Isobaric Vapor−Liquid Equilibria for Binary and Ternary Systems Composed of 2-Methoxy-2-methylpropane, Ethanol, 2-Methyl-2-propanol, and Octane at 101.3 kPa

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Isobaric vapor−liquid equilibria for two ternary systems, 2-methoxy-2-methylpropane (MTBE) + ethanol + 2-methyl-2-propanol and ethanol + 2-methyl-2-propanol + octane, and one binary system, ethanol + 2-methyl-2-propanol, have been measured at 101.3 kPa. The measurements were made in an equilibrium still with circulation of both the vapor and liquid phases. Both ternary systems and the binary system ethanol + 2-methyl-2-propanol do not form azeotropes. The three constituent binary systems of MTBE + ethanol, MTBE + 2-methyl-2-propanol, and 2-methyl-2-propanol + octane, which were measured in our previous work, are also not azeotropes. The other constituent system ethanol + octane, measured in our previous work, forms a minimum azeotrope. The experimental data for the binary systems were correlated with the nonrandom two-liquid (NRTL) equation. The NRTL equation yielded a good prediction of activity coefficients for the ternary systems from the parameters of the correlated binary systems.

Introduction

Ethers and alcohols used as gasoline additives have excellent antiknock qualities and are considered environmental protection substances. Gasoline including 2-methoxy-2-methylpropane (MTBE) has been used for a high-performance premium gasoline. In recent years, mixtures of ethers with alcohols have been considered for blending with gasoline. As a continuation of our studies[1,2] on the vapor−liquid equilibrium (VLE) of MTBE + octane + alcohols systems, the isobaric VLE for the ternary systems MTBE + ethanol + 2-methyl-2-propanol and ethanol + 2-methyl-2-propanol + octane and the constituent binary system ethanol + 2-methyl-2-propanol have been measured at 101.3 kPa. The measurements were made in an equilibrium still[3] with circulation of both the vapor and liquid phases. Data for the other four constituent binary systems of MTBE + ethanol,[1] MTBE + 2-methyl-2-propanol,[2] 2-methyl-2-propanol + octane,[2] and ethanol + octane[4] were reported in our previous studies. For the ethanol + 2-methyl-2-propanol system, one set of isobaric VLE data at 101.3 kPa is reported by Suska et al.[5] and one set of isothermal data at 313.15 K have been measured by Oracz.[6] No isobaric or isothermal VLE data have been reported previously for the MTBE + ethanol + 2-methyl-2-propanol and ethanol + 2-methyl-2-propanol + octane systems.

Experimental Section

Materials. Ethanol, 2-methyl-2-propanol, and octane, supplied by the Wako Pure Chemical Co. Ltd., and MTBE, supplied by the Merck−Dr. Th. Schuchardt & Co., were special grade reagents. Ethanol was used after a small quantity of water was removed with 3A molecular sieves. Gas-chromatographic analysis on all three materials indicated that each had a purity of at least 99.9 mol %. The measured physical properties of the compounds are listed in Table 1 along with the literature data. Refractive index values were determined with a digital refractometer by using the critical angle of total reflection method (Kyoto Electric RA-510, Japan). Refractive index was measured with an accuracy of ±0.00005.

Table 1. Normal Boiling Points, T_b, and Refractive Index, n_D, of the Components

	T_b/K			n_D(298.15 K)	
material	exptl	calc[a]	lit.	exptl	lit.
MTBE	328.14	328.36	328.11[b]	1.366 41	1.3663[b]
ethanol	351.44	351.45	351.443[c]	1.359 37	1.35941[c]
2-methyl-2-propanol	355.53	355.49	355.50[c]	1.384 90	1.39389[c]
octane	398.80	398.82	398.823[c]	1.395 15	1.39565[c]

[a] Calculated value using the Antoine constants with Table 2. [b] Arce et al.[11] [c] Riddick et al.[12]

Procedure. An all Pyrex-glass equilibrium still with circulation of vapor and liquid phases, developed in a previous study,[3] was used for the determination of VLE values. The overall charge of the apparatus was about 100 cm^3 of solution.

The temperature was measured with a calibrated platinum resistance thermometer (Pt 100Ω) with an accuracy of 0.03 K. A standard resistance thermometer (Chino Co. model R800-2, Japan), calibrated on the ITS-90 scale, was used for this calibration. The pressure in the apparatus was measured by means of a silicon resonant precision barometer (Tokyo Suzuki Seisakusho Co., model T60, Japan) with an accuracy of 0.015 kPa. Since the barometric pressure changed slightly, the experimental temperatures were corrected to 101.3 kPa.[1]

Analysis. The equilibrium composition of the samples was determined by using a gas chromatograph (GL Sciences model GC-380, Japan) equipped with a flame ionization detector and an autosampler. The column packing was Gasukuropack 54 (supplied by the GL Sciences Inc.). The

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Table 2. Antoine Constants of the Components[a]

material	*A*	*B*	*C*	ref
MTBE	6.120 19	1190.420	−39.040	*b*
ethanol	7.242 22	1595.811	−46.702	*c*
2-methyl-2-propanol	6.352 72	1105.198	−101.256	*c*
octane	6.043 94	1351.938	−64.030	*c*

[a] $\log(P/\text{kPa}) = A - B/[(T/\text{K}) + C]$. [e] Tsuji et al.[13] [f] Boublik et al.[14]

Table 3. Isobaric Vapor−Liquid Equilibrium Data, Temperature, *T*, Liquid Phase, x_1, and Vapor Phase, y_1, Mole Fractions, and Activity Coefficient, γ_i, for the Ethanol (1) + 2-Methyl-2-propanol (2) System at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
355.53	0.0000	0.0000		
355.43	0.0343	0.0371	0.9257	0.9998
355.35	0.0721	0.0779	0.9273	0.9997
355.29	0.0978	0.1056	0.9293	0.9997
355.24	0.1175	0.1269	0.9314	0.9993
355.12	0.1727	0.1861	0.9333	0.9986
354.95	0.2402	0.2586	0.9390	0.9973
354.78	0.3020	0.3249	0.9443	0.9951
354.70	0.3341	0.3595	0.9477	0.9928
354.49	0.3996	0.4296	0.9546	0.9889
354.41	0.4236	0.4556	0.9576	0.9861
354.26	0.4650	0.4993	0.9616	0.9828
354.02	0.5284	0.5661	0.9686	0.9757
353.87	0.5636	0.6027	0.9724	0.9710
353.76	0.5904	0.6306	0.9755	0.9663
353.67	0.6110	0.6510	0.9766	0.9646
353.43	0.6618	0.7017	0.9808	0.9579
353.35	0.6776	0.7182	0.9835	0.9519
353.22	0.7033	0.7430	0.9853	0.9483
352.97	0.7524	0.7902	0.9892	0.9373
352.58	0.8224	0.8544	0.9936	0.9209
352.48	0.8408	0.8706	0.9943	0.9169
352.26	0.8780	0.9023	0.9952	0.9115
352.18	0.8919	0.9140	0.9957	0.9084
352.06	0.9121	0.9309	0.9965	0.9020
351.94	0.9303	0.9457	0.9969	0.8978
351.91	0.9347	0.9492	0.9971	0.8969
351.87	0.9417	0.9549	0.9973	0.8944
351.71	0.9659	0.9739	0.9977	0.8915
351.44	1.0000	1.0000		

relationship between peak area and composition was determined from analysis of samples of known composition. The accuracies of liquid, x_i, and vapor, y_i, mole fractions are estimated to be 0.002 mole fraction.

Experimental Results

The activity coefficients γ_i were calculated with the equation

$$Py_i = \gamma_i P_i^{\text{S}} x_i \qquad (1)$$

In most cases it is preferable to calculate the activity coefficients by including fugacity coefficients and the Poynting factor correction. However, not all the required physical property data are available for MTBE to calculate these terms accurately. The activity coefficients were therefore calculated on the assumption of an ideal vapor phase. The vapor pressures of the pure components, P_i^{S}, were obtained using the Antoine equation constants, which are shown in Table 2.

Binary System. The binary VLE data for ethanol (1) + 2-methyl-2-propanol (2) are reported in Table 3 along with the activity coefficients calculated using eq 1. The values of ln γ_i are negative for the whole concentration range. The ethanol + 2-methyl-2-propanol system is nonazeotropic.

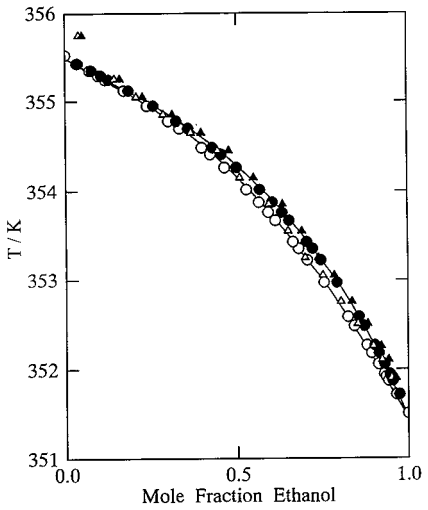

Figure 1. Temperature−composition diagram for ethanol (1) + 2-methyl-2-propanol (2) at 101.3 kPa. Present work: ○, x_1; ●, y_1. Suska et al.[5] at 101.3 kPa (1970): △, x_1; ▲, y_1. —, NRTL equation with parameters from Table 6.

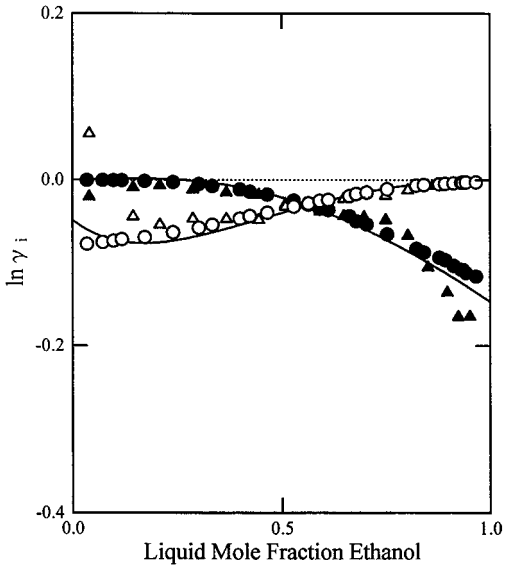

Figure 2. Activity coefficient−liquid composition diagram for ethanol (1) + 2-methyl-2-propanol (2) at 101.3 kPa. Present work: ○, ln γ_1; ●, ln γ_2. Suska et al.[5] at 101.3 kPa (1970): △, ln γ_1; ▲, ln γ_2. —, NRTL equation with parameters from Table 6.

The experimental VLE for the ethanol (1) + 2-methyl-2-propanol (2) system is shown graphically in Figures 1 and 2.

The three constituent binary systems of MTBE + ethanol, MTBE + 2-methyl-2-propanol, and 2-methyl-2-propanol + octane, which were measured in our previous work, are nonazeotropes. As seen in our previous work, the other constituent system, ethanol + octane, forms a minimum boiling azeotrope.

The experimental data were tested for thermodynamic consistency using the point test of Fredenslund et al.[7] and of Van Ness et al.[8] The area test is not employed in this case because this system is almost ideal. The results indicate that the experimental data for the binary system of ethanol + 2-methyl-2-propanol are thermodynamically consistent.

Ternary System. The experimental VLE data for the ternary system MTBE (1) + ethanol (2) + 2-methyl-2-propanol (3) at 101.3 kPa are reported in Table 4. The tie lines and isotherms based on the experimental data for the

Table 4. Isobaric Vapor−Liquid Equilibrium Data, Temperature, T, Liquid Phase, x_i, and Vapor Phase, y_i, Mole Fractions, and Activity Coefficient, γ_i, for MTBE (1) + Ethanol (2) + 2-Methyl-2-propanol (3) at 101.3 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
350.54	0.024	0.802	0.098	0.772	2.0951	0.9982	0.9080	340.01	0.234	0.516	0.539	0.343	1.5994	1.0634	0.9017
349.85	0.026	0.866	0.111	0.814	2.1712	1.0006	0.8871	342.46	0.242	0.201	0.531	0.149	1.4161	1.0694	0.9850
350.64	0.028	0.735	0.112	0.708	2.0460	0.9959	0.9186	337.80	0.246	0.679	0.555	0.415	1.6726	1.0751	0.8502
349.11	0.030	0.933	0.123	0.852	2.2030	1.0025	0.8618	343.37	0.247	0.091	0.526	0.069	1.3348	1.0598	1.0092
350.00	0.031	0.790	0.125	0.745	2.0660	0.9990	0.9054	341.21	0.247	0.384	0.532	0.272	1.4402	1.0753	0.9632
349.26	0.034	0.858	0.137	0.788	2.1374	1.0018	0.8875	340.16	0.251	0.392	0.560	0.264	1.5388	1.0726	0.9350
351.04	0.052	0.373	0.172	0.356	1.6668	0.9695	0.9811	338.52	0.253	0.567	0.568	0.355	1.6287	1.0690	0.8710
348.13	0.058	0.733	0.218	0.641	2.0346	0.9993	0.9070	340.78	0.266	0.284	0.568	0.199	1.4486	1.0829	0.9566
350.32	0.059	0.414	0.197	0.388	1.7098	0.9792	0.9705	341.67	0.273	0.155	0.568	0.114	1.3708	1.0991	0.9895
349.69	0.063	0.484	0.211	0.445	1.7418	0.9867	0.9583	342.11	0.274	0.102	0.564	0.075	1.3418	1.0710	1.0088
350.92	0.064	0.257	0.198	0.243	1.5524	0.9638	0.9900	337.15	0.282	0.607	0.591	0.365	1.5844	1.0885	0.8653
348.96	0.065	0.560	0.223	0.505	1.8425	0.9943	0.9436	338.65	0.282	0.429	0.593	0.276	1.5180	1.0919	0.9212
347.21	0.066	0.789	0.238	0.670	2.0340	1.0070	0.8820	342.08	0.284	0.067	0.571	0.049	1.3087	1.0704	1.0235
349.54	0.067	0.458	0.221	0.419	1.7364	0.9864	0.9640	337.90	0.294	0.460	0.606	0.289	1.5253	1.1011	0.8955
348.96	0.070	0.520	0.236	0.466	1.8024	0.9896	0.9456	339.32	0.294	0.315	0.600	0.209	1.4464	1.0963	0.9597
346.32	0.071	0.844	0.257	0.693	2.0830	1.0086	0.8623	340.24	0.308	0.172	0.606	0.121	1.3551	1.1154	0.9935
351.01	0.072	0.146	0.213	0.138	1.4826	0.9647	0.9930	337.09	0.315	0.470	0.620	0.290	1.4918	1.1180	0.9173
347.97	0.073	0.614	0.251	0.535	1.8936	1.0006	0.9278	337.64	0.323	0.390	0.627	0.247	1.4473	1.1229	0.9324
350.29	0.073	0.284	0.223	0.262	1.5678	0.9671	0.9865	340.71	0.327	0.075	0.613	0.054	1.2730	1.1200	1.0328
350.91	0.081	0.078	0.224	0.073	1.3862	0.9592	1.0048	336.34	0.329	0.501	0.637	0.297	1.5026	1.1126	0.8766
350.43	0.081	0.161	0.238	0.149	1.4915	0.9619	0.9926	338.14	0.334	0.290	0.637	0.190	1.3974	1.1347	0.9599
346.91	0.082	0.669	0.279	0.562	1.9313	1.0075	0.9043	338.64	0.335	0.347	0.641	0.220	1.3831	1.0767	0.8899
349.51	0.083	0.314	0.252	0.283	1.6011	0.9740	0.9802	338.71	0.347	0.192	0.646	0.130	1.3419	1.1492	0.9836
346.34	0.087	0.703	0.292	0.578	1.9387	1.0096	0.8947	339.12	0.355	0.130	0.647	0.091	1.2993	1.1545	1.0145
348.16	0.091	0.553	0.262	0.485	1.5779	1.0011	0.9527	339.49	0.357	0.084	0.647	0.059	1.2769	1.1451	1.0293
346.14	0.092	0.694	0.302	0.567	1.9026	1.0117	0.8971	334.73	0.365	0.549	0.661	0.309	1.4759	1.1341	0.8473
349.74	0.092	0.177	0.265	0.161	1.4980	0.9745	0.9900	339.17	0.369	0.084	0.658	0.059	1.2662	1.1709	1.0277
350.30	0.095	0.087	0.251	0.081	1.3542	0.9720	1.0068	335.86	0.372	0.427	0.660	0.260	1.3964	1.1639	0.9293
345.15	0.096	0.763	0.321	0.599	1.9842	1.0125	0.8711	336.56	0.375	0.320	0.667	0.202	1.3712	1.1729	0.9591
344.95	0.101	0.753	0.330	0.588	1.9509	1.0143	0.8720	336.00	0.381	0.359	0.674	0.220	1.3876	1.1653	0.9366
346.04	0.105	0.584	0.336	0.471	1.8599	1.0024	0.9116	337.52	0.399	0.162	0.685	0.108	1.2845	1.1934	1.0076
346.75	0.106	0.487	0.328	0.404	1.7512	1.0031	0.9407	337.53	0.403	0.147	0.687	0.099	1.2756	1.1933	1.0173
343.85	0.107	0.826	0.350	0.615	2.0190	1.0139	0.8421	334.34	0.403	0.471	0.682	0.272	1.3958	1.1838	0.8996
349.70	0.108	0.096	0.278	0.087	1.3411	0.9699	1.0079	337.97	0.406	0.095	0.688	0.065	1.2497	1.1957	1.0376
343.59	0.113	0.818	0.361	0.604	1.9939	1.0153	0.8402	336.06	0.409	0.270	0.690	0.172	1.3182	1.2108	0.9865
344.82	0.117	0.635	0.368	0.490	1.8853	1.0101	0.8855	336.10	0.417	0.247	0.697	0.159	1.3043	1.2171	0.9829
345.54	0.120	0.533	0.363	0.424	1.7764	1.0088	0.9260	334.77	0.425	0.357	0.702	0.214	1.3459	1.2012	0.9416
348.31	0.123	0.147	0.332	0.127	1.4636	0.9769	0.9918	334.40	0.426	0.394	0.702	0.229	1.3585	1.1859	0.9479
347.31	0.125	0.269	0.352	0.226	1.5667	0.9911	0.9732	335.89	0.453	0.181	0.718	0.119	1.2447	1.2649	1.0275
342.82	0.126	0.806	0.386	0.580	1.9501	1.0223	0.8501	335.77	0.461	0.167	0.722	0.111	1.2371	1.2783	1.0399
348.40	0.130	0.082	0.337	0.071	1.4031	0.9703	1.0027	336.37	0.462	0.107	0.725	0.072	1.2159	1.2714	1.0604
343.56	0.130	0.689	0.394	0.510	1.8851	1.0191	0.8742	336.56	0.464	0.082	0.727	0.056	1.2067	1.2695	1.0693
346.24	0.132	0.361	0.371	0.294	1.6248	1.0024	0.9643	333.90	0.466	0.337	0.724	0.201	1.3003	1.2474	0.9584
345.22	0.134	0.584	0.396	0.443	1.7587	0.9746	0.8696	334.24	0.467	0.301	0.725	0.184	1.2858	1.2586	0.9751
347.43	0.140	0.161	0.365	0.136	1.4508	0.9913	0.9907	334.35	0.474	0.276	0.729	0.172	1.2697	1.2721	0.9819
346.06	0.144	0.303	0.392	0.245	1.5738	1.0044	0.9662	332.79	0.476	0.433	0.720	0.249	1.3114	1.2620	0.9192
345.12	0.147	0.395	0.404	0.311	1.6292	1.0171	0.9546	332.75	0.507	0.358	0.741	0.212	1.2683	1.3004	0.9432
347.49	0.148	0.092	0.375	0.078	1.4072	0.9959	0.9968	334.06	0.513	0.206	0.752	0.133	1.2192	1.3338	1.0361
346.50	0.156	0.179	0.398	0.147	1.4635	1.0037	0.9863	333.92	0.514	0.222	0.748	0.143	1.2184	1.3433	1.0405
344.96	0.160	0.328	0.425	0.256	1.5838	1.0143	0.9609	334.45	0.518	0.157	0.760	0.103	1.2071	1.3392	1.0415
344.89	0.161	0.337	0.425	0.263	1.5819	1.0180	0.9607	335.08	0.521	0.091	0.762	0.062	1.1780	1.3530	1.0890
342.45	0.163	0.603	0.445	0.432	1.7647	1.0346	0.8969	332.47	0.528	0.335	0.752	0.199	1.2472	1.3254	0.9679
346.48	0.168	0.104	0.411	0.085	1.4016	0.9965	1.0004	332.59	0.534	0.309	0.755	0.187	1.2340	1.3398	0.9912
343.66	0.171	0.425	0.451	0.317	1.6359	1.0222	0.9365	331.71	0.544	0.381	0.770	0.207	1.2699	1.2512	0.8735
342.84	0.173	0.494	0.463	0.358	1.6988	1.0271	0.9137	334.55	0.551	0.091	0.774	0.063	1.1513	1.4014	1.1214
341.79	0.175	0.605	0.470	0.420	1.7653	1.0317	0.8785	332.43	0.575	0.242	0.772	0.155	1.1774	1.4300	1.0766
343.92	0.180	0.353	0.456	0.268	1.5646	1.0308	0.9522	332.79	0.585	0.177	0.789	0.115	1.1705	1.4293	1.0678
341.01	0.182	0.653	0.477	0.444	1.7670	1.0422	0.8729	332.90	0.588	0.161	0.790	0.107	1.1614	1.4490	1.0867
343.94	0.187	0.320	0.460	0.244	1.5126	1.0368	0.9663	333.58	0.591	0.101	0.792	0.071	1.1334	1.4776	1.1449
340.39	0.193	0.655	0.497	0.433	1.7619	1.0417	0.8601	332.98	0.595	0.138	0.799	0.092	1.1562	1.4551	1.0809
344.67	0.195	0.166	0.467	0.129	1.4472	1.0243	0.9857	333.24	0.609	0.089	0.806	0.062	1.1308	1.4932	1.1464
341.33	0.195	0.541	0.497	0.372	1.6925	1.0395	0.9015	333.00	0.615	0.103	0.806	0.071	1.1292	1.5067	1.1460
343.92	0.196	0.417	0.439	0.324	1.3846	1.0544	0.9847	331.57	0.647	0.176	0.812	0.118	1.1298	1.5549	1.1236
342.47	0.197	0.456	0.482	0.330	1.5726	1.0429	0.9326	330.63	0.650	0.270	0.798	0.173	1.1394	1.5561	1.0694
339.49	0.200	0.712	0.506	0.456	1.7816	1.0473	0.8436	331.06	0.662	0.198	0.816	0.131	1.1298	1.5661	1.1034
340.84	0.201	0.573	0.503	0.388	1.6935	1.0463	0.8900	331.42	0.669	0.154	0.821	0.106	1.1123	1.6085	1.1667
342.55	0.203	0.389	0.492	0.283	1.5557	1.0451	0.9441	331.25	0.700	0.117	0.839	0.084	1.0919	1.6847	1.2056
342.54	0.206	0.356	0.498	0.259	1.5529	1.0461	0.9473	330.43	0.703	0.189	0.829	0.129	1.1029	1.6653	1.1590
340.99	0.212	0.502	0.516	0.342	1.6384	1.0471	0.9085	331.19	0.709	0.104	0.845	0.075	1.0868	1.7093	1.2331
338.99	0.213	0.707	0.521	0.445	1.7515	1.0521	0.8432	329.95	0.747	0.162	0.845	0.119	1.0744	1.8469	1.1763
344.60	0.215	0.081	0.486	0.063	1.3652	1.0177	1.0036	330.62	0.773	0.064	0.876	0.051	1.0531	1.9223	1.3259
339.96	0.216	0.587	0.521	0.388	1.6782	1.0587	0.8842	329.35	0.809	0.116	0.878	0.090	1.0506	1.9915	1.3384
343.63	0.217	0.181	0.498	0.138	1.4280	1.0491	0.9850	329.71	0.825	0.069	0.895	0.057	1.0375	2.0993	1.4010
339.40	0.222	0.622	0.530	0.401	1.6894	1.0576	0.8688	328.74	0.882	0.073	0.922	0.059	1.0326	2.1278	1.3607

Table 5. Isobaric Vapor−Liquid Equilibrium Data, Temperature, T, Liquid Phase, x_i, and Vapor Phase, y_i, Mole Fractions, and Activity Coefficient, γ_i, for Ethanol (1) + 2-Methyl-2-propanol (2) + Octane (3) at 101.3 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
356.33	0.041	0.831	0.059	0.874	1.1820	1.0190	0.5034	353.89	0.257	0.099	0.669	0.128	2.3655	1.3800	0.3350
356.43	0.049	0.800	0.073	0.854	1.2231	1.0283	0.4698	354.76	0.259	0.499	0.360	0.494	1.2218	1.0200	0.6181
356.53	0.058	0.766	0.090	0.830	1.2712	1.0400	0.4379	354.75	0.270	0.319	0.472	0.346	1.5366	1.1183	0.4553
356.74	0.063	0.645	0.103	0.747	1.3327	1.1040	0.4868	354.50	0.274	0.598	0.329	0.567	1.0657	0.9872	0.8385
356.87	0.071	0.608	0.119	0.724	1.3623	1.1282	0.4632	354.49	0.276	0.564	0.345	0.537	1.1075	0.9912	0.7685
356.16	0.071	0.716	0.101	0.773	1.1831	1.0527	0.5735	354.58	0.282	0.303	0.494	0.325	1.5494	1.1127	0.4517
358.88	0.072	0.356	0.204	0.581	2.1130	1.4305	0.3292	354.32	0.285	0.222	0.561	0.250	1.7580	1.1783	0.4030
355.60	0.073	0.805	0.091	0.820	1.0571	1.0144	0.7259	353.16	0.285	0.066	0.719	0.081	2.3589	1.3569	0.3372
359.04	0.079	0.311	0.241	0.539	2.2780	1.5083	0.3141	354.47	0.295	0.431	0.421	0.423	1.2687	1.0231	0.5900
356.26	0.081	0.679	0.119	0.746	1.2190	1.0659	0.5465	354.12	0.311	0.286	0.529	0.293	1.5320	1.0805	0.4664
355.62	0.082	0.784	0.103	0.802	1.0730	1.0178	0.7044	354.24	0.314	0.507	0.397	0.476	1.1337	0.9868	0.7442
355.36	0.082	0.866	0.093	0.860	0.9787	0.9993	0.8861	353.93	0.314	0.212	0.583	0.228	1.6814	1.1437	0.4247
359.03	0.082	0.306	0.245	0.531	2.2211	1.5145	0.3196	352.83	0.317	0.071	0.722	0.082	2.1550	1.2729	0.3575
357.41	0.083	0.505	0.163	0.654	1.5574	1.2030	0.4113	352.89	0.339	0.096	0.705	0.104	1.9658	1.2012	0.3744
355.98	0.085	0.716	0.117	0.761	1.1533	1.0429	0.5999	354.04	0.343	0.424	0.458	0.396	1.2061	0.9900	0.6634
357.01	0.085	0.581	0.139	0.693	1.3127	1.1254	0.4724	353.33	0.355	0.192	0.624	0.192	1.6315	1.0872	0.4434
355.34	0.087	0.856	0.101	0.849	1.0000	0.9979	0.8795	353.95	0.357	0.446	0.452	0.412	1.1461	0.9829	0.7338
357.13	0.088	0.524	0.165	0.660	1.5107	1.1814	0.4224	353.85	0.359	0.363	0.501	0.341	1.2699	1.0012	0.6094
359.15	0.088	0.251	0.305	0.467	2.5708	1.6159	0.2991	353.56	0.374	0.272	0.566	0.261	1.3921	1.0366	0.5283
356.63	0.089	0.599	0.147	0.695	1.3443	1.1092	0.4846	353.88	0.375	0.504	0.436	0.458	1.0571	0.9689	0.9329
359.03	0.090	0.254	0.299	0.469	2.4878	1.6117	0.3071	353.63	0.385	0.355	0.521	0.325	1.2399	0.9852	0.6415
355.86	0.092	0.716	0.125	0.755	1.1435	1.0397	0.6152	353.77	0.404	0.505	0.456	0.454	1.0309	0.9617	1.0607
355.64	0.092	0.758	0.117	0.780	1.0770	1.0232	0.6840	353.31	0.406	0.284	0.574	0.260	1.3122	0.9984	0.5857
356.35	0.093	0.637	0.141	0.714	1.2497	1.0849	0.5177	352.10	0.409	0.084	0.735	0.080	1.7517	1.0812	0.4190
357.53	0.094	0.450	0.202	0.605	1.6898	1.2417	0.3914	353.55	0.420	0.445	0.489	0.395	1.0726	0.9585	0.9255
357.68	0.096	0.433	0.208	0.596	1.7074	1.2634	0.3814	352.72	0.426	0.176	0.659	0.162	1.4730	1.0292	0.5007
356.04	0.096	0.679	0.138	0.731	1.1923	1.0549	0.5705	353.11	0.434	0.280	0.588	0.250	1.2699	0.9820	0.6214
355.31	0.099	0.838	0.112	0.833	0.9742	1.0017	0.8700	353.40	0.434	0.401	0.518	0.353	1.1062	0.9549	0.8509
358.88	0.099	0.193	0.381	0.383	2.8774	1.7367	0.2924	353.51	0.445	0.458	0.502	0.402	1.0389	0.9500	1.0761
357.24	0.103	0.482	0.195	0.622	1.5157	1.2039	0.4124	353.48	0.445	0.455	0.502	0.401	1.0394	0.9536	1.0642
356.77	0.103	0.543	0.181	0.651	1.4293	1.1408	0.4521	352.91	0.448	0.263	0.605	0.231	1.2755	0.9728	0.6276
356.45	0.105	0.591	0.169	0.676	1.3263	1.1005	0.4920	352.60	0.457	0.199	0.653	0.175	1.3645	0.9857	0.5631
355.91	0.106	0.674	0.150	0.720	1.1877	1.0503	0.5840	351.72	0.457	0.070	0.753	0.063	1.6295	1.0491	0.4526
357.33	0.108	0.423	0.230	0.579	1.6972	1.2748	0.3776	353.16	0.468	0.382	0.545	0.330	1.0869	0.9487	0.9166
356.09	0.110	0.636	0.163	0.696	1.2359	1.0687	0.5420	353.72	0.472	0.486	0.510	0.437	0.9879	0.9633	1.3740
357.65	0.112	0.355	0.275	0.518	1.9284	1.3403	0.3576	352.94	0.476	0.320	0.582	0.273	1.1517	0.9457	0.7858
357.81	0.116	0.354	0.272	0.521	1.8377	1.3455	0.3556	351.56	0.483	0.069	0.758	0.060	1.5600	1.0158	0.4766
356.86	0.119	0.480	0.226	0.595	1.5462	1.1767	0.4211	352.95	0.484	0.334	0.578	0.284	1.1255	0.9417	0.8379
357.53	0.130	0.256	0.372	0.408	2.2666	1.4743	0.3304	353.17	0.490	0.403	0.549	0.346	1.0461	0.9411	1.0838
356.18	0.136	0.530	0.225	0.611	1.3824	1.1210	0.4778	353.15	0.491	0.400	0.550	0.343	1.0488	0.9425	1.0663
357.16	0.140	0.298	0.357	0.436	2.0413	1.3725	0.3445	351.54	0.498	0.075	0.756	0.064	1.5116	0.9989	0.4949
356.15	0.146	0.499	0.251	0.580	1.4280	1.1341	0.4638	352.16	0.504	0.174	0.685	0.146	1.3209	0.9558	0.6013
355.58	0.149	0.630	0.208	0.658	1.1864	1.0408	0.6042	352.73	0.515	0.320	0.600	0.267	1.1075	0.9298	0.9024
356.08	0.160	0.460	0.283	0.543	1.4799	1.1523	0.4472	353.44	0.516	0.439	0.557	0.384	0.9993	0.9489	1.4026
356.63	0.163	0.197	0.478	0.308	2.3994	1.4911	0.3208	352.33	0.534	0.238	0.652	0.195	1.1787	0.9271	0.7651
355.05	0.164	0.758	0.189	0.743	0.9995	0.9975	0.8924	352.42	0.537	0.261	0.640	0.214	1.1464	0.9247	0.8202
356.53	0.166	0.258	0.425	0.369	2.0978	1.3719	0.3438	351.39	0.538	0.080	0.758	0.065	1.4113	0.9616	0.5460
355.53	0.171	0.582	0.245	0.612	1.2213	1.0512	0.5769	352.71	0.545	0.337	0.606	0.279	1.0578	0.9270	1.0816
356.02	0.171	0.424	0.316	0.505	1.5437	1.1672	0.4318	352.20	0.563	0.239	0.661	0.193	1.1400	0.9176	0.8443
356.33	0.172	0.315	0.386	0.416	1.8506	1.2788	0.3736	353.14	0.563	0.387	0.599	0.335	0.9961	0.9489	1.4579
354.97	0.184	0.729	0.213	0.712	1.0049	0.9975	0.8863	351.18	0.568	0.075	0.767	0.059	1.3651	0.9339	0.5794
355.90	0.186	0.381	0.354	0.461	1.6038	1.1911	0.4198	352.38	0.578	0.288	0.643	0.233	1.0718	0.9177	1.0439
356.01	0.188	0.322	0.398	0.409	1.7681	1.2441	0.3874	351.59	0.600	0.150	0.724	0.116	1.2006	0.9045	0.7472
356.01	0.190	0.321	0.402	0.405	1.7752	1.2359	0.3867	351.47	0.628	0.152	0.730	0.116	1.1603	0.8940	0.8261
355.45	0.190	0.533	0.284	0.564	1.2755	1.0590	0.5518	352.30	0.637	0.281	0.678	0.225	1.0281	0.9105	1.3485
355.60	0.192	0.153	0.561	0.228	2.4774	1.4810	0.3213	351.82	0.638	0.214	0.701	0.166	1.0831	0.8959	1.0434
355.66	0.201	0.209	0.511	0.286	2.1555	1.3608	0.3414	351.72	0.659	0.208	0.712	0.159	1.0696	0.8892	1.1231
354.89	0.202	0.701	0.237	0.681	1.0238	0.9945	0.8721	352.42	0.687	0.270	0.716	0.219	1.0036	0.9170	1.6851
354.86	0.204	0.747	0.230	0.721	0.9857	0.9900	1.0211	351.21	0.695	0.143	0.754	0.104	1.0952	0.8686	1.0340
354.60	0.213	0.088	0.657	0.132	2.7243	1.5434	0.3135	350.66	0.696	0.061	0.795	0.044	1.1774	0.8661	0.8090
355.35	0.216	0.459	0.344	0.491	1.3675	1.0750	0.5108	351.75	0.700	0.210	0.733	0.160	1.0356	0.8856	1.3715
355.37	0.218	0.224	0.508	0.291	1.9989	1.3038	0.3619	351.71	0.718	0.202	0.745	0.154	1.0277	0.8868	1.4624
355.33	0.222	0.223	0.514	0.287	1.9923	1.2956	0.3610	352.35	0.722	0.244	0.749	0.197	1.0003	0.9152	1.8357
355.75	0.222	0.355	0.393	0.420	1.4953	1.1703	0.4391	351.08	0.722	0.132	0.768	0.095	1.0785	0.8647	1.1174
354.78	0.223	0.671	0.263	0.647	1.0359	0.9924	0.8648	351.92	0.748	0.204	0.769	0.158	1.0080	0.8964	1.7572
354.76	0.228	0.717	0.255	0.691	0.9808	0.9914	1.0273	351.13	0.764	0.137	0.784	0.100	1.0384	0.8695	1.4019
354.94	0.231	0.551	0.313	0.550	1.1805	1.0203	0.6429	351.11	0.783	0.130	0.796	0.094	1.0309	0.8643	1.4941
354.12	0.235	0.088	0.672	0.123	2.5702	1.4676	0.3211	351.85	0.786	0.178	0.801	0.138	1.0028	0.8988	1.9321
354.67	0.246	0.613	0.300	0.591	1.0767	0.9965	0.7926	351.31	0.818	0.129	0.822	0.096	1.0108	0.8756	1.8258
354.66	0.248	0.636	0.295	0.609	1.0515	0.9900	0.8490	351.35	0.845	0.115	0.846	0.086	1.0041	0.8821	2.0253
355.00	0.251	0.317	0.460	0.357	1.5968	1.1476	0.4310	350.38	0.857	0.047	0.848	0.032	1.0326	0.8378	1.5300
354.66	0.253	0.687	0.284	0.656	0.9910	0.9874	1.0243	350.76	0.911	0.045	0.891	0.032	1.0049	0.8651	2.1113

ternary system are shown in Figures 3 and 4, respectively. The experimental VLE data for the system of ethanol (1) + 2-methyl-2-propanol (2) + octane (3) at 101.3 kPa are reported in Table 5 and are shown graphically in Figures

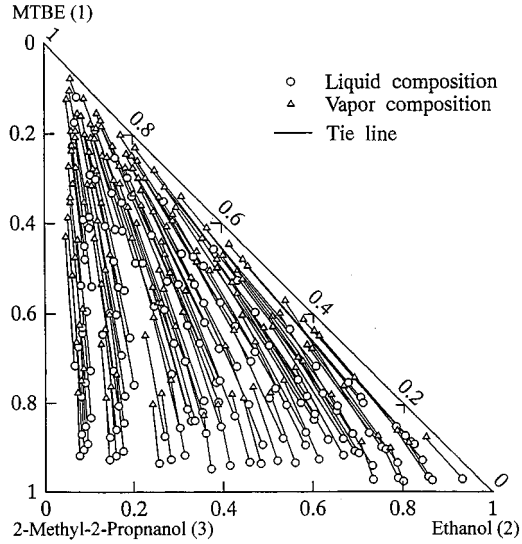

Figure 3. Tie lines for the ternary system MTBE (1) + ethanol (2) + 2-methyl-2-propanol (3) at 101.3 kPa: ○, liquid composition; △, vapor composition.

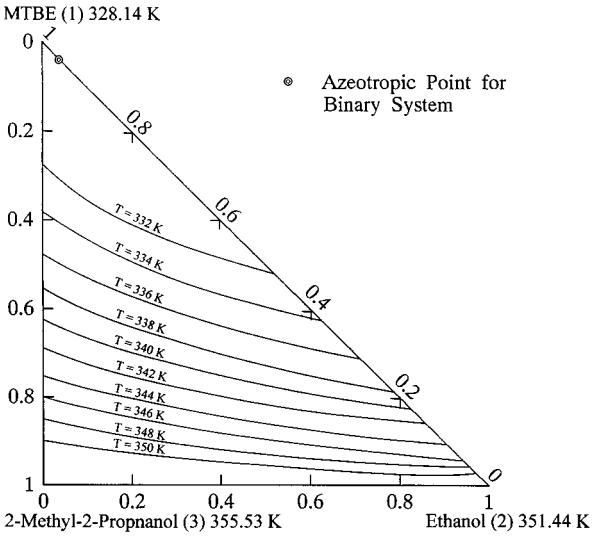

Figure 4. Isotherms for the ternary system MTBE (1) + ethanol (2) + 2-methyl-2-propanol (3) at 101.3 kPa.

Table 6. Parameters of the NRTL Equation for the Binary Systems

system	$g_{ij} - g_{ii}$ J·mol^{-1}	$g_{ij} - g_{jj}$ J·mol^{-1}	α_{ij}
MTBE (1) + ethanol (2)	791.988	2501.984	0.47
ethanol (1) + 2-methyl-2-propanol (2)	3108.461	−2282.054	0.47
MTBE (1) + 2-methyl-2-propanol (2)	−793.364	2825.310	0.47
2-methyl-2-propanol (1) + octane (2)	2355.785	2188.091	0.47
ethanol (1) + octane (2)	5419.983	5029.721	0.47

5 and 6. Each of these systems forms a nonazeotropic mixture.

Correlation and Prediction

The activity coefficients were correlated with the nonrandom two-liquid (NRTL) equation (eq 9) using the α term as either a fitting parameter or a fixed value. In the case of the systems containing an alcohol with a hydrocarbon or an ether, it was acceptable to correlate using the fixed value of 0.47 as the α term. The parameters in the equation were obtained by using the Marquardt method.[10] The sum of the squares of the relative deviations in the activity coefficients was minimized during optimization of the parameters.

The NRTL parameters, $g_{ij} - g_{ii}$, $g_{ij} - g_{jj}$, and α_{ij} for the five binary systems $i-j$ were determined on the basis of the experimental data. They are shown in Table 6. The calculated results using the NRTL equation are depicted by solid lines in Figures 1 and 2. The average absolute deviations and maximum deviations between the experimental and calculated vapor-phase compositions and temperatures for the constituent five binary systems are shown in Table 7.

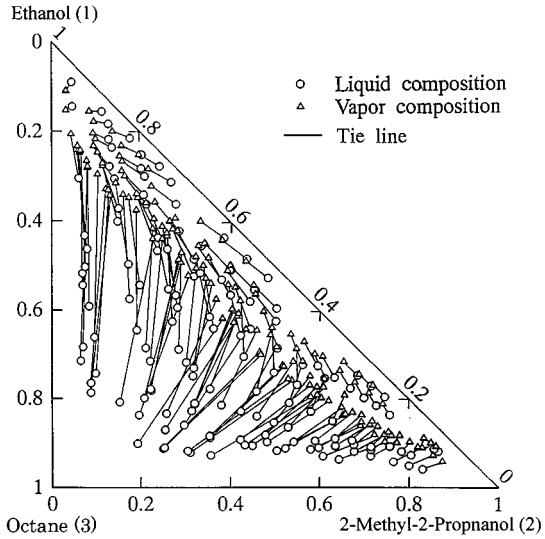

Figure 5. Tie lines for the ternary system ethanol (1) + 2-methyl-2-propanol (2) + octane (3) at 101.3 kPa: ○, liquid composition; △, vapor composition.

The prediction of the ternary VLE was carried out with the NRTL binary parameters in Table 6. For the MTBE (1) + ethanol (2) + 2-methyl-2-propanol (3) system, the average absolute deviations were 0.007 mole fraction in y_1, 0.004 mole fraction in y_2, and 0.27 K in temperature. Average absolute deviations of 0.006 mole fraction in y_1, 0.05 mole fraction in y_2, and 0.18 K in temperature were

Table 7. Deviations between Calculated and Experimental Vapor Mole Fractions, Δy_i, and Temperatures, ΔT, of the NRTL Equation for the Binary Systems

	deviation							
	average				maximum			
system	Δy_i	ΔT/K	$\Delta\gamma_1$	$\Delta\gamma_2$	Δy_i	ΔT/K	$\Delta\gamma_1$	$\Delta\gamma_2$
MTBE (1) + ethanol (2)[a]	0.006	0.13	0.0130	0.0365	0.023	0.46	0.0483	0.0645
ethanol (1) + 2-methyl-2-propanol (2)	0.001	0.02	0.0044	0.0022	0.002	0.05	0.0184	0.0044
MTBE (1) + 2-methyl-2-propanol (2)[b]	0.003	0.12	0.0279	0.0289	0.007	0.46	0.1066	0.0971
2-methyl-2-propanol (1) + octane (2)[b]	0.006	0.12	0.0122	0.1118	0.014	0.35	0.0467	0.2845
ethanol (1) + octane (2)[c]	0.006	0.07	0.0244	0.0512	0.014	0.31	0.0640	0.0885

[a] Reference 1. [b] Reference 2. [c] Reference 4.

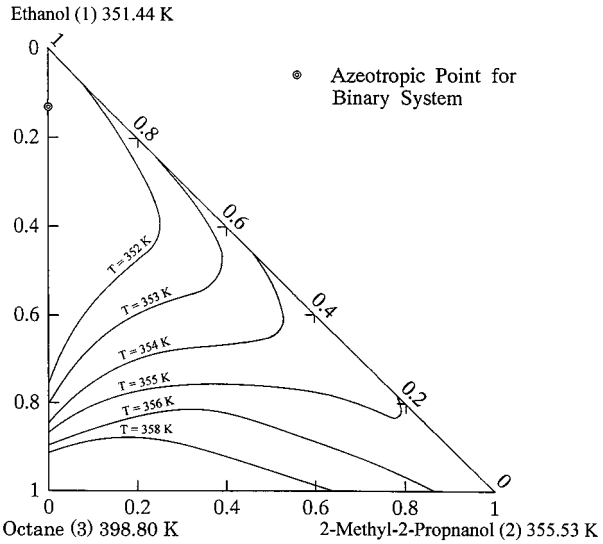

Figure 6. Isotherms for the ternary system ethanol (1) + 2-methyl-2-propanol (2) + octane (3) at 101.3 kPa.

determined for the ethanol (1) + 2-methyl-2-propanol (2) + octane (3) system.

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