Isothermal Vapor–Liquid Equilibria for Methanol + Ethanol + Water, Methanol + Water, and Ethanol + Water

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Isothermal vapor–liquid equilibria were measured for the ternary system methanol + ethanol + water and its constituent binary systems of methanol + water and ethanol + water at 323.15, 328.15, and 333.15 K. The apparatus that was used made it possible to control the measured temperature and total pressure by computer. The experimental binary data were correlated by the NRTL equation. The ternary system was predicted using the binary NRTL parameters with good accuracy.

Introduction

This paper discusses the vapor–liquid equilibria (VLE) that were measured for the ternary system of methanol + ethanol + water and its constituent binary systems of methanol + water and ethanol + water at 323.15, 328.15, and 333.15 K. For the ternary system, we previously reported the isobaric VLE at 101.3 kPa (Kurihara et al., 1993), and two data sets of isothermal VLE (298.15, 313.15 K) are available in the literature (Hall et al., 1979; Ratcliff and Chao, 1969).

Experimental Section

Apparatus and Procedure. A modified Rogalski–Malanoski equilibrium still (Hiaki et al., 1992) combined with an isothermal VLE measuring apparatus, which was similar to that described in the literature (Hiaki et al., 1994), was used. The apparatus consisted of an equilibrium still for samples, an ebulliometer for a reference substance (water), a Hewlett-Packard Model 3421A acquisition data/control unit, an NEC personal computer, six solenoid valves, three pressure transducers, three surge tanks, cold traps, a refrigerator, and a vacuum pump. An attractive feature of this apparatus is that the temperature in the system can be kept constant accurately using a computer in conjunction with the six solenoid valves and three pressure transducers.

The equilibrium temperature was measured with a calibrated platinum resistance thermometer with an ac-

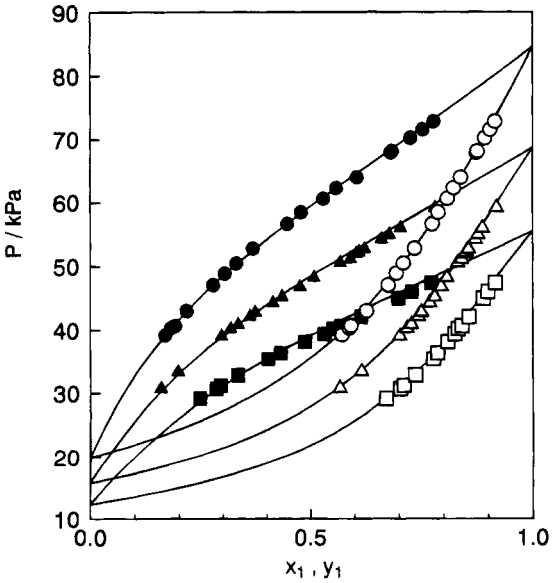

Figure 1. Pressure–composition diagram for methanol (1) + water (2): (■) x_1 and (□) y_1 at 323.15 K; (▲) x_1 and (△) y_1 at 328.15 K; (●) x_1 and (○) y_1 at 333.15 K; (—) NRTL equation.

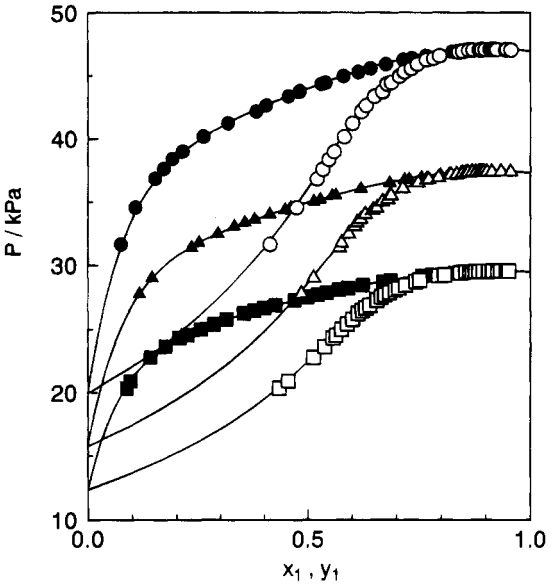

Figure 2. Pressure–composition diagram for ethanol (1) + water (2): (■) x_1 and (□) y_1 at 323.15 K; (▲) x_1 and (△) y_1 at 328.15 K; (●) x_1 and (○) y_1 at 333.15 K; (—) NRTL equation.

Table 1. Densities, ρ, and Normal Boiling Points, T_b, of the Components

component	ρ(298.15 K)/(g cm^{-3}) exptl	ρ(298.15 K)/(g cm^{-3}) lit.[a]	T_b/K exptl	T_b/K lit.[a]
methanol	0.7867	0.786 37	337.69	337.696
ethanol	0.7851	0.784 93	351.48	351.443
water	0.9972	0.997 05	373.15	373.15

[a] Riddick et al., 1986.

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Table 2. Isothermal Vapor–Liquid Equilibrium Data, Vapor Pressure, P, Liquid Phase, x_1, and Vapor Phase, y_1, Mole Fractions, and Activity Coefficients, γ_i, for Methanol (1) + Water (2)

P/kPa	x_1	y_1	γ_1	γ_2	P/kPa	x_1	y_1	γ_1	γ_2	P/kPa	x_1	y_1	γ_1	γ_2
							323.15 K							
29.119	0.2470	0.6710	1.4425	1.0270	36.276	0.4316	0.7873	1.2022	1.0956	42.049	0.6145	0.8569	1.0623	1.2599
30.620	0.2842	0.7029	1.3799	1.0259	38.085	0.4872	0.8100	1.1494	1.1389	44.916	0.6989	0.8890	1.0336	1.3367
31.135	0.2940	0.7109	1.3714	1.0291	39.341	0.5314	0.8254	1.1085	1.1831	45.943	0.7290	0.8991	1.0246	1.3810
32.790	0.3338	0.7373	1.3182	1.0436	40.160	0.5513	0.8326	1.0998	1.2092	47.334	0.7730	0.9160	1.0135	1.4143
35.321	0.4028	0.7772	1.2388	1.0636	40.612	0.5688	0.8410	1.0886	1.2087					
							328.15 K							
30.710	0.1587	0.5660	1.6198	1.0022	44.237	0.4137	0.7693	1.2089	1.1005	52.227	0.6091	0.8502	1.0675	1.2654
33.368	0.1980	0.6154	1.5318	1.0121	45.184	0.4346	0.7799	1.1911	1.1120	52.664	0.6217	0.8557	1.0612	1.2701
39.038	0.2961	0.7019	1.3632	1.0453	46.743	0.4753	0.7947	1.1472	1.1562	54.245	0.6600	0.8709	1.0472	1.3024
40.215	0.3171	0.7182	1.3410	1.0492	48.181	0.5078	0.8079	1.1245	1.1888	54.956	0.6781	0.8770	1.0395	1.3278
40.835	0.3339	0.7280	1.3104	1.0543	50.500	0.5669	0.8315	1.0855	1.2421	55.980	0.7032	0.8866	1.0318	1.3525
42.143	0.3610	0.7432	1.2762	1.0708	51.100	0.5897	0.8401	1.0665	1.2590	59.208	0.7808	0.9183	1.0165	1.3958
42.760	0.3733	0.7504	1.2640	1.0767	51.974	0.6030	0.8495	1.0723	1.2457					
							333.15 K							
39.223	0.1686	0.5714	1.6014	1.0105	50.428	0.3303	0.7101	1.2998	1.0901	63.998	0.6044	0.8383	1.0583	1.3062
40.344	0.1814	0.5867	1.5712	1.0178	52.784	0.3681	0.7345	1.2616	1.1074	67.924	0.6804	0.8733	1.0378	1.3449
40.646	0.1910	0.5914	1.5152	1.0258	56.652	0.4461	0.7742	1.1757	1.1532	68.141	0.6835	0.8751	1.0384	1.3430
42.984	0.2167	0.6268	1.4953	1.0232	58.427	0.4775	0.7877	1.1518	1.1853	70.229	0.7255	0.8922	1.0271	1.3776
47.023	0.2773	0.6751	1.3745	1.0559	60.614	0.5282	0.8085	1.1077	1.2284	71.597	0.7530	0.9039	1.0215	1.3916
48.852	0.3039	0.6943	1.3390	1.0714	62.260	0.5572	0.8216	1.0953	1.2525	72.832	0.7776	0.9141	1.0171	1.4055

Table 3. Isothermal Vapor–Liquid Equilibrium Data, Vapor Pressure, P, Liquid Phase, x_1, and Vapor Phase, y_1, Mole fractions, and Activity Coefficients, γ_i, for Ethanol (1) + Water (2)

P/kPa	x_1	y_1	γ_1	γ_2	P/kPa	x_1	y_1	γ_1	γ_2	P/kPa	x_1	y_1	γ_1	γ_2
							323.15 K							
20.333	0.0874	0.4341	3.4513	1.0187	27.284	0.4691	0.6563	1.2973	1.4273	29.487	0.8454	0.8555	1.0119	2.2319
20.904	0.0967	0.4549	3.3591	1.0192	27.535	0.4987	0.6660	1.2495	1.4825	29.480	0.8559	0.8639	1.0090	2.2551
22.796	0.1411	0.5120	2.8214	1.0463	27.701	0.5218	0.6741	1.2158	1.5257	29.478	0.8638	0.8699	1.0067	2.2808
23.663	0.1756	0.5372	2.4675	1.0731	27.881	0.5421	0.6840	1.1950	1.5551	29.498	0.8713	0.8769	1.0067	2.2856
24.336	0.2065	0.5562	2.2331	1.0995	28.101	0.5692	0.6971	1.1688	1.5971	29.517	0.8801	0.8849	1.0063	2.2957
24.570	0.2253	0.5636	2.0935	1.1181	28.216	0.5907	0.7050	1.1436	1.6439	29.538	0.8911	0.8948	1.0057	2.3121
25.024	0.2552	0.5761	1.9235	1.1505	28.448	0.6242	0.7205	1.1148	1.7106	29.531	0.9031	0.9065	1.0051	2.3094
25.436	0.2856	0.5890	1.7856	1.1822	28.711	0.6697	0.7434	1.0817	1.8037	29.560	0.9136	0.9151	1.0039	2.3544
25.815	0.3133	0.6008	1.6845	1.2124	28.828	0.6868	0.7523	1.0716	1.8439	29.566	0.9263	0.9273	1.0035	2.3644
26.259	0.3535	0.6133	1.5497	1.2689	29.195	0.7586	0.7940	1.0366	2.0159	29.558	0.9344	0.9337	1.0014	2.4221
26.481	0.3773	0.6226	1.4861	1.2967	29.253	0.7811	0.8081	1.0266	2.0754	29.558	0.9480	0.9470	1.0011	2.4432
26.694	0.3999	0.6311	1.4325	1.3258	29.406	0.8299	0.8429	1.0129	2.1990	29.548	0.9528	0.9512	1.0001	2.4777
26.898	0.4258	0.6397	1.3738	1.3637										
							328.15 K							
27.774	0.1161	0.4841	3.1244	1.0261	35.215	0.5273	0.6801	1.2188	1.5091	37.325	0.8436	0.8554	1.0136	2.1901
29.017	0.1445	0.5123	2.7731	1.0470	35.507	0.5541	0.6845	1.1768	1.5908	37.352	0.8502	0.8595	1.0112	2.2235
31.391	0.2338	0.5712	2.0638	1.1119	35.516	0.5626	0.6874	1.1642	1.6073	37.378	0.8616	0.8688	1.0093	2.2493
31.767	0.2506	0.5760	1.9644	1.1375	36.055	0.6194	0.7138	1.1142	1.7173	37.393	0.8714	0.8775	1.0083	2.2614
32.475	0.2938	0.5923	1.7605	1.1866	36.530	0.6841	0.7480	1.0706	1.8465	37.395	0.8798	0.8848	1.0070	2.2757
33.048	0.3306	0.6058	1.6278	1.2318	36.779	0.7174	0.7667	1.0533	1.9244	37.416	0.8854	0.8891	1.0061	2.2992
33.350	0.3551	0.6106	1.5411	1.2745	36.812	0.7276	0.7714	1.0458	1.9581	37.415	0.8925	0.8946	1.0042	2.3297
33.611	0.3777	0.6191	1.4803	1.3022	36.973	0.7558	0.7937	1.0402	1.9804	37.421	0.9002	0.9019	1.0039	2.3363
34.012	0.4123	0.6294	1.3946	1.3576	37.172	0.7979	0.8211	1.0246	2.0872	37.425	0.9131	0.9130	1.0020	2.3803
34.343	0.4470	0.6465	1.3338	1.3898	37.223	0.8165	0.8340	1.0184	2.1363	37.437	0.9342	0.9331	1.0012	2.4189
34.519	0.4598	0.6557	1.3216	1.3929	37.307	0.8334	0.8470	1.0154	2.1741	37.412	0.9566	0.9550	1.0000	2.4662
35.017	0.5127	0.6682	1.2249	1.5096										
							333.15 K							
31.647	0.0742	0.4130	3.7957	1.0037	43.756	0.4808	0.6682	1.3001	1.3988	46.998	0.8538	0.8616	1.0113	2.2317
34.540	0.1071	0.4742	3.2893	1.0172	44.336	0.5298	0.6788	1.2140	1.5151	46.987	0.8646	0.8715	1.0099	2.2372
36.840	0.1511	0.5196	2.7208	1.0425	44.447	0.5390	0.6887	1.2136	1.5017	47.020	0.8823	0.8860	1.0067	2.2855
37.611	0.1705	0.5326	2.5221	1.0597	44.935	0.5800	0.7070	1.1700	1.5687	47.045	0.8873	0.8908	1.0070	2.2878
38.387	0.1899	0.5473	2.3738	1.0726	45.282	0.6141	0.7175	1.1299	1.6590	47.048	0.8966	0.8987	1.0054	2.3137
38.999	0.2133	0.5587	2.1909	1.0939	45.557	0.6417	0.7333	1.1115	1.6975	47.060	0.9091	0.9095	1.0037	2.3524
40.175	0.2606	0.5814	1.9209	1.1373	45.881	0.6764	0.7468	1.0813	1.7974	47.055	0.9154	0.9151	1.0029	2.3712
41.230	0.3168	0.6006	1.6741	1.2052	46.218	0.7156	0.7674	1.0577	1.8931	47.055	0.9206	0.9195	1.0020	2.3957
42.157	0.3813	0.6209	1.4693	1.2918	46.338	0.7347	0.7834	1.0542	1.8951	47.044	0.9255	0.9242	1.0015	2.4039
42.635	0.4036	0.6316	1.4276	1.3170	46.547	0.7656	0.7968	1.0335	2.0218	47.026	0.9458	0.9444	1.0010	2.4238
43.368	0.4548	0.6502	1.3260	1.3917	46.868	0.8246	0.8395	1.0176	2.1504	47.039	0.9479	0.9467	1.0015	2.4180
43.730	0.4794	0.6688	1.3043	1.3917	46.915	0.8353	0.8477	1.0153	2.1756	46.994	0.9583	0.9562	0.9997	2.4807

curacy of ±0.01 K. The pressure in the still was determined by measuring the bubble point of water and referring to the vapor pressure data on water (Bridgeman and Aldrich, 1964). The accuracy was estimated to be ±0.03 kPa.

Analysis. Vapor and liquid samples were analyzed with a Simazu gas chromatograph type GC-8AIT equipped with a thermal conductivity cell. Porapak QS was used as the column packing and helium as the carrier gas. The compositions were determined by the relative area method with an accuracy of ±0.001 mole fraction.

Materials. Methanol and ethanol were special grade pure reagents (Wako Pure Chemical Industry, Ltd.) and were used after removing traces of water with 3A molecular

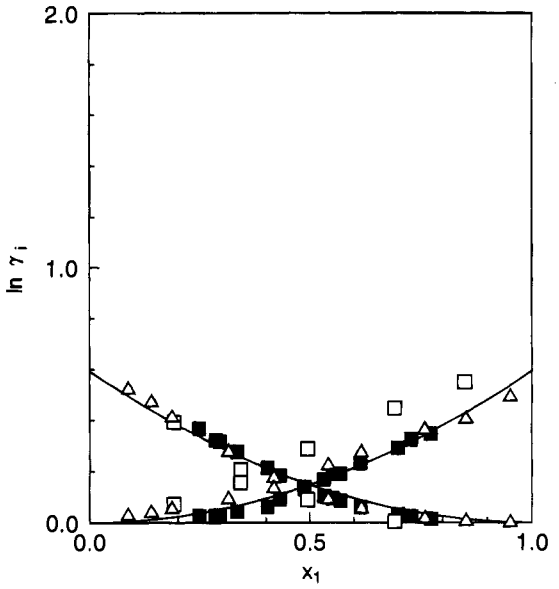

Figure 3. Activity coefficient–liquid composition diagram for methanol (1) + water (2) at 323.15 K: (■) this work; (□) Dulitskaya (1945); (△) McGlashan and Williamson (1976); (—) NRTL equation.

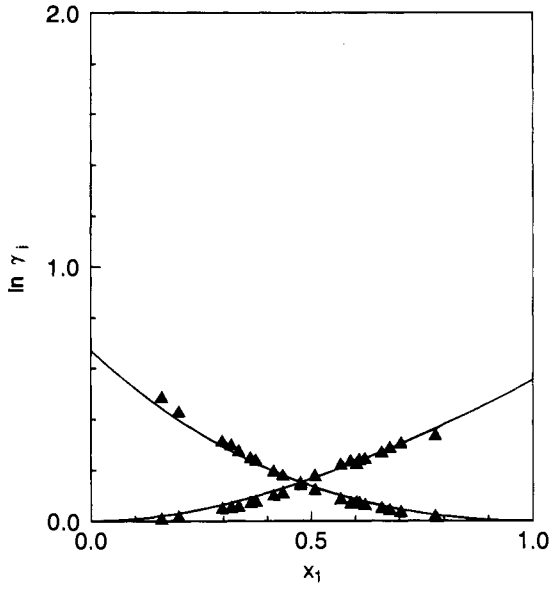

Figure 4. Activity coefficient–liquid composition diagram for methanol (1) + water (2) at 328.15 K: (▲) this work; (—) NRTL equation.

Table 4. Antoine Constants of the Components[a]

component	A	B	C
methanol	7.253 25	1608.512	−31.143
ethanol	7.242 15	1596.044	−46.655
water	7.115 72	1684.123	−43.568

[a] $\log(P/\text{kPa}) = A - B/[(T/\text{K}) + C]$.

sieves. The water was passed through an ion exchanger and distilled. The purity of the materials was checked by gas chromatography and found to be better than 99.9 mol %. In Table 1, some measured properties of the purified reagents are shown with the literature values.

Experimental Results

Binary Systems. The VLE data at 323.15, 328.15, and 333.15 K for the methanol + water and ethanol + water systems are showed in Tables 2 and 3 and Figures 1–8.

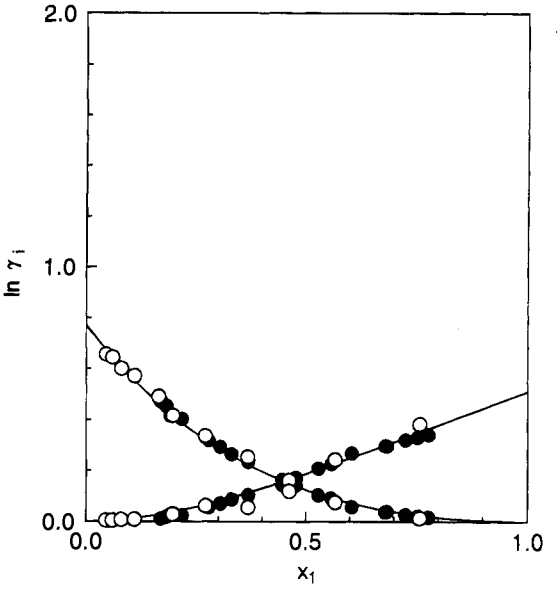

Figure 5. Activity coefficient–liquid composition diagram for methanol (1) + water (2) at 333.15 K: (●) this work; (○) Broul et al. (1969); (—) NRTL equation.

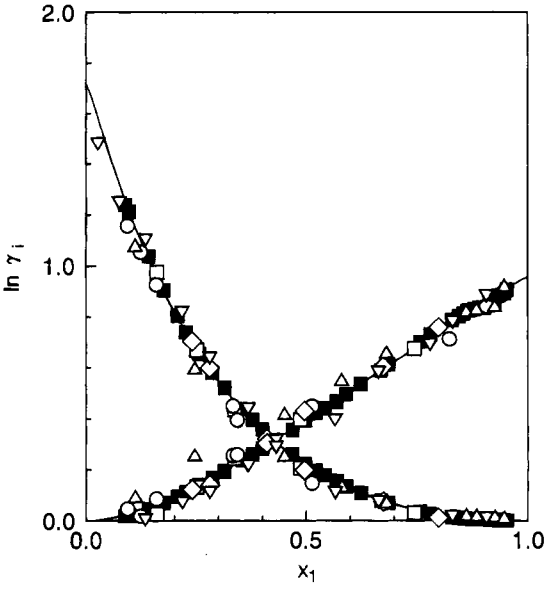

Figure 6. Activity coefficient–liquid composition diagram for ethanol (1) + water (2) at 323.15 K: (■) this work; (○) Jones et al. (1943); (□) Dulitskaya (1945); (◇) Nikol'skaya (1946); (△) Udovenko and Fatkulina (1952); (▽) Dutta Choudhury (1976); (—) NRTL equation.

Table 5. Azeotropic Composition $x_{1(az)}$ in Mole Fraction and Pressure $P_{(az)}$ for Ethanol (1) + Water (2) at Three Temperatures

T/K	$x_{1(az)}$	$P_{(az)}$/kPa
323.15	0.932	29.57
328.15	0.920	37.44
333.15	0.910	47.05

The activity coefficients, γ_i, in the tables and figures were evaluated by the following equation:

$$\phi_i P y_i = \gamma_i P_i^S \phi_i^S \exp[v_i^L(P - P_i^S)/RT] \quad (1)$$

where ϕ_i and ϕ_i^S are the fugacity coefficients of component i in the mixture and the pure vapor, respectively. They were calculated using the second virial coefficients obtained by the Tsonopoulos method (Tsonopoulos, 1974). The liquid molar volumes v_i^L were calculated by the modified Rackett

Table 6. Isothermal Vapor–Liquid Equilibrium Data, Vapor Pressure, P, Liquid Phase, x_i, and Vapor Phase, y_i, Mole fractions, and Activity Coefficients, γ_i, for Methanol (1) + Ethanol (2) + Water (3)

P/kPa	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	P/kPa	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
						323.15 K									
20.921	0.0140	0.0821	0.0649	0.4107	1.7759	3.5746	0.9807	30.987	0.1724	0.3455	0.2999	0.4280	0.9818	1.3014	1.4128
27.718	0.0390	0.3902	0.0774	0.5773	1.0036	1.3934	1.3546	33.564	0.1735	0.7274	0.2713	0.6483	0.9545	1.0116	2.2053
28.902	0.0392	0.5385	0.0705	0.6406	0.9476	1.1670	1.5981	30.513	0.1835	0.2343	0.3545	0.3497	1.0740	1.5447	1.2520
30.148	0.0502	0.6936	0.0848	0.7110	0.9278	1.0478	1.9438	32.966	0.1855	0.5583	0.2863	0.5355	0.9256	1.0701	1.8542
30.717	0.0579	0.7886	0.0956	0.7712	0.9237	1.0179	2.1583	33.380	0.1862	0.6220	0.2882	0.5669	0.9397	1.0292	2.0401
22.176	0.0753	0.0480	0.2984	0.2161	1.6082	3.4074	0.9920	33.602	0.2123	0.5383	0.3224	0.5072	0.9281	1.0710	1.8564
27.586	0.0897	0.2404	0.1962	0.4457	1.1010	1.7383	1.1910	30.610	0.2492	0.0619	0.5777	0.1269	1.2928	2.1288	1.0597
28.447	0.0957	0.3111	0.1885	0.4803	1.0219	1.4917	1.2830	35.878	0.2851	0.5647	0.4187	0.4788	0.9572	1.0274	1.9811
29.719	0.1043	0.4371	0.1815	0.5323	0.9425	1.2279	1.4986	33.532	0.2870	0.2486	0.4812	0.2896	1.0227	1.3221	1.3367
24.676	0.1109	0.0617	0.3591	0.2145	1.4603	2.9226	1.0270	37.666	0.3276	0.6447	0.4743	0.5051	0.9899	0.9952	2.2694
32.175	0.1126	0.8125	0.1832	0.7492	0.9527	1.0042	2.3531	36.509	0.3959	0.1881	0.5886	0.2002	0.9860	1.3127	1.4965
30.949	0.1133	0.5766	0.1853	0.5962	0.9218	1.0846	1.7632	38.298	0.4222	0.3218	0.5865	0.2759	0.9654	1.1075	1.6635
31.591	0.1198	0.6711	0.1922	0.6464	0.9226	1.0306	1.9730	42.562	0.5342	0.3998	0.6776	0.2851	0.9776	1.0205	1.9463
30.457	0.1637	0.2995	0.3012	0.4091	1.0210	1.4110	1.3277	44.984	0.6649	0.1583	0.8100	0.1127	0.9913	1.0754	1.5891
33.197	0.1700	0.6708	0.2642	0.6109	0.9384	1.0228	2.1078								
						328.15 K									
23.344	0.0411	0.0221	0.2197	0.1469	1.8522	4.2003	0.9993	41.574	0.2662	0.2629	0.4370	0.3159	1.0040	1.3356	1.3803
37.529	0.0488	0.6165	0.0826	0.6707	0.9360	1.0938	1.7524	38.264	0.2758	0.0261	0.6285	0.0576	1.2850	2.2636	1.0879
34.300	0.0528	0.2876	0.1129	0.5196	1.0826	1.6644	1.2094	44.882	0.2774	0.5955	0.3985	0.5108	0.9469	1.0265	2.0313
33.662	0.0548	0.2409	0.1261	0.4896	1.1437	1.8384	1.1623	40.927	0.2874	0.1285	0.5354	0.1965	1.1220	1.6743	1.1881
35.015	0.0556	0.3401	0.1100	0.5377	1.0222	1.4861	1.2919	44.421	0.2954	0.4529	0.4292	0.4138	0.9481	1.0828	1.7550
24.334	0.0564	0.0211	0.2740	0.1302	1.7539	4.0618	0.9950	46.707	0.3363	0.5429	0.4720	0.4474	0.9620	1.0252	1.9762
38.921	0.0601	0.7876	0.0996	0.7678	0.9498	1.0152	2.1502	46.124	0.3508	0.4160	0.4956	0.3660	0.9565	1.0815	1.7338
24.944	0.0657	0.0190	0.3080	0.1124	1.7344	3.9902	0.9999	43.472	0.3610	0.1177	0.6104	0.1551	1.0805	1.5301	1.2368
36.609	0.1068	0.3221	0.2037	0.4725	1.0295	1.4402	1.3135	44.330	0.3791	0.1123	0.6321	0.1427	1.0861	1.5038	1.2414
40.194	0.1070	0.7474	0.1719	0.7068	0.9503	1.0162	2.1246	48.174	0.3856	0.4997	0.5276	0.3989	0.9667	1.0234	1.9573
39.340	0.1168	0.5707	0.1867	0.5884	0.9258	1.0854	1.7934	46.406	0.3977	0.2670	0.5712	0.2554	0.9783	1.1831	1.5188
38.130	0.1561	0.3031	0.2810	0.4174	1.0114	1.4069	1.3456	47.786	0.4067	0.3810	0.5538	0.3220	0.9545	1.0752	1.7706
41.571	0.1569	0.7036	0.2444	0.6447	0.9524	1.0176	2.0966	49.840	0.4461	0.4387	0.5879	0.3425	0.9626	1.0345	1.9088
41.080	0.1800	0.5276	0.2792	0.5268	0.9374	1.0965	1.7266	49.126	0.4464	0.3535	0.5989	0.2903	0.9662	1.0732	1.7229
39.590	0.2031	0.2859	0.3534	0.3723	1.0143	1.3800	1.3447	47.014	0.4531	0.1100	0.6838	0.1209	1.0413	1.3771	1.3290
43.320	0.2188	0.6506	0.3274	0.5730	0.9526	1.0182	2.0956	50.410	0.4861	0.3283	0.6388	0.2611	0.9706	1.0657	1.7219
38.505	0.2208	0.1430	0.4474	0.2483	1.1495	1.7914	1.1650	50.994	0.4872	0.3810	0.6337	0.2917	0.9716	1.0374	1.8290
42.714	0.2373	0.4912	0.3567	0.4672	0.9439	1.0850	1.7549	56.400	0.6877	0.1116	0.8321	0.0825	0.9974	1.1046	1.5187
39.773	0.2545	0.1347	0.4946	0.2196	1.1381	1.7360	1.1771	59.840	0.7697	0.1068	0.8770	0.0711	0.9950	1.0532	1.5919
38.320	0.2638	0.0433	0.5957	0.0925	1.2751	2.1942	1.0904								
						333.15 K									
31.483	0.0342	0.0436	0.1604	0.2539	1.7848	3.9516	1.0001	50.450	0.1996	0.3759	0.3180	0.4305	0.9634	1.2307	1.4946
45.826	0.0428	0.5176	0.0734	0.6304	0.9437	1.1918	1.5447	49.758	0.2025	0.3110	0.3397	0.3892	1.0008	1.3271	1.3861
46.735	0.0477	0.5830	0.0793	0.6587	0.9325	1.1268	1.6593	52.421	0.2842	0.2394	0.4642	0.2913	1.0255	1.3575	1.3446
41.075	0.0512	0.2024	0.1234	0.4703	1.1914	2.0447	1.1178	58.782	0.3434	0.5724	0.4790	0.4627	0.9793	1.0069	2.0404
33.965	0.0535	0.0485	0.2254	0.2437	1.7277	3.6729	1.0041	57.624	0.3831	0.3091	0.5428	0.2904	0.9757	1.1485	1.5615
47.991	0.0546	0.6869	0.0877	0.7068	0.9246	1.0527	1.9108	57.020	0.3929	0.2338	0.5707	0.2370	0.9901	1.2269	1.4681
48.542	0.0583	0.7452	0.0938	0.7413	0.9366	1.0290	2.0416	55.733	0.4013	0.0937	0.6574	0.1197	1.0921	1.5128	1.2288
49.034	0.0630	0.8082	0.1031	0.7822	0.9621	1.0108	2.1904	61.204	0.4112	0.5073	0.5516	0.3951	0.9797	1.0088	2.0060
41.933	0.0710	0.1914	0.1728	0.4382	1.2278	2.0556	1.1056	59.751	0.4226	0.3367	0.5759	0.2908	0.9722	1.0934	1.6553
35.893	0.0734	0.0539	0.2714	0.2395	1.6010	3.4282	1.0058	58.663	0.4592	0.1065	0.6914	0.1179	1.0553	1.3776	1.2869
37.595	0.0938	0.0597	0.3091	0.2304	1.4933	3.1156	1.0224	63.960	0.4876	0.4325	0.6293	0.3230	0.9839	1.0094	1.9130
45.871	0.0976	0.3552	0.1773	0.5011	1.0007	1.3822	1.3479	65.489	0.5288	0.3923	0.6687	0.2860	0.9866	1.0082	1.8834
43.204	0.1029	0.1835	0.2350	0.3903	1.1864	1.9663	1.1339	61.681	0.5382	0.0530	0.7747	0.0556	1.0595	1.3704	1.2789
39.641	0.1130	0.0645	0.3522	0.2226	1.4880	2.9342	1.0243	67.166	0.5740	0.3476	0.7105	0.2470	0.9898	1.0070	1.8234
48.175	0.1340	0.4094	0.2259	0.4948	0.9743	1.2418	1.4736	64.401	0.5981	0.0517	0.8042	0.0488	1.0322	1.2854	1.3503
41.369	0.1350	0.0701	0.3866	0.2161	1.4257	2.7323	1.0334	69.374	0.6311	0.2981	0.7579	0.2054	0.9910	1.0073	1.8006
49.236	0.1353	0.4930	0.2176	0.5385	0.9495	1.1461	1.6163	67.856	0.6522	0.1290	0.8004	0.1004	0.9912	1.1143	1.5379
44.910	0.1436	0.1734	0.3130	0.3421	1.1761	1.8940	1.1334	69.793	0.6845	0.1389	0.8183	0.1021	0.9923	1.0812	1.5729
50.522	0.1530	0.5503	0.2357	0.5575	0.9327	1.0898	1.7624	66.993	0.6897	0.1355	0.8226	0.0997	0.9928	1.0853	1.5557
43.353	0.1608	0.0778	0.4234	0.2077	1.3726	2.4768	1.0496	72.935	0.7419	0.1497	0.8511	0.1010	0.9939	1.0352	1.6122
51.806	0.1689	0.6112	0.2594	0.5805	0.9529	1.0468	1.8890	75.471	0.7855	0.1584	0.8755	0.0998	0.9982	0.9989	1.6629
45.052	0.1862	0.0855	0.4493	0.2003	1.3062	2.2565	1.0830	75.470	0.8184	0.0459	0.9144	0.0309	1.0007	1.0676	1.5208

equation (Spencer and Adler, 1978; Moon, 1990). The vapor pressures of the pure components, P_i^S, were calculated from the Antoine equation constants given in Table 4. The Antoine constants were determined from the vapor pressure data of the pure components measured in this work. The average relative deviations between the values calculated by the Antoine equation and the experimental values are less than 0.01% in all cases.

The ethanol + water system forms a maximum pressure azeotrope. The azeotropic points at each temperature were determined from the experimental VLE data by a graphical technique (Hiaki et al., 1986). The azeotropic composition and pressure are shown in Table 5 and are compared with the literature values in Figure 9.

The experimental VLE data were examined by the thermodynamic consistency test (Kojima et al., 1990) which was proposed in our previous paper. The results indicate that the reported data for both systems are thermodynamically consistent.

For the methanol + water and ethanol + water systems at the temperatures investigated in this paper, there are three and seven data sets, respectively, which contain pressure, liquid composition, and vapor composition, available in the literature. However, these data are not

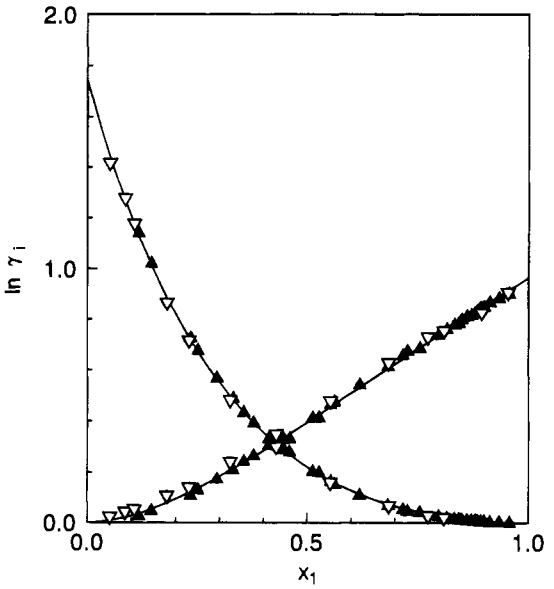

Figure 7. Activity coefficient–liquid composition diagram for ethanol (1) + water (2) at 328.15 K: (▲) this work; (▽) Mertl (1972); (—) NRTL equation.

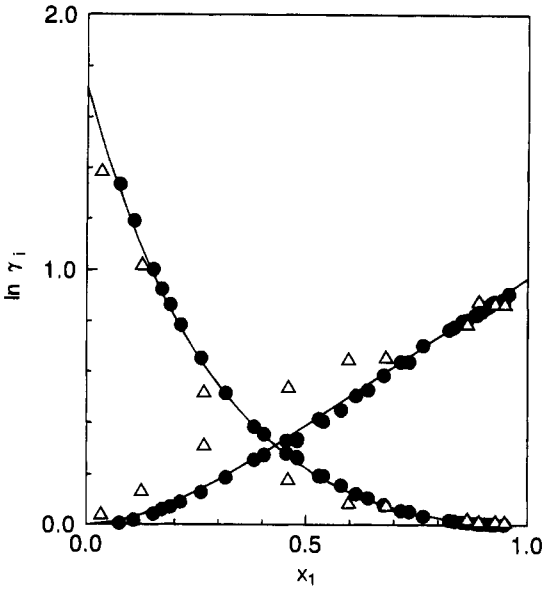

Figure 8. Activity coefficient–liquid composition diagram for ethanol (1) + water (2) at 333.15 K: (●) this work; (△) Udovenko and Fatkulina (1952); (—) NRTL equation.

Table 7. NRTL Parameters and Deviations between the Calculated and Experimental Vapor-Phase Mole Fractions, Δy_i, and Pressures, ΔP[a]

NRTL parameter	methanol (1) + water (2)	ethanol (1) + water (2)	methanol (1) + ethanol (2) + water (3)
		323.15 K	
$(g_{12} - g_{22})$/K	102.6158	36.1146	
$(g_{21} - g_{11})$/K	101.5526	529.9113	no ternary parameters
α_{12}	0.4	0.4	
		328.15 K	
$(g_{12} - g_{22})$/K	31.2103	38.6321	
$(g_{21} - g_{11})$/K	189.8366	535.0587	no ternary parameters
α_{12}	0.4	0.4	
		333.15 K	
$(g_{12} - g_{22})$/K	−36.3387	42.4320	
$(g_{21} - g_{11})$/K	294.9389	530.8664	no ternary parameters
α_{12}	0.4	0.4	

	Δy_1	ΔP/%	Δy_1	ΔP/%	Δy_1	Δy_2	ΔP/%
			323.15 K				
average	0.005	1.49	0.002	0.17	0.006	0.004	0.71
maximum	0.009	2.35	0.004	1.03	0.026	0.010	1.82
			328.15 K				
average	0.004	1.04	0.002	0.16	0.004	0.002	0.64
maximum	0.014	2.03	0.007	0.30	0.016	0.007	1.15
			333.15 K				
average	0.003	0.38	0.004	0.21	0.003	0.003	0.53
maximum	0.009	0.95	0.013	0.92	0.008	0.012	1.52

[a] $\Delta y_i = \Sigma_k|y_{i,\text{exptl}} - y_{i,\text{calcd}}|_k/N$, $\Delta P = 100\Sigma_k(|(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}|_k/N$, N = number of data points.

consistent with our proposed test. Figures 3–8 show the comparisons of the activity coefficients calculated from all literature VLE data and our results.

Ternary System. Table 6 gives the experimental VLE data for the system methanol + ethanol + water system at 323.15, 328.15, and 333.15 K.

Correlation and Prediction

The activity coefficients of the binary systems were correlated by the NRTL equation (Renon and Prausnitz, 1968) for each equilibrium temperature. The correlation procedure was based on the minimization of the following objective function:

$$F = \sum_{k=1}^{N}\left[\left(\frac{\gamma_{1,\text{calcd}} - \gamma_{1,\text{exptl}}}{\gamma_{1,\text{exptl}}}\right)_k^2 + \left(\frac{\gamma_{2,\text{calcd}} - \gamma_{2,\text{exptl}}}{\gamma_{2,\text{exptl}}}\right)_k^2\right] \quad (2)$$

where N is the number of data points. The mixture nonrandomness parameter α_{12} was set as 0.4 as recommended by Walas (Walas, 1984). Table 7 lists the estimated parameters of the binary systems and the deviations between the calculated and experimental vapor-phase compositions and total pressures. The calculated results are shown by the solid lines in Figures 1–8.

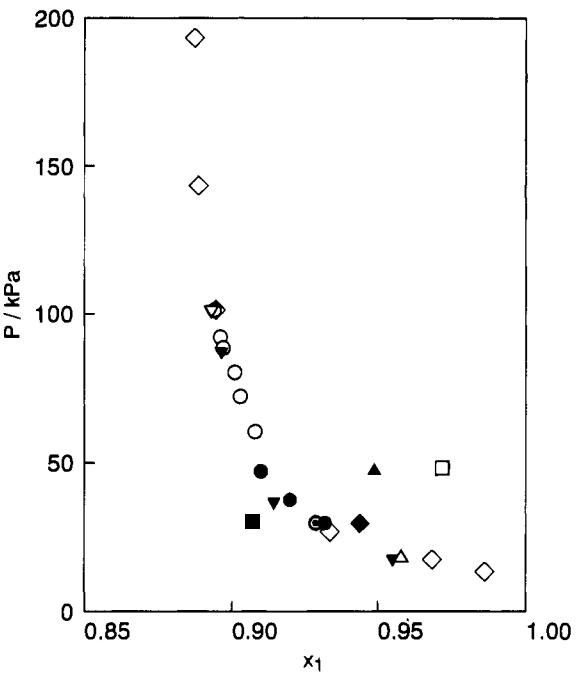

Figure 9. Azeotropic pressure–liquid composition diagram for ethanol (1) + water (2): (●) this work; (▼) Vrevskii (1910); (◇) Wade and Merriman (1911); (□) Jones et al. (1943); (▲) Udovenko and Fatkulna (1952); (◆) Wilson et al. (1979); (⊙) Baláczar-Ortiz (1979); (■) Dutta Choudhury (1976); (○) Tochigi et al. (1985); (△) Zielkiewicz and Konitz (1991); (▽) Kurihara et al. (1993).

The VLE for the ternary methanol + ethanol + water system was predicted with the binary NRTL parameters listed in Table 7. In the prediction, the parameters τ_{12}, τ_{21}, and α_{12} for the methanol + ethanol system were equated to 0 at the calculated pressure range, because the values γ_1 and γ_2 are close to 1 (Kurihara et al., 1993) which indicates that this system is nearly an ideal solution. The agreement between the predicted and experimental values was good.

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