.380 66	0.003 29	0.3309	1.356 47	0.007 29	0.1933	1.373 46	0.007 81
0.2833	1.362 52	0.006 03	0.1176	1.379 62	0.004 01	0.4129	1.353 92	0.008 30	0.1958	1.373 40	0.007 89
0.7877	1.341 32	0.007 63	0.1507	1.378 71	0.005 03	0.5160	1.349 98	0.008 82	0.2127	1.373 18	0.008 62
0.8889	1.334 08	0.004 96	0.9072	1.337 27	0.007 75	0.6131	1.345 82	0.008 87	0.2263	1.372 72	0.008 93
0.9372	1.330 08	0.003 14	0.9312	1.334 43	0.006 31	0.7124	1.340 79	0.008 15	0.9020	1.333 10	0.007 40
0.9717	1.326 87	0.001 49	0.9506	1.331 49	0.004 51	0.8026	1.335 00	0.006 26	0.9306	1.329 86	0.005 77
1.0000	1.324 10	0.000 00	0.9714	1.328 42	0.002 65	0.9054	1.328 00	0.003 72	0.9528	1.327 07	0.004 23
						1.0000	1.320 18	0.000 00			
methanol (1) + octane (2)			ethanol (1) + hexane (2)			methanol (1) + octane (2)			ethanol (1) + hexane (2)		
0.0000	1.391 96	0.000 00	0.1149	1.367 94	0.000 09	0.0000	1.386 87	0.000 00	0.1149	1.362 06	−0.000 19
0.0326	1.391 76	0.002 01	0.1963	1.367 02	0.000 18	0.0459	1.386 53	0.002 72	0.1963	1.361 13	−0.000 22
0.0752	1.391 07	0.004 21	0.3056	1.365 84	0.000 37	0.0735	1.386 08	0.004 11	0.3056	1.359 93	−0.000 21
0.0853	1.390 92	0.004 75	0.4076	1.364 70	0.000 50	0.1026	1.385 64	0.005 61	0.4076	1.358 83	−0.000 18
0.9421	1.335 43	0.007 40	0.4950	1.363 73	0.000 62	0.9451	1.330 35	0.006 51	0.4950	1.357 94	−0.000 10
0.9534	1.333 43	0.006 17	0.6069	1.362 35	0.000 64	0.9636	1.327 28	0.004 67	0.6069	1.356 76	−0.000 04
0.9716	1.329 85	0.003 82	0.6986	1.361 17	0.000 61	0.9773	1.324 77	0.003 08	0.6986	1.355 80	0.000 01
			0.8034	1.359 75	0.000 49				0.8034	1.354 67	0.000 04
			0.9052	1.358 22	0.000 24				0.9052	1.353 52	0.000 02
			1.0000	1.356 80	0.000 00				1.0000	1.352 45	0.000 00
ethanol (1) + heptane (2)			ethanol (1) + octane (2)			ethanol (1) + heptane (2)			ethanol (1) + octane (2)		
0.1191	1.379 98	0.000 56	0.1208	1.389 91	0.002 20	0.1191	1.374 60	0.000 92	0.1208	1.384 79	0.002 08
0.2042	1.378 47	0.001 23	0.2035	1.388 29	0.003 49	0.2042	1.373 27	0.001 64	0.2035	1.383 22	0.003 35
0.3024	1.376 74	0.002 03	0.3035	1.386 17	0.004 88	0.3024	1.371 67	0.002 41	0.3035	1.381 21	0.004 79
0.4031	1.374 87	0.002 74	0.4031	1.383 82	0.006 03	0.4031	1.369 88	0.003 04	0.4031	1.378 92	0.005 92
0.4887	1.373 10	0.003 17	0.5030	1.381 05	0.006 78	0.4887	1.368 19	0.003 42	0.5030	1.376 20	0.006 64
0.5972	1.370 49	0.003 35	0.6010	1.377 85	0.007 02	0.5972	1.365 57	0.003 41	0.6010	1.373 05	0.006 87
0.7027	1.367 51	0.003 08	0.7048	1.373 79	0.006 61	0.7027	1.362 67	0.003 06	0.7048	1.369 01	0.006 40
0.7956	1.364 55	0.002 50	0.7959	1.369 52	0.005 54	0.7956	1.359 81	0.002 43	0.7959	1.364 78	0.005 30
0.8890	1.361 10	0.001 45	0.9049	1.363 30	0.003 16	0.8890	1.356 57	0.001 44	0.9049	1.358 77	0.003 05
$T = 308.15$ K						$T = 318.15$ K					
methanol (1) + hexane (2)			methanol (1) + heptane (2)			methanol (1) + hexane (2)			methanol (1) + heptane (2)		
0.0000	1.366 40	0.000 00	0.0000	1.379 42	0.000 00	0.0000	1.360 49	0.000 00	0.0000	1.374 10	0.000 00
0.0877	1.364 67	0.002 14	0.0321	1.378 86	0.001 28	0.1386	1.358 16	0.003 62	0.0559	1.373 14	0.002 20
0.1386	1.363 82	0.003 54	0.0559	1.378 54	0.002 32	0.1996	1.356 80	0.004 87	0.0875	1.372 62	0.003 46
0.1996	1.362 53	0.004 95	0.0875	1.377 64	0.003 22	0.3151	1.353 79	0.006 82	0.1176	1.372 07	0.004 62
0.3151	1.359 40	0.006 92	0.1176	1.377 00	0.004 31	0.3851	1.351 55	0.007 58	0.1707	1.370 99	0.006 54
0.3435	1.358 59	0.007 36	0.1707	1.375 83	0.006 17	0.4930	1.347 59	0.008 25	0.1976	1.370 33	0.007 40
0.7381	1.342 14	0.008 34	0.9072	1.334 71	0.007 17	0.6061	1.342 87	0.008 38	0.2301	1.369 40	0.008 30
0.7877	1.339 03	0.007 42	0.9306	1.331 86	0.005 66	0.6960	1.338 33	0.007 70	0.2697	1.368 11	0.009 25
0.8889	1.331 63	0.004 49	0.9506	1.329 14	0.004 08	0.7877	1.333 10	0.006 40	0.8375	1.337 30	0.010 53
0.9372	1.327 77	0.002 77				0.8889	1.326 33	0.003 97	0.8701	1.334 02	0.009 09
1.0000	1.322 23	0.000 00				1.0000	1.317 59	0.000 00	0.9072	1.330 07	0.007 24
									0.9506	1.324 60	0.004 22
methanol (1) + octane (2)			ethanol (1) + hexane (2)			methanol (1) + octane (2)			ethanol (1) + hexane (2)		
0.0000	1.390 52	0.000 0	0.1149	1.364 96	−0.000 07	0.0000	1.384 55	0.000 00	0.1149	1.359 10	−0.000 20
0.0326	1.389 72	0.001 43	0.1963	1.364 04	−0.000 03	0.0326	1.384 12	0.001 75	0.1963	1.358 18	−0.000 28
0.0752	1.388 61	0.003 23	0.3056	1.362 82	0.000 05	0.0752	1.383 51	0.004 00	0.3056	1.357 05	−0.000 28
0.0853	1.388 68	0.003 99	0.4076	1.361 73	0.000 18	0.0853	1.383 36	0.004 52	0.4076	1.356 04	−0.000 24
0.1136	1.387 87	0.005 11	0.4950	1.360 76	0.000 25	0.1136	1.382 93	0.005 99	0.4950	1.355 20	−0.000 17
0.9323	1.335 15	0.008 30	0.6069	1.359 47	0.000 29	0.1209	1.382 69	0.006 24	0.6069	1.354 13	−0.000 08
0.9421	1.333 41	0.007 23	0.6986	1.358 37	0.000 28	0.1435	1.382 34	0.007 40	0.6986	1.353 21	−0.000 06
0.9534	1.331 48	0.006 07	0.8034	1.357 09	0.000 24	0.1638	1.381 94	0.008 36	0.8034	1.352 16	−0.000 02
0.9716	1.328 08	0.003 91	0.9052	1.355 78	0.000 14	0.1784	1.381 55	0.008 95	0.9052	1.351 15	0.000 02
			1.0000	1.354 51	0.000 00	0.9323	1.330 27	0.008 15	1.0000	1.350 15	0.000 00
						0.9421	1.328 77	0.007 30			
						0.9534	1.326 71	0.006 00			
						0.9716	1.323 30	0.003 81			
ethanol (1) + heptane (2)			ethanol (1) + octane (2)			ethanol (1) + heptane (2)			ethanol (1) + octane (2)		
0.1191	1.377 38	0.000 93	0.1208	1.387 67	0.001 50	0.1191	1.372 24	0.000 99	0.1208	1.382 38	0.001 99
0.2042	1.376 01	0.001 68	0.2035	1.385 84	0.002 65	0.2042	1.370 87	0.001 66	0.2035	1.380 85	0.003 30
0.3024	1.374 33	0.002 44	0.3035	1.383 64	0.004 05	0.3024	1.369 11	0.002 25	0.3035	1.378 80	0.004 69
0.4031	1.372 50	0.003 12	0.4031	1.381 23	0.005 23	0.4031	1.367 16	0.002 71	0.4031	1.376 56	0.005 88
0.4887	1.370 75	0.003 50	0.5030	1.378 51	0.006 10	0.4887	1.365 35	0.002 95	0.5030	1.373 77	0.006 52
0.5972	1.368 21	0.003 67	0.6010	1.375 37	0.006 49	0.5972	1.362 84	0.003 04	0.6010	1.370 60	0.006 72
0.7027	1.365 34	0.003 42	0.7048	1.371 38	0.006 24	0.7027	1.360 02	0.002 75	0.7048	1.366 53	0.006 23
0.7956	1.362 40	0.002 80	0.7959	1.367 15	0.005 29	0.7956	1.357 26	0.002 21	0.7959	1.362 33	0.005 16
0.8890	1.359 06	0.001 79	0.9049	1.361 01	0.003 08	0.8890	1.354 20	0.001 39	0.9049	1.356 35	0.002 93

Table 3. Densities, Speeds of Sound, Isentropic Compressibilities, Excess Molar Volumes, and Changes of Isentropic Compressibilities on Mixing of Binary Mixtures at Different Temperatures

x_1	ρ/ (g·cm^{-3})	u/ (m·s^{-1})	κ_S/ (T Pa^{-1})	V^E/ (cm^3·mol^{-1})	$\delta\kappa_S$/ (T Pa^{-1})	x_1	ρ/ (g·cm^{-3})	u/ (m·s^{-1})	κ_S/ (T Pa^{-1})	V^E/ (cm^3·mol^{-1})	$\delta\kappa_S$/ (T Pa^{-1})
		T = 303.15 K						T = 313.15 K			
		methanol (1) + hexane (2)						methanol (1) + hexane (2)			
0.0000	0.6504	1054.6	1382.4	0.000	0	0.0000	0.6412	1010.0	1529.0	0.000	0
0.1276	0.6542	1042.8	1405.6	0.349	61	0.1134	0.6442	998.5	1557.0	0.381	69
0.2053	0.6577	1039.4	1407.4	0.419	86	0.2010	0.6480	994.6	1559.9	0.474	104
0.2501	0.6599	1038.1	1406.1	0.463	98	0.2844	0.6523	992.2	1557.3	0.536	131
0.7787	0.7132	1033.3	1313.3	0.488	163	0.4044	0.6600	990.1	1545.5	0.577	163
0.8556	0.7303	1040.8	1264.1	0.380	136	0.4968	0.6673	989.8	1529.7	0.601	180
0.9354	0.7552	1057.9	1183.1	0.163	79	0.5938	0.6767	989.4	1509.7	0.620	196
1.0000	0.7818	1085.8	1084.9	0	0	0.7071	0.6912	990.8	1473.9	0.598	201
						0.8015	0.7081	996.6	1421.8	0.499	183
						0.9039	0.7344	1013.9	1324.6	0.301	123
						1.0000	0.7724	1053.2	1167.2	0.000	0
		methanol (1) + heptane (2)						methanol (1) + hexane (2)			
0.0000	0.6753	1108.9	1204.2	0.000	0	0.0000	0.6668	1066.9	1317.5	0.000	0
0.0539	0.6760	1101.8	1218.5	0.200	21	0.0748	0.6677	1057.5	1339.3	0.299	33
0.0847	0.6767	1099.4	1222.7	0.258	29	0.1222	0.6688	1053.9	1346.3	0.391	47
0.1232	0.6776	1096.7	1227.1	0.335	38	0.2041	0.6711	1049.1	1353.9	0.512	67
0.9061	0.7475	1062.2	1185.7	0.358	90	0.9081	0.7382	1027.0	1284.3	0.410	103
0.9311	0.7548	1065.3	1167.4	0.288	74	0.9274	0.7443	1030.1	1266.2	0.316	88
0.9613	0.7652	1071.5	1138.2	0.180	49	0.9621	0.7560	1038.1	1227.4	0.194	54
		methanol (1) + octane (2)						methanol (1) + octane (2)			
0.0000	0.6945	1151.6	1085.7	0.000	0	0.0000	0.6864	1110.8	1180.8	0.000	0
0.0524	0.6948	1144.7	1098.4	0.202	13	0.0561	0.6866	1103.1	1196.9	0.245	17
0.0598	0.6949	1144.0	1099.6	0.217	14	0.0726	0.6868	1101.7	1199.6	0.285	20
0.0699	0.6951	1143.2	1100.9	0.225	15	0.0922	0.6871	1100.0	1202.9	0.321	23
0.9479	0.7617	1074.9	1136.2	0.269	51	0.9425	0.7508	1040.4	1230.5	0.304	63
0.9485	0.7618	1074.9	1136.2	0.272	51	0.9498	0.7530	1041.1	1225.1	0.276	57
0.9720	0.7697	1077.7	1118.6	0.176	34	0.9678	0.7592	1043.9	1208.8	0.184	41
		ethanol (1) + hexane (2)						ethanol (1) + hexane (2)			
0.1055	0.6552	1047.0	1392.3	0.324	49	0.1180	0.6467	1001.6	1541.3	0.357	65
0.2038	0.6614	1045.1	1384.1	0.415	77	0.1967	0.6516	1000.6	1532.9	0.447	91
0.3093	0.6694	1045.5	1366.6	0.437	99	0.2614	0.6562	1000.9	1521.3	0.486	108
0.3996	0.6773	1047.3	1346.1	0.440	112	0.3019	0.6594	1001.4	1512.4	0.489	117
0.5073	0.6882	1051.2	1315.0	0.438	121	0.3904	0.6670	1003.6	1488.6	0.501	132
0.5965	0.6989	1056.1	1282.7	0.410	122	0.4607	0.6739	1006.4	1465.1	0.489	140
0.7028	0.7140	1065.2	1234.4	0.367	113	0.5948	0.6894	1014.9	1408.3	0.450	143
0.7981	0.7308	1077.1	1179.4	0.273	94	0.7000	0.7043	1024.5	1352.8	0.408	134
0.8940	0.7513	1094.9	1110.3	0.178	60	0.7981	0.7216	1039.0	1283.6	0.309	108
1.0000	0.7807	1125.7	1010.7	0.000	0	0.8975	0.7433	1059.3	1198.9	0.183	67
						1.0000	0.7721	1092.1	1086.0	0.000	0
		ethanol (1) + heptane (2)						ethanol (1) + heptane (2)			
0.0979	0.6783	1100.3	1217.6	0.280	32	0.1029	0.6698	1057.1	1335.9	0.334	42
0.1984	0.6826	1096.1	1219.3	0.411	53	0.1700	0.6725	1053.3	1340.4	0.445	62
0.3090	0.6885	1093.3	1215.0	0.476	71	0.3114	0.6798	1050.7	1332.5	0.544	87
0.4076	0.6948	1091.6	1207.8	0.507	82	0.4046	0.6857	1049.4	1324.2	0.576	100
0.5084	0.7026	1090.8	1196.1	0.500	90	0.5071	0.6936	1049.6	1308.8	0.562	109
0.5984	0.7109	1090.9	1182.0	0.483	93	0.6072	0.7029	1050.6	1289.0	0.535	112
0.7142	0.7241	1093.1	1155.8	0.436	90	0.7078	0.7145	1053.8	1260.4	0.473	107
0.7984	0.7362	1096.9	1129.0	0.373	79	0.7995	0.7277	1059.2	1224.9	0.389	92
0.8984	0.7549	1106.1	1082.7	0.222	52	0.8985	0.7465	1070.4	1169.2	0.210	60
		ethanol (1) + octane (2)						ethanol (1) + octane (2)			
0.1124	0.6968	1141.4	1101.6	0.317	24	0.1121	0.6884	1100.1	1200.3	0.384	30
0.2080	0.6998	1136.0	1107.2	0.432	37	0.2049	0.6913	1094.9	1206.7	0.491	45
0.3034	0.7035	1131.7	1109.8	0.499	47	0.3070	0.6952	1090.4	1209.8	0.566	58
0.3806	0.7070	1128.8	1110.0	0.540	53	0.3906	0.6991	1087.1	1210.3	0.591	66
0.4922	0.7132	1124.3	1109.3	0.559	60	0.4967	0.7051	1083.5	1208.1	0.595	74
0.5969	0.7205	1120.4	1105.6	0.550	65	0.5897	0.7115	1080.7	1203.3	0.588	78
0.6888	0.7286	1117.1	1099.8	0.511	66	0.6880	0.7199	1078.4	1194.5	0.560	79
0.8004	0.7416	1114.8	1085.0	0.405	59	0.7921	0.7317	1077.4	1177.4	0.468	72
0.8972	0.7573	1115.8	1060.7	0.234	42	0.8970	0.7480	1079.9	1146.3	0.313	51
		T = 308.15 K						T = 318.15 K			
		methanol (1) + hexane (2)						methanol (1) + hexane (2)			
0.0000	0.6461	1032.4	1452.3	0.000	0	0.0000	0.6365	987.8	1610.0	0.000	0
0.0585	0.6473	1024.7	1471.2	0.251	38	0.1298	0.6400	975.5	1641.9	0.436	84
0.1092	0.6490	1021.5	1476.6	0.358	60	0.2093	0.6434	972.1	1644.6	0.538	118
0.1952	0.6527	1017.2	1480.7	0.449	92	0.2822	0.6472	970.1	1641.8	0.585	144
0.2721	0.6566	1014.6	1479.6	0.506	116	0.4044	0.6550	968.0	1629.4	0.624	181
0.7469	0.7046	1013.8	1380.8	0.366	172	0.4983	0.6624	967.4	1613.2	0.648	202
0.7930	0.7131	1015.4	1360.2	0.340	167	0.5984	0.6722	967.3	1589.9	0.657	219
0.8493	0.7254	1021.6	1320.8	0.298	145	0.7059	0.6862	969.0	1551.9	0.611	224
0.9001	0.7395	1031.4	1271.1	0.204	112	0.7986	0.7024	977.2	1490.9	0.536	200
0.9485	0.7557	1045.6	1210.5	0.111	67	0.9048	0.7305	996.8	1377.8	0.260	129
1.0000	0.7771	1068.9	1126.2	0.000	0	1.0000	0.7676	1037.3	1210.7	0.000	0

Table 3 (Continued)

x_1	ρ/ (g·cm^{-3})	u/ (m·s^{-1})	κ_S/ (T Pa^{-1})	V^E/ (cm^3·mol^{-1})	$\delta\kappa_S$/ (T Pa^{-1})	x_1	ρ/ (g·cm^{-3})	u/ (m·s^{-1})	κ_S/ (T Pa^{-1})	V^E/ (cm^3·mol^{-1})	$\delta\kappa_S$/ (T Pa^{-1})
T = 308.15 K						T = 313.15 K					
methanol (1) + heptane (2)						methanol (1) + heptane (2)					
0.0000	0.6710	1087.7	1259.6	0.000	0	0.0000	0.6625	1045.6	1380.5	0.000	0
0.0847	0.6723	1077.9	1280.1	0.280	32	0.0826	0.6633	1035.5	1406.1	0.375	40
0.0906	0.6724	1077.4	1281.2	0.299	34	0.1940	0.6661	1028.6	1419.0	0.575	71
0.1544	0.6740	1073.5	1287.4	0.412	49	0.2578	0.6682	1025.2	1423.8	0.643	87
0.9073	0.7430	1044.7	1233.3	0.375	96	0.8468	0.7195	1004.7	1376.8	0.527	140
0.9299	0.7498	1047.9	1214.6	0.296	80	0.8712	0.7247	1006.0	1363.5	0.481	131
0.9589	0.7598	1054.1	1184.4	0.183	54	0.9600	0.7515	1020.8	1276.9	0.142	59
methanol (1) + octane (2)						methanol (1) + octane (2)					
0.0000	0.6904	1132.9	1128.6	0.000	0	0.0000	0.6822	1090.3	1233.1	0.000	0
0.0430	0.6906	1125.3	1143.5	0.176	15	0.0645	0.6826	1082.8	1249.5	0.243	18
0.0523	0.6907	1124.5	1145.0	0.102	17	0.0984	0.6829	1079.1	1257.5	0.355	27
0.0933	0.6912	1119.0	1155.3	0.304	27	0.1796	0.6841	1070.2	1276.2	0.534	47
0.9323	0.7528	1058.3	1185.9	0.312	61	0.9313	0.7428	1022.5	1287.7	0.359	75
0.9491	0.7575	1058.1	1179.2	0.267	54	0.9675	0.7541	1027.1	1257.1	0.204	46
0.9702	0.7647	1062.4	1158.6	0.170	34	0.9766	0.7576	1029.2	1246.2	0.148	35
ethanol (1) + hexane (2)						ethanol (1) + hexane (2)					
0.1072	0.6508	1025.8	1460.3	0.312	51	0.1079	0.6414	979.8	1623.9	0.351	66
0.1943	0.6562	1024.2	1452.7	0.408	79	0.2037	0.6473	978.4	1613.7	0.473	102
0.3073	0.6644	1024.7	1433.5	0.486	106	0.3068	0.6548	979.4	1592.2	0.549	131
0.3915	0.6718	1026.5	1412.6	0.474	119	0.4002	0.6630	982.1	1563.6	0.544	147
0.5043	0.6832	1031.1	1376.7	0.461	130	0.5068	0.6740	987.4	1521.7	0.509	157
0.6099	0.6960	1037.7	1334.3	0.426	130	0.5988	0.6853	994.2	1476.4	0.448	156
0.7041	0.7097	1046.6	1286.3	0.371	121	0.7032	0.7006	1005.5	1411.8	0.359	142
0.7933	0.7252	1058.5	1230.6	0.303	102	0.7922	0.7165	1019.3	1343.4	0.250	117
0.9006	0.7485	1079.8	1145.9	0.172	61	0.8992	0.7395	1042.4	1244.4	0.150	70
1.0000	0.7764	1110.5	1044.4	0.000	0	1.000	0.7676	1075.7	1125.8	0.000	0
ethanol (1) + heptane (2)						ethanol (1) + heptane (2)					
0.0960	0.6738	1080.5	1271.2	0.306	32	0.0974	0.6649	1036.3	1400.4	0.410	45
0.1970	0.6781	1076.4	1272.8	0.439	56	0.1943	0.6689	1032.4	1402.7	0.555	72
0.3132	0.6843	1073.5	1268.2	0.508	76	0.3109	0.6750	1029.5	1397.7	0.630	96
0.4102	0.6905	1072.2	1259.7	0.541	88	0.4098	0.6814	1028.7	1386.7	0.635	111
0.5101	0.6982	1071.4	1246.9	0.540	97	0.5053	0.6887	1029.1	1371.1	0.628	119
0.6057	0.7071	1072.4	1229.8	0.516	100	0.6139	0.6988	1030.9	1346.6	0.594	122
0.7101	0.7191	1075.1	1203.2	0.462	96	0.7129	0.7105	1034.7	1314.5	0.505	116
0.7999	0.7321	1079.8	1171.6	0.378	84	0.8035	0.7236	1041.0	1275.3	0.423	99
0.8996	0.7510	1089.9	1120.9	0.208	55	0.9041	0.7428	1053.7	1212.6	0.244	62
ethanol (1) + octane (2)						ethanol (1) + octane (2)					
0.1009	0.6923	1123.1	1145.2	0.319	25	0.1062	0.6840	1080.2	1252.9	0.385	31
0.2193	0.6960	1116.5	1152.5	0.464	42	0.2079	0.6870	1074.3	1261.2	0.537	50
0.3099	0.6995	1112.5	1155.0	0.536	52	0.3074	0.6908	1069.9	1264.6	0.607	64
0.3891	0.7032	1109.3	1155.7	0.563	60	0.3959	0.6949	1066.5	1265.3	0.637	75
0.4929	0.7090	1105.4	1154.2	0.579	67	0.4850	0.6998	1063.7	1262.9	0.651	82
0.5977	0.7163	1101.9	1149.7	0.569	71	0.5952	0.7073	1060.8	1256.3	0.640	87
0.6964	0.7250	1099.2	1141.5	0.532	72	0.6939	0.7160	1059.1	1245.1	0.582	86
0.8042	0.7378	1097.7	1124.8	0.415	64	0.7970	0.7278	1058.7	1225.8	0.486	78
0.9016	0.7538	1099.7	1097.0	0.235	44	0.8969	0.7440	1062.2	1191.4	0.273	54

tive index of the sample. A PolyScience bath controller model 9010 with a temperature stability of $\pm 10^{-2}$ K was used to thermostat the refractometer. Apparatus calibration (DSA-48 and ABBEMAT) was realized periodically using ambient air and Millipore quality water. Accuracies in the calculation of mole fractions, excess molar volumes, changes of refractive indices on mixing, and changes of isentropic compressibilities on mixing were estimated to be better than $\pm 10^{-4}$, $\pm 9 \times 10^{-3}$ cm^3·mol^{-1}, $\pm 10^{-4}$, and ± 1 TPa^{-1}, respectively. Further information on the experimental technique and mode of operation has been described previously (Iglesias et al., 1996; Orge et al., 1997).

3. Results and Discussion

The values of refractive indices and changes of refractive indices on mixing are reported in Table 2. Densities, speeds of sound, isentropic compressibilities (calculated by means of the Laplace equation $K_s = \rho^{-1} \cdot u^{-2}$, excess molar volumes, and changes of isentropic compressibilities on mixing are reported in Table 3.

The values of the changes of refractive indices on mixing, the excess molar volumes, and the changes of isentropic compressibilities on mixing have been computed using the following equation

$$\delta Q_{ij} = Q_{ij} - \sum_{i=1}^{n_c} x_i \cdot Q_i \qquad (1)$$

In this equation, δQ_{ij} is the derived property, Q_{ij} is the property of the mixture, Q_i is the property of the pure compound, x_i is the mole fraction of component i, and n_c is the number of components in the mixture. Excess and derived properties were correlated using the Redlich−Kister expression (eq 2) by the unweighted least-squares method.

$$\delta Q = x_i \cdot x_j \cdot \sum_{p=0}^{m} B_p \cdot (x_i - x_j)^p \qquad (2)$$

In this equation x_i, and x_j are the mole fractions of the

Table 4. Parameters B_i of Eq 2 and Root-Mean-Square Deviations σ

	B_0	B_1	B_2	B_3	B_4	B_5	σ
			T=303.15 K				
			methanol (1) + hexane (2)				
δn_D	0.03375	0.01325	0.01122				0.00007
V^E/(cm^3·mol^{-1})	2.3123	0.8157	1.2855	−1.6704			0.012
$\delta\kappa_S$/(T Pa^{-1})	592.87	342.53	456.70	102.34			0.1
			methanol (1) + heptane (2)				
δn_D	0.05264	0.03270	0.01981				0.00012
V^E/(cm^3·mol^{-1})	1.5851	0.5190	3.3191				0.006
$\delta\kappa_S$/(T Pa^{-1})	205.68	198.46	765.64	336.58			0.4
			methanol (1) + octane (2)				
δn_D	0.07240	0.04182	0.03345				0.00005
V^E/(cm^3·mol^{-1})	−3.6369	0.7793	10.5172				0.002
$\delta\kappa_S$/(T Pa^{-1})	−362.19	−160.65	1260.60	746.76			0.1
			ethanol (1) + hexane (2)				
δn_D	0.00244	0.00150	−0.00095				0.00001
V^E/(cm^3·mol^{-1})	1.7491	−0.0254	0.7289	−1.2201	1.1391		0.005
$\delta\kappa_S$/(T Pa^{-1})	483.58	102.82	105.01	−47.90	72.69		0.1
			ethanol (1) + heptane (2)				
δn_D	0.01284	0.00643	−0.00442				0.00002
V^E/(cm^3·mol^{-1})	2.0032	−0.0984	1.2253	−0.4671			0.005
$\delta\kappa_S$/(T Pa^{-1})	357.53	128.76	165.30				0.5
			ethanol (1) + octane (2)				
δn_D	0.02702	0.01096	0.00227	−0.00123			0.00001
V^E/(cm^3·mol^{-1})	2.2344	0.1735	1.0096	−0.9013			0.005
$\delta\kappa_S$/(T Pa^{-1})	243.08	106.49	132.84	40.93	61.92		0.2
			T=308.15 K				
			methanol (1) + hexane (2)				
δn_D	0.03705	0.01195					0.00011
V^E/(cm^3·mol^{-1})	1.9201	−1.2786	1.2394	3.5420	8.6955	−4.6136	0.005
$\delta\kappa_S$/(T Pa^{-1})	638.34	219.94	436.88	582.11	63.28	−487.09	0.8
			methanol (1) + heptane (2)				
δn_D	0.05636	0.02662	0.01045				0.00008
V^E/(cm^3·mol^{-1})	2.8295	1.3570	1.7958	−1.2283			0.002
$\delta\kappa_S$/(T Pa^{-1})	298.61	233.59	715.46	323.74			0.2
			methanol (1) + octane (2)				
δn_D	0.08982	0.04946					0.00010
V^E/(cm^3·mol^{-1})	1.0647	0.6626	4.5917				0.005
$\delta\kappa_S$/(T Pa^{-1})	675.70	408.69					2.9
			ethanol (1) + hexane (2)				
δn_D	0.00097	0.00140	−0.00087				0.00001
V^E/(cm^3·mol^{-1})	1.8447	−0.4982	1.1354	−0.5008			0.007
$\delta\kappa_S$/(T Pa^{-1})	518.31	107.27	113.62	−21.85	33.84		0.2
			ethanol (1) + heptane (2)				
δn_D	0.01415	0.00593	−0.00119				0.00001
V^E/(cm^3·mol^{-1})	2.1521	−0.0428	1.1351	−0.9957			0.006
$\delta\kappa_S$/(T Pa^{-1})	384.29	143.17	156.05				0.5
			ethanol (1) + octane (2)				
δn_D	0.02435	0.01346	0.00038	0.00054			0.00001
V^E/(cm^3·mol^{-1})	2.3215	0.1699	1.1607	−1.0349			0.006
$\delta\kappa_S$/(T Pa^{-1})	270.38	111.79	123.88	41.97	90.57		0.1
			T=313.15 K				
			methanol (1) + hexane (2)				
δn_D	0.03543	0.08682					0.00010
V^E/(cm^3·mol^{-1})	2.4092	0.5746	1.9001	−1.3063			0.006
$\delta\kappa_S$/(T Pa^{-1})	724.76	366.95	487.93	126.88			0.8
			methanol (1) + heptane (2)				
δn_D	0.05275	0.00767	0.02044	0.02284			0.00007
V^E/(cm^3·mol^{-1})	2.3474	0.4502	3.0289				0.012
$\delta\kappa_S$/(T Pa^{-1})	379.83	237.27	701.86	356.49			0.7
			methanol (1) + octane (2)				
δn_D	0.05020	0.00630	0.05451	0.03763			0.00003
V^E/(cm^3·mol^{-1})	1.1961	2.2879	5.0057	−2.1601			0.002
$\delta\kappa_S$/(T Pa^{-1})	−77.60	42.97	1036.02	552.38			0.2
			ethanol (1) + hexane (2)				
δn_D	−0.00041	0.00136	−0.00050				0.00001
V^E/(cm^3·mol^{-1})	1.9244	−0.3953	1.2955	−0.9363			0.005
$\delta\kappa_S$/(T Pa^{-1})	569.63	106.68	163.96	−64.02			0.7
			ethanol (1) + heptane (2)				
δn_D	0.01360	0.00401	−0.00326				0.00002
V^E/(cm^3·mol^{-1})	2.2624	−0.2264	1.1565	−0.8577			0.007
$\delta\kappa_S$/(T Pa^{-1})	431.84	124.96	196.29				0.6
			ethanol (1) + octane (2)				
δn_D	0.02651	0.01008	0.00082				0.00002
V^E/(cm^3·mol^{-1})	2.3693	−0.1559	1.8414				0.012
$\delta\kappa_S$/(T Pa^{-1})	298.07	118.44	142.97	46.79	85.90		0.1

Table 4 (Continued)

	B_0	B_1	B_2	B_3	B_4	B_5	σ
			T=318.15 K				
			methanol (1) + hexane (2)				
δn_D	0.03336	0.00655	0.00325				0.00003
$V^E/(cm^3 \cdot mol^{-1})$	2.6023	0.5062	1.7693	−1.7445			0.014
$\delta\kappa_S/(T\ Pa^{-1})$	811.46	441.21	479.85				1.0
			methanol (1) + heptane (2)				
δn_D	0.05002	0.01763	0.03327	0.01198	−0.01733		0.00003
$V^E/(cm^3 \cdot mol^{-1})$	3.3114	1.3870	1.6673	−2.7372			0.011
$\delta\kappa_S/(T\ Pa^{-1})$	551.38	323.70	283.35	243.34	380.05		0.3
			methanol (1) + octane (2)				
δn_D	0.07309	0.02864	0.02741	0.01800			0.00005
$V^E/(cm^3 \cdot mol^{-1})$	2.2933	−0.8477	3.4251	2.3478			0.003
$\delta\kappa_S/(T\ Pa^{-1})$	84.72	−205.30	871.95	971.97			0.5
			ethanol (1) + hexane (2)				
δn_D	−0.00069	0.00138	−0.00057				0.00001
$V^E/(cm^3 \cdot mol^{-1})$	2.0298	−1.1652	0.7892				0.012
$\delta\kappa_S/(T\ Pa^{-1})$	628.56	93.35	93.17	−70.75	103.01		0.4
			ethanol (1) + heptane (2)				
δn_D	0.01192	0.00304					0.00002
$V^E/(cm^3 \cdot mol^{-1})$	2.5226	−0.3802	1.1161	−1.1040	1.1709		0.008
$\delta\kappa_S/(T\ Pa^{-1})$	474.04	136.76	199.34				0.7
			ethanol (1) + octane (2)				
δn_D	0.02608	0.00962					0.00002
$V^E/(cm^3 \cdot mol^{-1})$	2.5972	0.0774	1.4899	−1.1474			0.007
$\delta\kappa_S/(T\ Pa^{-1})$	331.62	125.29	144.31	62.67	94.17		0.2

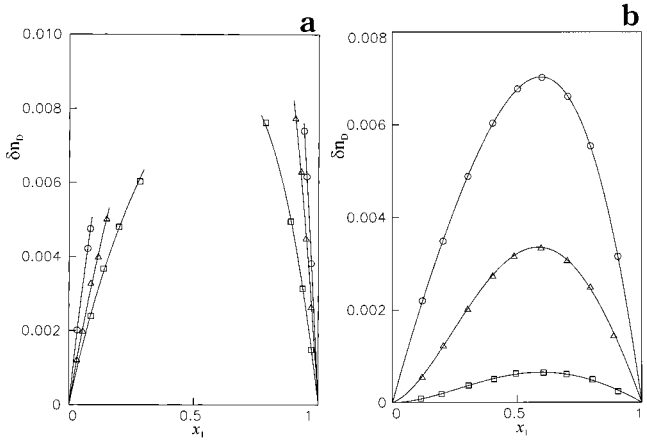

Figure 1. Changes of refractive indices on mixing at 303.15 K for (a) methanol and (b) ethanol with (□) hexane, (△) heptane, and (○) octane.

components, m is the degree of the polynomial, and B_p are the adjustable parameters. The degree of this polynomial, m was optimized by applying the F-test (Bevington, 1969). These parameters are compiled in Table 4 as well as the root-mean-square deviations calculated according to the expression

$$\sigma = \left(\sum_{i}^{n_{DAT}} \frac{(\delta Q_{exp} - \delta Q_{cal})^2}{n_{DAT}} \right)^{1/2} \quad (3)$$

where δQ_{exp} is the experimental value, δQ_{cal} is the calculated value, and n_{DAT} is the number of experimental data points. Figure 1 shows the experimental and correlated data of changes of refractive indices on mixing for the binary mixtures methanol or ethanol plus *n*-alkanes at 303.15 K. In the methanol + *n*-alkane binary mixtures there is an immiscibility region that has been studied in a previous paper (Orge et al., 1997). All binary mixtures have a positive deviation of their derived properties, and the maximun tends to correspond to the largest aliphatic chain. Parts a and b of Figures 2 show the excess molar volumes

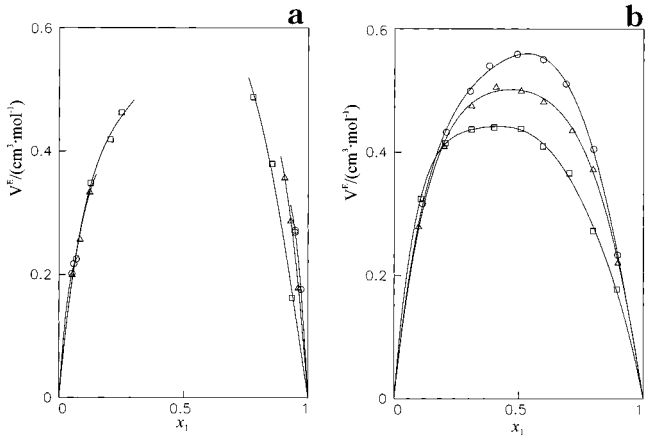

Figure 2. Excess molar volumes at 303.15 K for (a) methanol and (b) ethanol with (□) hexane, (△) heptane, and (○) octane.

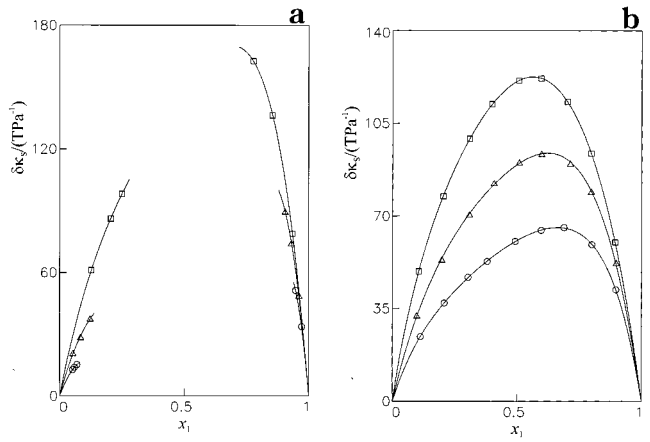

Figure 3. Changes of isentropic compressibilities on mixing at 303.15 K for (a) methanol and (b) ethanol with (□) hexane, (△) heptane, and (○) octane.

of the binaries methanol or ethanol plus *n*-alkanes at 303.15 K, respectively. The changes of isentropic compressibilities on mixing of the mentioned binary mixtures are

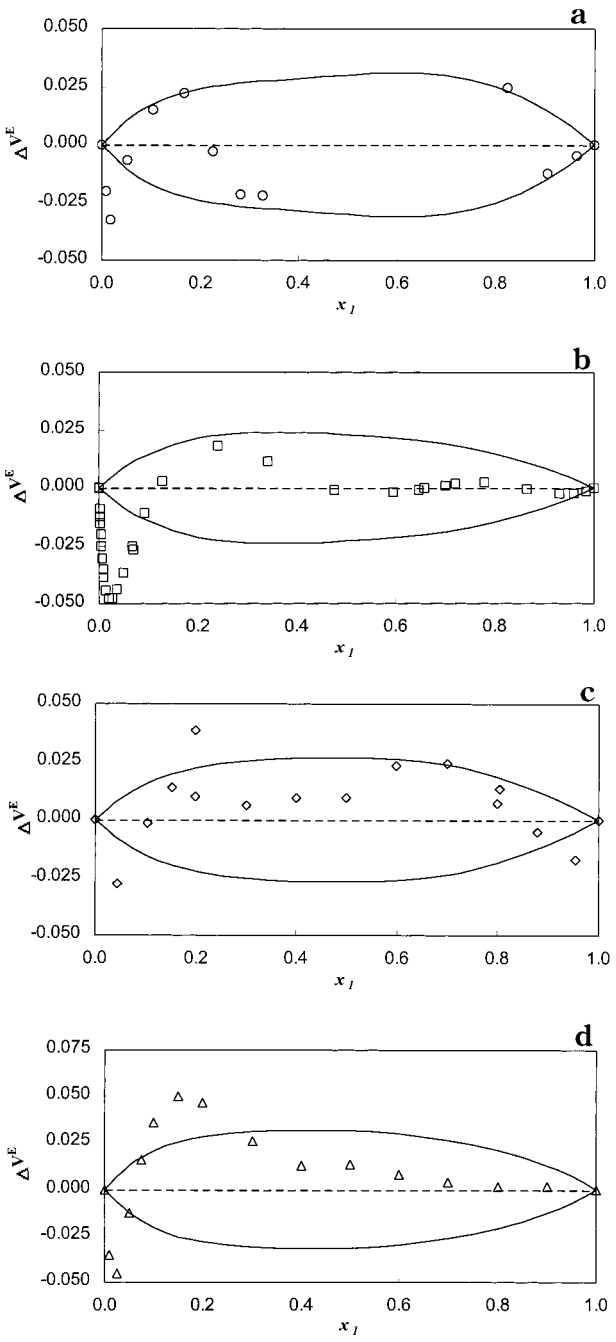

Figure 4. Deviations ΔV^E for (a) methanol + hexane at 313.15 K, (b) ethanol + hexane at 308.15 K, (c) ethanol + heptane at 308.15 K, and (d) ethanol + heptane at 318.15 K: (—) $\pm 0.05 \times V^E$ (eq 2); (○) Liu et al., 1991; (□) Marsh and Burfitt, 1975; (◇) Papaloannou et al., 1991; (△) Van Ness et al., 1967.

plotted in Figure 3. These derived properties also tend to increase with temperature.

In the open literature there are several authors that have measured some of these systems. The systems compared were methanol + hexane at 313.15 K (Liu et al., 1991), ethanol + hexane at 308.15 K (Marsh and Burfitt, 1975), ethanol + heptane at 308.15 K (Papaloannou et al., 1991), and ethanol + heptane at 318.15 K (Van Ness et al., 1967). Figure 4 shows the deviations (eq 4) between our correlated data (eq 2) and other authors' experimental data.

$$\Delta V^E = V^E_{RK} - V^E_{lit} \tag{4}$$

In this equation V^E_{lit} is the other authors' excess molar volumes and V^E_{RK} is the value of the excess molar volumes calculated by the Redlich−Kister equation (eq 2), using our correlation parameters, at the same mole fraction.

Literature Cited

Bevington, P. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969.

Iglesias, M.; Orge, B.; Tojo, J. Refractive Indices, Densities and Excess Properties on Mixing of the Systems Acetone + Methanol + Water and Acetone + Methanol + 1-Butanol at 298.15 K. *Fluid Phase Equilib.* **1996**, *126*, 203−223.

Liu, A.; Pusicha, K.; Demiriz, A. M.; Kohler, F. Model for Alkanol + Alkane Mixtures: Extension and Experimental Verification. *J. Solution Chem.* **1991**, *20*, 39−56.

Marsh, K. N.; Burfitt, C. Excess Volumes for Alcohols + Nonpolar Solvents. I. Ethanol + Cyclohexane, + *n*-Hexane, + Benzene, + Carbon Tetrachloride, + Cyclopentane, and + *p*-Xylene. *J. Chem. Thermodyn.* **1975**, *7*, 955−968.

Orge, B.; Iglesias, M.; Rodríguez, A.; Canosa, J. M.; Tojo, J. Mixing Properties of (Methanol, Ethanol, or 1-Propanol) with (Pentane, Hexane, Heptane and Octane) at 298.15 K. *Fluid Phase Equilib.* **1997**, *133*, 213−227.

Papaloannou, D.; Ziakas, D.; Panayiotou, C. Volumetric Properties of Binary Mixtures. I. 2-Propanone + 2,2,4-Trimethylpentane and *n*-Heptane + Ethanol Mixtures. *J. Chem. Eng. Data* **1991**, *36*, 35−39.

Redlich, O.; Kister, A. T. Thermodynamics on Nonelectrolytic Solutions. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

TRC Thermodynamic Tables; Thermodynamic Research Center, Texas A&M University: College Station, TX, 1994.

Van Ness, H. C.; Soczek, C. A.; Kochar, N. K. Thermodynamic Excess Properties for Ethanol-*n*-Heptane. *J. Chem. Eng. Data* **1967**, *12*, 346−351.

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