

# Isobaric Vapor-Liquid Equilibria for Methanol + Ethanol + Water and the Three Constituent Binary Systems

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Vapor-liquid equilibrium data for methanol + ethanol + water and its three constituent binary systems methanol + ethanol, ethanol + water, and methanol + water were measured at 101.3 kPa using a liquid-vapor ebullition-type equilibrium still. The experimental binary data were correlated by the NRTL equation. The ternary system methanol + ethanol + water was predicted by means of the binary NRTL parameters with good accuracy.

## Introduction

The objective of this paper is to experimentally determine the vapor-liquid equilibrium (VLE) data for the ternary system methanol + ethanol + water and its three constituent binary systems at 101.3 kPa. For this ternary system, two data sets of isothermal VLE (298.15, 313.05 K) and three datasets of isobaric VLE at 101.3 kPa were reported previously (1-5). The isobaric VLE data of ref 3, however, cover only a region below 0.02 mole fraction of water, and the experimental data of refs 4 and 5 indicate that some tie lines of the ternary system cross. It was accordingly felt that the VLE data for the system methanol + ethanol + water at 101.3 kPa should be measured anew.

## Experimental Section

**Apparatus and Procedure.** A liquid-vapor ebullition-type equilibrium still (6) was used for the measurement of the VLE. Vapor and liquid samples were analyzed with a Shimadzu gas chromatograph type GC-3BT 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 (7) with an accuracy of  $\pm 0.001$  in mole fraction.

The equilibrium temperature was measured with a calibrated platinum resistance thermometer. The accuracy was estimated to be  $\pm 0.01$  K. Pressure in the still was measured by a Fortin-type mercury barometer. Since the barometric pressure slightly varied during the measurements, the experimental equilibrium temperatures were corrected to 101.3 kPa.

**Materials.** Methanol and ethanol were special grade pure reagents (Wako Pure Chemical Industry, Ltd.) and were used after removing traces of water with molecular sieves 3A. Water was used after ion exchange and distillation. The purity of the materials was checked by gas chromatography and found to be better than 99.9 mol %. In Table I, densities and normal boiling points of the purified reagents are shown and compared with the literature values.

## Experimental Results

**Binary Systems.** Table II and Figures 1-3 give the experimental VLE data at 101.3 kPa for the three binary systems methanol + ethanol, ethanol + water, and methanol + water. The published data (9, 10), which were recom-

Table I. Densities  $\rho$  and Normal boiling Points  $T_b$  of the Components

component	$\rho(298.15\text{K})/(\text{g cm}^{-3})$		$T_b/\text{K}$	
	exptl	lit. (8)	exptl	lit. (8)
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

Table II. Isobaric Vapor-Liquid Equilibrium Data (Liquid-Phase Mole Fraction  $x_b$ , Vapor-Phase Mole Fraction  $y_b$ , and Temperature  $T$ ) and Activity Coefficients  $\gamma_i$  for Binary Systems at 101.3 kPa

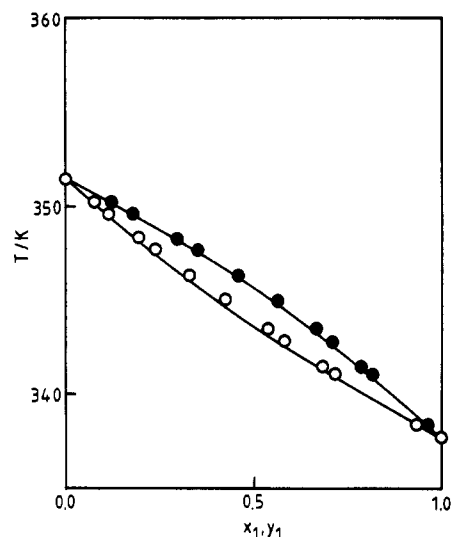
$x_1$	$y_1$	$T/\text{K}$	$\gamma_1$	$\gamma_2$	$x_1$	$y_1$	$T/\text{K}$	$\gamma_1$	$\gamma_2$
Methanol (1) + Ethanol (2)									
0.074	0.119	350.26	1.018	0.997	0.529	0.663	343.50	1.010	0.977
0.113	0.177	349.63	1.013	0.996	0.581	0.709	342.83	1.007	0.975
0.195	0.292	348.36	1.013	0.991	0.682	0.792	341.47	1.008	0.970
0.238	0.349	347.68	1.016	0.989	0.717	0.818	341.06	1.005	0.970
0.329	0.459	346.35	1.014	0.983	0.935	0.963	338.41	1.002	0.958
0.424	0.561	344.98	1.010	0.981					
Ethanol (1) + Water (2)									
0.056	0.366	362.19	4.434	1.004	0.704	0.759	351.74	1.068	1.844
0.091	0.448	359.26	3.705	1.016	0.715	0.764	351.70	1.060	1.879
0.189	0.539	356.33	2.386	1.067	0.798	0.818	351.41	1.028	2.072
0.286	0.582	354.89	1.795	1.164	0.843	0.851	351.37	1.014	2.188
0.323	0.600	354.46	1.664	1.196	0.847	0.854	351.37	1.013	2.200
0.331	0.605	354.41	1.640	1.197	0.849	0.856	351.36	1.013	2.200
0.419	0.627	353.59	1.385	1.346	0.884	0.886	351.34	1.008	2.270
0.512	0.666	352.85	1.237	1.479	0.908	0.907	351.33	1.005	2.338
0.620	0.712	352.16	1.120	1.686	0.922	0.920	351.33	1.003	2.373
Methanol (1) + Water (2)									
0.019	0.137	369.56	2.437	1.000	0.462	0.768	347.09	1.177	1.181
0.077	0.368	362.72	1.998	1.003	0.501	0.787	346.38	1.141	1.205
0.133	0.492	358.38	1.780	1.014	0.586	0.826	344.70	1.087	1.275
0.140	0.508	357.76	1.782	1.014	0.638	0.848	343.83	1.058	1.322
0.205	0.594	354.51	1.586	1.030	0.651	0.852	343.59	1.051	1.349
0.260	0.647	352.45	1.461	1.046	0.679	0.864	343.11	1.040	1.376
0.310	0.683	350.86	1.367	1.075	0.717	0.882	342.41	1.031	1.397
0.320	0.690	350.58	1.350	1.079	0.803	0.922	340.89	1.018	1.418
0.358	0.713	349.54	1.293	1.105	0.879	0.952	339.66	1.006	1.501
0.420	0.746	348.07	1.215	1.151	0.951	0.981	338.46	1.002	1.549

mended by Moon (11), are also plotted in Figures 2 and 3. The activity coefficients  $\gamma_i$  of component  $i$  were evaluated with eq 1 where  $\phi_i$  and  $\phi_i^s$ , the fugacity coefficients of

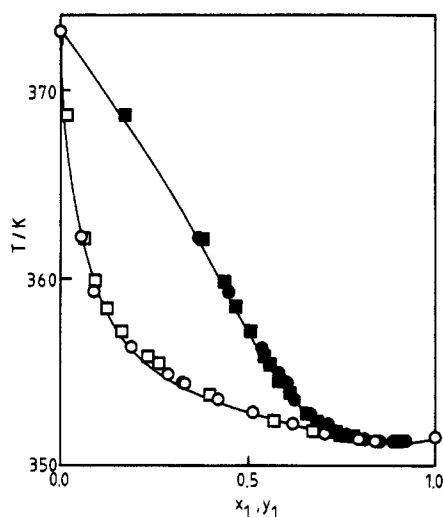
$$\phi_i P y_i = \gamma_i P_i^s \phi_i^s \exp[v_i^L(P - P_i^s)/RT] \quad (1)$$

component  $i$  in the mixture and pure vapor, respectively, were calculated by using the second virial coefficients obtained by the Tsonopoulos method (12). The vapor pressures of the

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**Figure 1.** Vapor-liquid equilibrium temperature  $T$  against the liquid-phase mole fraction  $x_1$  and vapor-phase mole fraction  $y_1$  for the methanol (1) + ethanol (2) system at 101.3 kPa. Key: (○, ●) this work; (—) calculated results as an ideal solution.



**Figure 2.** Vapor-liquid equilibrium temperature  $T$  against the liquid-phase mole fraction  $x_1$  and vapor-phase mole fraction  $y_1$  for the ethanol (1) + water (2) system at 101.3 kPa. Key: (○, ●) this work; (□, ■) Carey and Lewis (9); (—) correlated results with NRTL equation.

**Table III.** Antoine Constants of the Components<sup>a</sup>

component	A	B	C
methanol	7.206 02	1582.271	-33.424 (13)
ethanol	7.287 81	1623.220	-44.170 (14)
water	7.196 21	1730.630	-39.724 (15)

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

pure components,  $P_i^s$ , were calculated by the Antoine equation using the constants given in Table III. The liquid molar volumes  $v_i^L$  were evaluated by the Rackett equation (16). The calculated activity coefficients are listed in Table II.

In the methanol + ethanol system, the values of both  $\gamma_i$ , in the range from 0.958 to 1.018, close to 1 indicate that this system at atmospheric pressure is nearly an ideal solution. Therefore, this system has been treated as an ideal solution in this work.

The binary experimental VLE data for the ethanol + water and methanol + water systems were examined by the

**Table IV.** Azeotropic Composition  $x_{1(\text{AZ})}$  in Mole Fraction and Temperature  $T_{(\text{AZ})}$  for the Ethanol (1) + Water (2) System at 101.3 kPa

exptl		lit.	
$x_{1(\text{AZ})}$	$T_{(\text{AZ})}/\text{K}$	$x_{1(\text{AZ})}$	$T_{(\text{AZ})}/\text{K}$
0.893	351.33	0.904	351.324 (18)
		0.8940	351.30 (19)
		0.8945	351.28 (20)
		0.8950	351.27 (21)
		0.894	351.34 (22)
		0.895	351.25 (23)

**Table V.** Isobaric Vapor-Liquid Equilibrium Data (Liquid-Phase Mole Fraction  $x_i$ , Vapor-Phase Mole Fraction  $y_i$ , and Temperature  $T$ ) and Activity Coefficients  $\gamma_i$  for the Methanol (1) + Ethanol (2) + Water (3) System at 101.3 kPa

$x_1$	$x_2$	$y_1$	$y_2$	$T/\text{K}$	$\gamma_1$	$\gamma_2$	$\gamma_3$
0.015	0.009	0.098	0.084	368.03	2.314	5.184	1.007
0.024	0.680	0.038	0.723	351.43	0.962	1.066	1.852
0.027	0.298	0.053	0.541	354.09	1.090	1.649	1.235
0.028	0.015	0.156	0.124	365.19	2.155	5.056	1.004
0.032	0.914	0.050	0.895	350.87	0.968	1.002	2.403
0.040	0.078	0.137	0.353	358.38	1.648	3.515	1.001
0.043	0.146	0.114	0.429	355.96	1.382	2.492	1.073
0.046	0.538	0.072	0.625	351.78	0.940	1.150	1.644
0.050	0.805	0.076	0.791	350.63	0.950	1.015	2.180
0.065	0.417	0.109	0.554	352.20	0.993	1.295	1.443
0.096	0.740	0.143	0.716	350.02	0.950	1.023	2.094
0.118	0.642	0.175	0.644	349.95	0.949	1.064	1.840
0.122	0.796	0.182	0.743	349.53	0.968	1.006	2.277
0.122	0.349	0.205	0.468	351.55	1.017	1.340	1.407
0.128	0.221	0.246	0.386	352.52	1.126	1.683	1.236
0.130	0.074	0.345	0.227	354.88	1.435	2.708	1.069
0.178	0.600	0.258	0.575	349.08	0.956	1.051	1.902
0.188	0.277	0.316	0.376	350.75	1.046	1.398	1.354
0.195	0.013	0.540	0.043	354.53	1.515	2.959	1.061
0.236	0.708	0.339	0.614	347.82	0.990	0.998	2.244
0.238	0.260	0.378	0.334	349.91	1.018	1.367	1.397
0.240	0.459	0.344	0.454	348.64	0.960	1.104	1.726
0.261	0.224	0.419	0.293	349.72	1.036	1.402	1.372
0.314	0.398	0.441	0.381	347.62	0.975	1.112	1.659
0.314	0.552	0.431	0.474	346.93	0.977	1.024	1.964
0.367	0.176	0.554	0.207	347.87	1.039	1.354	1.387
0.418	0.228	0.580	0.227	346.62	0.999	1.203	1.525
0.446	0.077	0.675	0.094	346.95	1.077	1.457	1.334
0.449	0.464	0.580	0.372	344.96	0.987	1.033	1.662
0.457	0.084	0.675	0.100	346.65	1.062	1.438	1.368
0.490	0.392	0.624	0.305	344.53	0.988	1.020	1.845
0.535	0.258	0.677	0.211	344.36	0.988	1.080	1.668
0.570	0.034	0.782	0.035	344.81	1.054	1.337	1.395
0.605	0.213	0.743	0.169	343.35	0.995	1.091	1.558
0.641	0.108	0.791	0.090	343.06	1.010	1.160	1.545
0.731	0.190	0.834	0.128	341.24	0.999	1.009	1.700
0.788	0.062	0.895	0.044	340.90	1.007	1.078	1.457
0.865	0.044	0.935	0.032	339.70	1.002	1.160	1.371

thermodynamic consistency test (11, 17) which was proposed in our previous paper. The results indicate that the reported data for both systems are thermodynamically consistent.

The ethanol + water system shows a minimum boiling azeotrope. The azeotropic point was determined from the experimental VLE data by a graphical method (6). The azeotropic composition and temperature are compared with the literature values in Table IV.

**Ternary Systems.** Table V and Figure 4 show the experimental VLE data for the methanol + ethanol + water system at 101.3 kPa. The tails of the solid arrows in Figure 4 represent experimental liquid compositions, and the heads of the arrows show experimental vapor compositions on the same tie line.

#### Correlation and Prediction

The activity coefficients  $\gamma_i$  for the three binary systems were correlated by the NRTL equation (24). Table VI lists

**Table VI. NRTL Parameters and Deviations between Calculated and Experimental Vapor-Phase Mole Fractions  $\Delta y_i$  and Temperatures  $\Delta T^a$** 

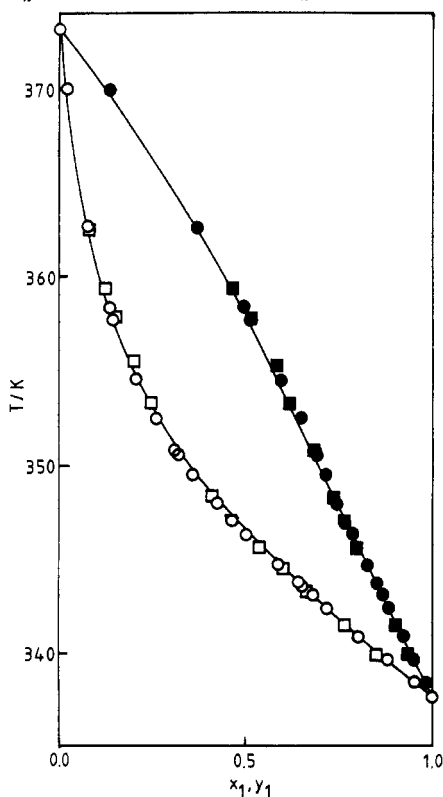
NRTL parameter/ (J mol <sup>-1</sup> )	methanol (1) + ethanol (2)	ethanol (1) + water (2)	methanol (1) + water (2)	methanol (1) + ethanol (2) + water (3)						
$g_{12} - g_{22}$	0.0	206.7	-788.2	no ternary parameters						
$g_{21} - g_{11}$	0.0	5270.3	3641.5							
$\alpha_{12}$	0.0	0.4	0.4							
	methanol (1) + ethanol (2)		ethanol (1) + water (2)		methanol (1) + water (2)		methanol (1) + ethanol (2) + water (3)			
	$\Delta y_1$	$\Delta T/K$	$\Delta y_1$	$\Delta T/K$	$\Delta y_1$	$\Delta T/K$	$\Delta y_1$	$\Delta y_2$	$\Delta y_3$	$\Delta T/K$
average	0.005	0.04	0.006	0.08	0.008	0.18	0.003	0.003	0.003	0.14
maximum	0.008	0.08	0.017	0.27	0.017	0.37	0.008	0.019	0.019	0.35

$$^a \Delta y_i = \sum_k |(y_{i,\text{exptl}} - y_{i,\text{calcd}})|_k / N, \Delta T = \sum_k |(T_{\text{exptl}} - T_{\text{calcd}})|_k / N, N = \text{number of data points}, R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}.$$

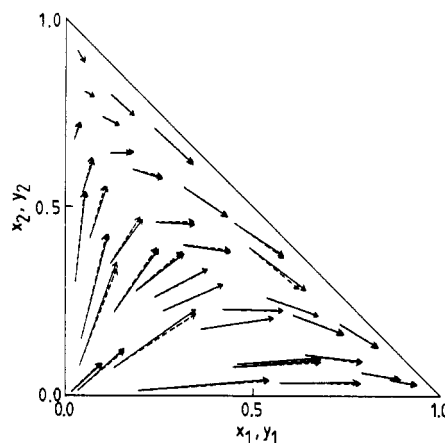
**Table VII. NRTL Parameters Recommended in the DECHEMA Chemical Data Series and Deviations between Calculated and Experimental Vapor-Phase Mole Fractions  $\Delta y_i$  and Temperature  $\Delta T^a$** 

NRTL parameter/ (J mol <sup>-1</sup> )	methanol (1) + ethanol (2)	ethanol (1) + water (2)	methanol (1) + water (2)	methanol (1) + ethanol (2) + water (3)						
$g_{12} - g_{22}$	-108.8	-3791.4 + 4.1451T	-2999.0 + 6.1204T	no ternary parameters						
$g_{21} - g_{11}$	53.3	4458.8 + 8.4420T	1661.7 + 4.2493T							
$\alpha_{12}$	0.3356	0.1448	0.2442							
	methanol (1) + ethanol (2)		ethanol (1) + water (2)		methanol (1) + water (2)		methanol (1) + ethanol (2) + water (3)			
	$\Delta y_1$	$\Delta T/K$	$\Delta y_1$	$\Delta T/K$	$\Delta y_1$	$\Delta T/K$	$\Delta y_1$	$\Delta y_2$	$\Delta y_3$	$\Delta T/K$
average	0.002	0.03	0.004	0.21	0.004	0.16	0.004	0.005	0.006	0.11
maximum	0.004	0.05	0.022	0.89	0.010	0.41	0.016	0.023	0.022	0.67

$$^a \Delta y_i = \sum_k |(y_{i,\text{exptl}} - y_{i,\text{calcd}})|_k / N, \Delta T = \sum_k |(T_{\text{exptl}} - T_{\text{calcd}})|_k / N, N = \text{number of data points}, R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}.$$

**Figure 3. Vapor-liquid equilibrium temperature  $T$  against the liquid-phase mole fraction  $x_1$  and vapor-phase mole fraction  $y_1$  for the methanol (1) + ethanol (2) + water (3) system at 101.3 kPa. Key: (O, ●) this work; (□, ■) Verhoeye and Schepper (10); (—) correlated results with NRTL equation.**

the NRTL parameters  $g_{12} - g_{22}$ ,  $g_{21} - g_{11}$ , and  $\alpha_{12}$  of the binary systems and deviations between experimental and calculated vapor-phase compositions and bubble point temperatures. In Figures 1-3, the calculated results are shown by solid lines.

**Figure 4. Vapor-liquid equilibrium tie lines (tails of arrows represent liquid-phase mole fractions  $x_1$  and  $x_2$ , and heads of arrows represent vapor-phase mole fractions  $y_1$  and  $y_2$ ) for the methanol (1) + ethanol (2) + water (3) system at 101.3 kPa. Key: (—) experimental values; (- - -) predicted results with NRTL equation.**

In the calculations, the parameters  $g_{12} - g_{22}$ ,  $g_{21} - g_{11}$ , and  $\alpha_{12}$  for the methanol + ethanol system were given a zero value.

The VLE of the ternary system methanol + ethanol + water was predicted by means of the binary NRTL parameters listed in Table VI. The predictions are also illustrated by the broken arrows in Figure 4.

Table VII also gives deviations between experimental and calculated vapor-phase compositions and bubble point temperatures, when the NRTL parameters recommended in the DECHEMA Chemistry Data Series (15) are used for the calculations of the VLE of the studied four systems. The calculated results in Table VI were more accurate than those in Table VII for the ternary and ethanol + water systems, but the result of the methanol + water system was opposite. This is due to the fixed parameters  $\alpha_{12}$  used for the correlation in this work.

Predictions of the ternary VLE data of the literature based on the NRTL parameters evaluated in this work and recommended in ref 15 give the maximum deviations of vapor-phase compositions 0.077 and 0.082 for ref 3 and 0.045 and 0.055 for ref 4.

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