Isobaric Vapor−Liquid Equilibria for 2-Methoxy-2-methylpropane + Ethanol + Octane and Constituent Binary Systems at 101.3 kPa

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Isobaric vapor−liquid equilibria for 2-methoxy-2-methylpropane (MTBE) + ethanol + octane and for the constituent binary systems MTBE + ethanol and MTBE + octane were measured at 101.3 kPa. The measurements were made in an equilibrium still with circulation of both the vapor and liquid phases. The ternary system of MTBE + ethanol + octane forms a nonazeotrope. The binary system of MTBE (1) + ethanol (2) forms a minimum boiling azeotrope. The azeotropic data are x_1(AZ) = 0.955 mole fraction and T(AZ) = 327.94 K. The experimental data of binary systems were correlated with the nonrandom two-liquid (NRTL) equations. The NRTL equation yielded a good prediction of activity coefficients for the ternary system from the parameters of correlated binary systems.

Introduction

Ethers and alcohols used as gasoline additives have excellent antiknock properties and are environmentally acceptable substances. Gasoline blended with about 7−15% 2-methoxy-2-methyl propane (MTBE) has been used for high-performance premium gasoline. On the other hand, recommendations for gasoline additives include not only pure MTBE but also mixtures with alcohols for high-octane gasoline. In this research, isobaric vapor−liquid equilibrium (VLE) data for the ternary system MTBE + ethanol + octane and for the constituent binary systems MTBE + ethanol and MTBE + octane were measured at 101.3 kPa. The measurements were made in an equilibrium still (Hiaki et al., 1992) with circulation of both the vapor and liquid phases. For MTBE + ethanol, one set of isobaric VLE at 101.3 kPa is reported by Arce et al. (1996). VLE for the system MTBE + octane at 94 kPa has been measured by Wisniak et al. (1997). Another constituent binary system of ethanol + octane was reported in our previous study (Hiaki et al., 1994). No VLE data have been reported previously for MTBE + ethanol + octane.

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]	1.36641	1.3663[b]
ethanol	351.44	351.45	351.443[c]	1.35937	1.35941[c]
octane	398.80	398.82	398.823[c]	1.39515	1.39565[c]

[a] Calculated value using the Antoine constants with Table 2. [b] Arce et al. (1996). [c] Riddick et al. (1986).

Table 2. Antoine Constants of the Components[a]

material	A	B	C	lit.
MTBE	6.120 19	1190.420	−39.040	*b*
ethanol	7.242 22	1595.811	−46.702	*c*
octane	6.043 94	1351.938	−64.030	*c*

[a] $\log(P/\text{kPa}) = A - B/[(T/\text{K}) + C]$. [b] Tsuji et al. (1998). [c] Boublik et al. (1984).

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 MTBE (1) + Ethanol (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
351.44	0.0000	0.0000		
345.39	0.0752	0.2673	2.0935	1.0116
340.75	0.1558	0.4363	1.8926	1.0346
338.26	0.2145	0.5204	1.7749	1.0560
337.31	0.2437	0.5516	1.7049	1.0690
336.01	0.2837	0.5875	1.6167	1.0943
333.94	0.3699	0.6498	1.4695	1.1616
332.79	0.4299	0.6879	1.3880	1.2044
331.79	0.4967	0.7200	1.2983	1.2809
330.76	0.6051	0.7537	1.1503	1.5007
329.42	0.7011	0.8075	1.1102	1.6469
329.20	0.7250	0.8186	1.0953	1.7020
328.91	0.7620	0.8339	1.0718	1.8248
328.84	0.7739	0.8409	1.0662	1.8450
328.57	0.8117	0.8584	1.0518	2.0074
328.38	0.8385	0.8745	1.0415	2.0875
328.15	0.8875	0.9034	1.0194	2.3207
328.00	0.9262	0.9317	1.0147	2.5221
327.99	0.9341	0.9374	1.0110	2.5879
327.95	0.9535	0.9537	1.0123	2.7291
327.95	0.9695	0.9683	1.0215	2.8780
328.14	1.0000	1.0000		

Experimental Section

Materials. Ethanol and octane, supplied by the Wako Pure Chemical Co. Ltd., and MTBE, by the Merck-Dr. Th. Schuchardt & Co., were special grade reagents. Ethanol was used after their minute water content was removed with molecular sieves 3A. Gas-chromatographic analysis on all three materials indicated that each had a purity of at least 99.9 mol %. The measured physical properties of compounds are listed in Table 1 along with the literature data. Refractive index values were determined with a digital refractometer, using the critical angle of total

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Table 4. 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 MTBE (1) + Octane (3) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
398.80	0.0000	0.0000		
380.19	0.1088	0.4690	1.0092	1.0189
377.93	0.1259	0.5156	1.0163	1.0219
370.27	0.1838	0.6398	1.0322	1.0344
363.08	0.2587	0.7401	1.0310	1.0611
359.52	0.2924	0.7804	1.0555	1.0640
356.39	0.3322	0.8113	1.0506	1.0844
353.19	0.3749	0.8412	1.0468	1.0889
349.16	0.4404	0.8756	1.0482	1.1193
345.14	0.5153	0.9046	1.0389	1.1581
342.47	0.5673	0.9206	1.0393	1.2013
340.41	0.6114	0.9346	1.0405	1.1961
338.94	0.6441	0.9423	1.0420	1.2243
336.02	0.7223	0.9582	1.0339	1.2824
333.72	0.7881	0.9710	1.0363	1.2919
332.08	0.8377	0.9777	1.0161	1.3673
329.88	0.9114	0.9894	1.0235	1.3236
329.01	0.9467	0.9938	1.0184	1.3329
328.14	1.0000	1.0000		

Table 5. Results of the Consistency Tests for the VLE of MTBE (1) + Ethanol (2) and MTBE (1) + Octane (3) at 101.3 kPa

test	criterion of consistency (character: +)	MTBE + ethanol	MTBE + octane
point test[a]	$\Delta y < 0.01$	0.0034	0.0028
area test[b,c]	$(D - J) < 10\%$	−7.02	

[a] Van Ness, et al. (1973). [b] Herington (1951). [c] Redlich and Kister (1948).

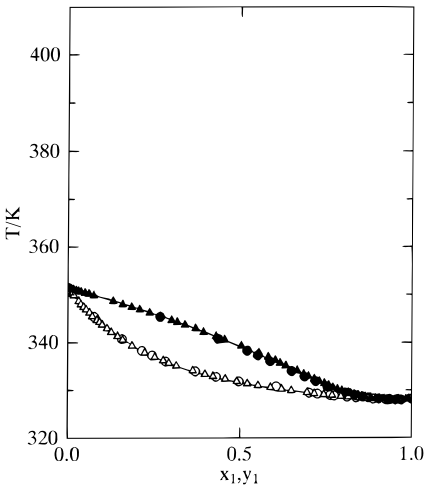

Figure 1. Temperature−composition diagram for MTBE (1) + ethanol (2) at 101.3 kPa: (present work) (○) x_1, (●) y_1; (Arce et al. at 101.32 kPa (1996)) (△) x_1, (▲) y_1, (−) NRTL equation with parameters from Table 7.

reflection method (Kyoto Electric RA-510, Japan). The refractive index was measured with an accuracy of ±0.00005.

Procedure. An equilibrium still (Hiaki et al., 1992) with a provision for both vapor and liquid recirculation was used for the measurements. The still has a total capacity of about 100 cm^3. The pressure, P, in the still was measured by means of a Fortin type mercury barometer. Since the barometric pressure changed slightly, the experimental temperatures were corrected to 101.3 kPa with the following equation

$$T = T_a + \frac{1}{\sum_{i=1}^{n} \frac{B_i x_i}{(T_a + C_i)^2}} \cdot \frac{101.3 - H_0}{H_0} \qquad (1)$$

where T_a is the experimental temperature at the measured atmospheric pressure obtained with a mercury barometer, B_i and C_i are the Antoine constants of component i, x_i is the mole fraction in liquid phase, and H_0 is the measured atmospheric pressure.

The equilibrium temperature T was measured with a calibrated platinum resistance thermometer (Pt, 100 Ω) with an accuracy of 0.03 K. A standard resistance thermometer (Chino Co. model R 800-2, Japan), which is based on ITS-90, was used for this calibration.

Analysis. The equilibrium composition of the samples was determined using a gas chromatograph (GL Sciences model GC-380, Japan) equipped with a flame ionization detector and autosampler. The column packing was BX-10 (supplied by GL Sciences Inc.). The relationship between peak area and composition was determined from the

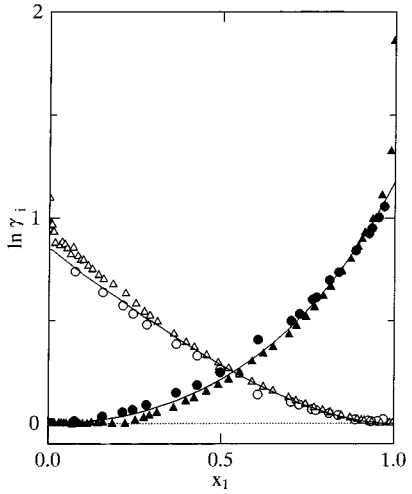

Figure 2. Activity coefficient−liquid composition diagram for MTBE (1) + ethanol (2) at 101.3 kPa: (present work) (○) ln γ_1, (●) ln γ_2; (Arce et al. at 101.32 kPa (1996)) (△) ln γ_1, (▲) ln γ_2, (−) NRTL equation with parameters from Table 7.

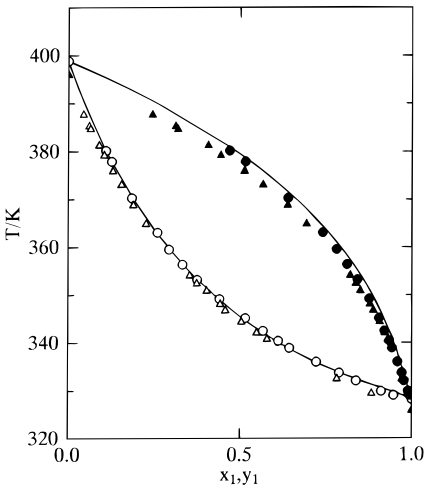

Figure 3. Temperature−composition diagram for MTBE (1) + octane (3) at 101.3 kPa: (present work) (○) x_1, (●) y_1; (Wisniak et al. at 94 kPa (1997)) (△) x_1, (▲) y_1, (−) NRTL equation with parameters from Table 7.

Table 6. Isobaric Vapor−Liquid Equilibrium Data, Temperature T, Liquid Phase x_i, and Vapor Phase y_i, Mole Fractions, and Activity Coefficient γ_i for the MTBE (1) + Ethanol (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
347.81	0.0389	0.9191	0.1385	0.7999	1.9350	0.9955	7.7178	339.74	0.2819	0.5514	0.5002	0.4426	1.2248	1.2864	2.4924
348.49	0.0424	0.6782	0.0975	0.7556	1.2236	1.2372	2.6878	342.07	0.2840	0.3699	0.4583	0.4556	1.0358	1.7828	1.6376
348.16	0.0455	0.7183	0.1089	0.7520	1.2828	1.1776	3.0483	344.61	0.2863	0.1763	0.4728	0.4198	0.9834	3.1017	1.1905
350.94	0.0463	0.2666	0.0882	0.7301	0.9451	2.7627	1.2340	337.43	0.2897	0.6533	0.5597	0.4144	1.4309	1.1228	3.6219
347.49	0.0466	0.9056	0.1532	0.7819	1.8004	1.0000	7.2334	339.17	0.2914	0.5609	0.5163	0.4318	1.2419	1.2619	2.6056
347.82	0.0488	0.7567	0.1226	0.7474	1.3618	1.1262	3.5032	338.30	0.3028	0.5810	0.5403	0.4168	1.2874	1.2234	2.8446
347.49	0.0509	0.8957	0.1723	0.7597	1.8542	0.9824	6.7765	345.05	0.3038	0.1378	0.5103	0.3837	0.9901	3.5719	1.1132
350.35	0.0517	0.3066	0.0974	0.7278	0.9525	2.4504	1.2986	338.03	0.3080	0.5855	0.5504	0.4101	1.2960	1.2046	2.8840
349.86	0.0566	0.3425	0.1069	0.7239	0.9677	2.2248	1.3675	340.86	0.3085	0.3982	0.4934	0.4322	1.0644	1.6537	1.7540
348.15	0.0587	0.6076	0.1255	0.7284	1.1406	1.3400	2.2518	343.19	0.3182	0.2006	0.5038	0.4008	0.9841	2.7637	1.2499
347.61	0.0649	0.6618	0.1452	0.7185	1.2146	1.2434	2.6267	336.96	0.3197	0.6097	0.5768	0.3951	1.3589	1.1733	3.2409
346.75	0.0718	0.7217	0.1709	0.7066	1.3346	1.1710	3.2567	336.40	0.3284	0.6154	0.5954	0.3824	1.3855	1.1498	3.3035
347.77	0.0727	0.5811	0.1486	0.7090	1.1114	1.3987	2.1700	336.28	0.3343	0.6134	0.5954	0.3834	1.3638	1.1609	3.3909
345.64	0.0758	0.8787	0.2364	0.7104	1.8047	1.0104	6.6870	336.41	0.3371	0.5975	0.5924	0.3825	1.3427	1.1840	3.1973
346.20	0.0773	0.7628	0.1940	0.6967	1.4325	1.1185	3.8352	342.00	0.3579	0.1986	0.5490	0.3678	0.9919	2.7032	1.2460
347.29	0.0780	0.6216	0.1654	0.6998	1.1708	1.3162	2.4082	337.86	0.3655	0.4618	0.5769	0.3762	1.1569	1.4194	2.1360
348.14	0.0810	0.4972	0.1481	0.7020	0.9880	1.6000	1.8522	345.64	0.3757	0.0681	0.6499	0.2468	0.9984	4.5178	1.0598
346.78	0.0850	0.6629	0.1876	0.6873	1.2362	1.2374	2.7169	336.37	0.3777	0.5199	0.6086	0.3600	1.2324	1.2828	2.5600
345.02	0.0899	0.8593	0.2624	0.6825	1.7222	1.0206	6.3738	338.84	0.3834	0.3600	0.5706	0.3708	1.0510	1.7076	1.7098
348.62	0.0924	0.3465	0.1712	0.6756	0.9862	2.1640	1.3957	335.33	0.3877	0.5475	0.6345	0.3440	1.2937	1.2189	2.8882
347.06	0.0927	0.5675	0.1899	0.6778	1.1431	1.4158	2.1179	340.65	0.3905	0.2167	0.5780	0.3488	0.9975	2.4893	1.3086
356.69	0.0938	0.0749	0.2189	0.5626	0.9882	6.0542	0.9903	337.97	0.3919	0.3980	0.5877	0.3613	1.0777	1.5482	1.8706
348.08	0.1010	0.3792	0.1872	0.6645	1.0010	1.9869	1.4887	336.39	0.3920	0.4885	0.6141	0.3522	1.2015	1.3387	2.3569
350.14	0.1051	0.2029	0.1958	0.6362	0.9480	3.2678	1.1683	342.93	0.3924	0.1077	0.6262	0.2869	1.0001	3.7284	1.1083
354.38	0.1060	0.0913	0.2305	0.5706	0.9804	5.5030	1.0158	336.32	0.3940	0.4873	0.6166	0.3499	1.2011	1.3354	2.3663
347.48	0.1120	0.4205	0.2023	0.6564	0.9931	1.8133	1.6135	335.31	0.3997	0.5239	0.6330	0.3431	1.2516	1.2707	2.7214
343.54	0.1174	0.8489	0.3325	0.6318	1.7370	1.0114	6.5605	334.68	0.4033	0.5477	0.6496	0.3346	1.2988	1.2194	2.9013
349.18	0.1194	0.2401	0.2150	0.6272	0.9416	2.8290	1.2293	339.48	0.4086	0.2566	0.5927	0.3428	1.0097	2.1652	1.4133
352.51	0.1196	0.1172	0.2436	0.5720	0.9683	4.6260	1.0623	337.31	0.4142	0.3879	0.6094	0.3449	1.0891	1.5752	1.8460
346.17	0.1339	0.4767	0.2516	0.6227	1.0741	1.6032	1.8160	338.14	0.4147	0.3312	0.6014	0.3447	1.0407	1.7689	1.6272
344.04	0.1372	0.7041	0.3086	0.6031	1.3618	1.1416	3.3867	343.46	0.4156	0.0781	0.6746	0.2365	1.0007	4.1412	1.0944
345.08	0.1421	0.5797	0.2834	0.6074	1.1743	1.3421	2.2995	334.78	0.4197	0.5139	0.6499	0.3301	1.2484	1.2804	2.6958
341.96	0.1474	0.8097	0.3939	0.5701	1.7213	1.0242	5.5671	339.05	0.4293	0.2390	0.6081	0.3303	1.0031	2.2918	1.3915
343.03	0.1479	0.7429	0.3478	0.5828	1.4661	1.0904	4.0277	341.20	0.4335	0.1203	0.6568	0.2701	1.0001	3.3784	1.1192
345.35	0.1484	0.5197	0.2805	0.6044	1.1075	1.4775	2.0172	338.26	0.4388	0.2745	0.6207	0.3242	1.0220	2.0176	1.4844
344.25	0.1536	0.6185	0.3126	0.5893	1.2281	1.2632	2.6059	336.71	0.4486	0.3544	0.6354	0.3220	1.0663	1.6492	1.7684
344.49	0.1613	0.5597	0.3091	0.5859	1.1500	1.3763	2.2621	335.67	0.4494	0.4142	0.6469	0.3202	1.1208	1.4710	2.0653
343.29	0.1644	0.6576	0.3465	0.5687	1.3084	1.1933	2.9949	338.97	0.4671	0.1770	0.6555	0.2831	0.9896	2.6434	1.2894
352.69	0.1744	0.0780	0.3692	0.4598	0.9957	5.5173	0.9924	336.79	0.4700	0.3006	0.6540	0.3024	1.0524	1.8327	1.5600
345.66	0.1784	0.3591	0.3111	0.5680	1.0103	1.9796	1.4986	337.30	0.4785	0.2542	0.6481	0.3015	1.0082	2.1133	1.5159
340.76	0.1821	0.7644	0.4377	0.5250	1.5960	1.0455	4.8319	340.30	0.4861	0.0975	0.7114	0.2215	0.9976	3.5685	1.1489
350.98	0.1916	0.0914	0.3854	0.4572	0.9915	5.0014	1.0150	335.72	0.4920	0.3250	0.6690	0.2942	1.0696	1.7392	1.7374
344.96	0.1919	0.3839	0.3352	0.5520	1.0334	1.8527	1.5672	337.44	0.5084	0.1918	0.6862	0.2635	0.9974	2.4267	1.3357
347.54	0.1964	0.1771	0.3486	0.5135	0.9772	3.3708	1.1754	335.55	0.5145	0.3001	0.6826	0.2812	1.0339	1.7875	1.6758
340.74	0.2067	0.6940	0.4379	0.5092	1.4142	1.1232	3.6975	335.76	0.5186	0.2740	0.6837	0.2779	1.0283	1.9313	1.5847
344.09	0.2074	0.4149	0.3625	0.5338	1.0606	1.7185	1.6751	334.15	0.5291	0.3456	0.7012	0.2731	1.0951	1.6276	1.8950
354.14	0.2095	0.0481	0.4813	0.3471	1.0373	6.3769	0.9504	338.23	0.5398	0.1101	0.7404	0.2050	0.9954	3.1972	1.2090
339.76	0.2143	0.7241	0.4757	0.4879	1.5209	1.0712	4.2566	336.59	0.5401	0.1864	0.7110	0.2446	1.0046	2.4196	1.3482
339.45	0.2210	0.7246	0.4862	0.4817	1.5277	1.0758	4.3279	335.93	0.5485	0.2083	0.7132	0.2467	1.0068	2.2337	1.3986
347.91	0.2252	0.1288	0.4151	0.4612	1.0037	4.0996	1.0083	333.64	0.5565	0.3249	0.7186	0.2582	1.0683	1.6493	1.8208
342.78	0.2310	0.4661	0.4033	0.5069	1.1023	1.5357	1.9066	334.68	0.5568	0.2619	0.7164	0.2517	1.0344	1.9122	1.5753
351.77	0.2370	0.0590	0.5004	0.3462	1.0194	5.6963	0.9793	334.11	0.5643	0.2930	0.7188	0.2544	1.0463	1.7787	1.7256
345.17	0.2394	0.2259	0.4040	0.4816	0.9935	2.7266	1.2510	338.09	0.5678	0.0834	0.7787	0.1681	0.9930	3.4600	1.1830
338.43	0.2475	0.7030	0.5238	0.4493	1.5211	1.0840	4.1602	334.99	0.5842	0.2008	0.7384	0.2274	1.0141	2.2402	1.4134
338.86	0.2500	0.6796	0.5090	0.4554	1.4349	1.1082	3.7785	333.07	0.6065	0.2765	0.7454	0.2328	1.0393	1.7993	1.7813
341.71	0.2501	0.4984	0.4380	0.4838	1.1410	1.4328	2.0858	336.36	0.6204	0.0903	0.8032	0.1554	0.9944	3.2033	1.1985
348.10	0.2537	0.1112	0.4625	0.4074	0.9824	4.1445	1.0647	333.35	0.6312	0.2156	0.7651	0.2108	1.0249	2.0817	1.5023
343.30	0.2581	0.3349	0.4226	0.4800	1.0134	1.9712	1.5010	330.45	0.6327	0.3019	0.7715	0.2174	1.1216	1.7331	1.8239
349.83	0.2630	0.0698	0.5198	0.3401	1.0084	5.1094	1.0165	335.19	0.6675	0.0822	0.8330	0.1314	0.9874	3.1108	1.2414
346.41	0.2766	0.1212	0.4848	0.3957	0.9920	3.9561	1.1031	334.53	0.6724	0.0993	0.8251	0.1437	0.9979	2.9187	1.2343
337.46	0.2807	0.6704	0.5566	0.4198	1.4654	1.1054	3.8443	332.74	0.7291	0.1075	0.8461	0.1322	0.9984	2.6872	1.2946

analysis of samples of known composition. The accuracy of liquid, x_i, and vapor, y_i, mole fractions is estimated to be 0.002 mole fraction.

Experimental Results

The activity coefficients γ_i were calculated using the following equation:

$$Py_i = \gamma_i P_i^S x_i \qquad (2)$$

Essentially, it is better to calculate the activity coefficients including the Poynting factor. However, there is a scarcity of physical properties for the substance of MTBE to calculate them exactly. Thus, the activity coefficients were calculated for the ideal vapor-phase assumption. 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 two binary VLE data for MTBE (1) + ethanol (2) and MTBE (1) + octane (3) are reported in Tables 3 and 4 along with the activity coefficients calculated using eq 2. The MTBE (1) + ethanol (2) forms a

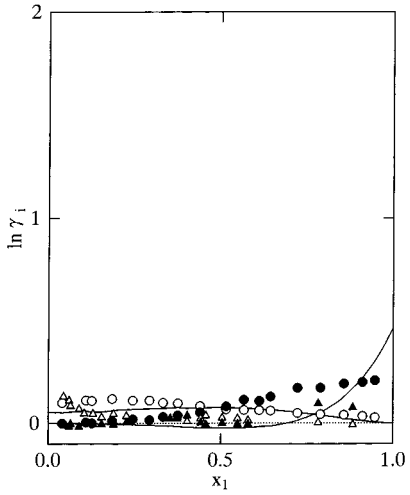

Figure 4. Activity coefficient−liquid composition diagram for MTBE (1) + octane (3) at 101.3 kPa: (present work) (○) ln γ_1, (●) ln γ_2; (Wisniak et al. at 94 kPa (1997)) (△) ln γ_1, (▲) ln γ_2, (−) NRTL equation with parameters from Table 7.

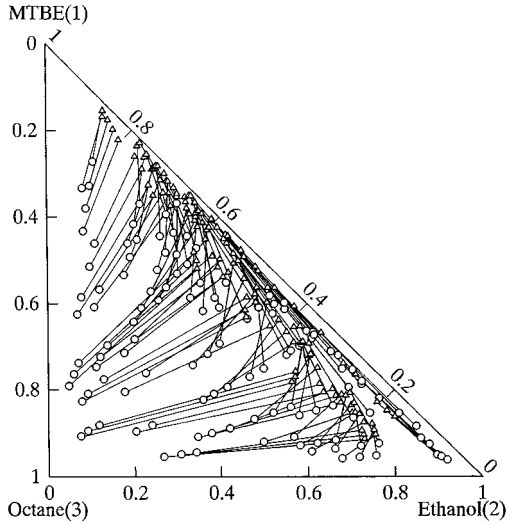

Figure 5. Tie lines for the ternary system MTBE (1) + ethanol (2) + octane (3) at 101.3 kPa: (○) liquid composition; (△) vapor composition.

minimum boiling azeotrope. The azeotropic data are x_1(AZ) = 0.955 mole fraction and T(AZ) = 327.94 K. The system of MTBE (1) + octane (3) does not form an azeotrope. The system of ethanol (2) + octane (3), reported in our previous paper (Hiaki et al., 1994), forms a minimum boiling azeotrope. The experimental VLE for two binary systems are shown in Figures 1−4.

The experimental data were tested for thermodynamic consistency using the point test of Van Ness et al. (1973) and the area test of Herington (1951) and of Redlich and Kister (1948). The results of the consistency tests for the VLE of MTBE (1) + ethanol (2) and MTBE (1) + octane (3) are shown in Table 5. For MTBE (1) + octane (3), which is almost an ideal solution, the area test is not a reliable test for VLE data because of the experimental noise observed in activity coefficients. Thus, Table 5 does not include the area test result of the MTBE (1) + octane (3) system. Those results indicate that the experimental data for three binary systems are thermodynamically consistent.

Ternary System. The experimental VLE data for ternary system MTBE (1) + ethanol (2) + octane (3) at 101.3 kPa are reported in Table 6. The tie lines and isotherms based on the experimental data for the ternary system are shown in Figures 5 and 6. This ternary system does not form an azeotropic mixture.

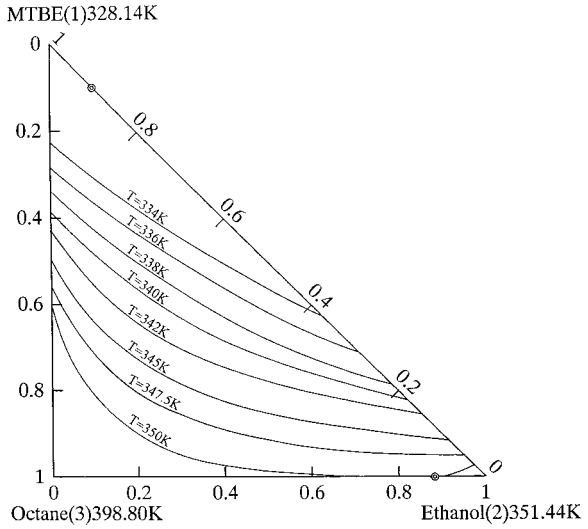

Figure 6. Isotherms for the ternary system MTBE (1) + ethanol (2) + octane (3) at 101.3 kPa.

Table 7. Parameters of the NRTL Equation for the Experimental Three 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	2501.98	0.47
ethanol (2) + octane (3)	5419.98	5029.72	0.47
MTBE (1) + octane (3)	−2196.83	4487.00	0.47

Table 8. Deviations Between Calculated and Experimental Vapor Mole Fractions Δy_i and Temperatures ΔT of the NRTL Equation for Three Binary Systems

		deviation			
		average		maximum	
system	$i-j$	Δy_i	ΔT	$\lvert\Delta y_i\rvert$	$\lvert\Delta T\rvert$
MTBE (i) + ethanol (j)	1−2	0.006	0.13	0.023	0.46
ethanol (i) + octane (j)	2−3	0.006	0.07	0.014	0.31
MTBE (i) + octane (j)	1−3	0.014	0.18	0.020	0.41

Correlation and Prediction

The activity coefficients were correlated with the nonrandom two-liquid (NRTL) equation (Renon and Prausnitz, 1968). The parameters in each of these equations are obtained by using the Marquardt algorithm (Marquardt, 1963). The sum of the squares of relative deviations in activity coefficients was minimized during optimization of the parameters.

The NRTL parameters, $g_{ij} - g_{ii}$, $g_{ij} - g_{jj}$, and a_{ij} of three binary systems $i - j$ determined on the basis of the experimental data, are shown in Table 7. The deviations between the experimental and calculated vapor-phase compositions and temperatures for the three binary systems are shown in Table 8. The calculated results using the NRTL equation are shown by solid lines in Figures 1 and 2.

The prediction of ternary VLE was carried out with the NRTL binary parameters in Table 7. Average absolute deviations were 0.009 mole fraction in y_1, 0.010 mole fraction in y_2, and 0.82 K in temperature.

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