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Vapor−Liquid Equilibrium Data for Methanol + 1,3-Dioxolane + Water and Constituent Binary Systems at 101.3 kPa

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Isobaric vapor−liquid equilibria were measured at atmospheric pressure for the ternary system methanol + 1,3-dioxolane + water and its constituent binary systems methanol + 1,3-dioxolane and 1,3-dioxolane + water. Parameters for the Wilson and NRTL equations were determined from binary data, and the prediction for the ternary system was compared with experimental results. For this ternary system, the NRTL equation gave better results than the Wilson equation.

Introduction

Polyacetal resin, a material used in the manufacture of car and electrical and electronic components, is industrially synthesized by the copolymerization of trioxane and 1,3-dioxolane. The liquid waste after reaction contains 1,3-dioxolane, methanol, and water. Distillation is used to separate out the 1,3-dioxolane from this liquid mixture, because it is essential to recycle the 1,3-dioxolane that has failed to polymerize. For the design of this distillation, knowledge of the vapor−liquid equilibrium (VLE) data for the ternary system methanol + 1,3-dioxolane + water is needed.

The present study reports experimental VLE data for the ternary system methanol + 1,3-dioxolane + water and its constituent binary mixtures methanol + 1,3-dioxolane and 1,3-dioxolane + water at 101.3 kPa. For the other constituent binary mixture, methanol + water, isobaric VLE data at 101.3 kPa have already been reported by the authors.[1] VLE data for the methanol + 1,3-dioxolane + water system are not available in the literature.

We also confirm whether this ternary system exhibits a valley in the liquid composition versus bubble point temperature surface from the behavior of the experimental vapor−liquid tie lines. Naka et al. defined the term *valley* as a curve that divides the patterns of vapor−liquid tie lines.[2,3] It is important to take into account the existence of the valley in addition to the azeotrope, because the composition profiles of distillation columns are restricted by the valley.

Table 1. Antoine Constants[a] and Liquid Molar Volumes[b] of Components

component	A	B	C	$10^6 v^L/m^3 \cdot mol^{-1}$
methanol	6.685 50	1290.449	−61.940	40.73
1,3-dioxolane	6.148 59	1196.197	−59.834	69.89
water	6.196 28	1154.545	−97.619	18.07

[a] $\log(P/\text{kPa}) = A - B/[(T/\text{K}) + C]$. [b] The value is published by Gmehling and Onken.[14]

Experimental Section

Apparatus and Procedure. In this VLE measurement, we used a modified Rogalski−Malanowski equilibrium still.[4,5] This still is a vapor−liquid recirculation type and mainly consists of a boiling flask, Cottrell pump, thermometer well, equilibrium chamber, condenser, and withdrawal of condensed vapor and liquid samples. The boiling flask has a capacity of about 70 cm^3. An electric cartridge heater was inserted into the boiling flask, and a little glass dust was put on the wall of the heat-transfer surface to stabilize the boiling. The equilibrium still was opened to the atmosphere, and the atmospheric pressure in the still was measured using a Fortin type mercury barometer. The accuracy of this mercury barometer is ±0.013 kPa (±0.1 mmHg). The equilibrium temperature was measured with a calibrated platinum resistance thermometer with an accuracy of ±0.01 K. The experimental equilibrium temperatures were corrected to 101.3 kPa by the equation[6]

$$T = T_{\text{expt}} + \frac{1}{\sum_{i=1}^{\text{NC}} B_i x_i/(T_{\text{expt}} + C_i)^2} \frac{101.3 - P_{\text{expt}}}{P_{\text{expt}}} \tag{1}$$

where NC is the number of components. This was carried out because the atmospheric pressure fluctuated slightly during the measurements. In this equation, T_{expt}/K is the experimental temperature at the actual atmospheric pressure P_{expt}/kPa, B_i and C_i are the Antoine constants of component i, as listed in Table 1, and x_i is the mole fraction in the liquid phase. The reproducibility of the equilibrium temperatures was within 0.01 K over the entire mole fraction range.

Analysis. Vapor and liquid samples were analyzed with a Shimadzu gas chromatograph, model GC-14APT, equipped with a thermal conductivity detector. TSG-1 (15%) was used as the column packing, and helium was used as the carrier gas. The compositions were determined by the relative area method with an accuracy of ±0.001 mole fraction.

Materials. Methanol and 1,3-dioxolane were special grade pure chemicals (Wako Pure Chemical Industry, Ltd.) and were used after removal of any traces of water with molecular 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

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Table 2. Densities, ρ, and Normal Boiling Points, T_b, of the Components

	ρ(298.15 K)/g·cm^{-3}		T_b/K	
component	expt	lit.	expt	lit.[a]
methanol	0.7867	0.786 37[a]	337.69	337.696[a]
1,3-dioxolane	1.0586	1.058 65[b]	348.57	348.549[c]
water	0.9972	0.997 05[a]	373.13	373.15[a]

[a] Riddick et al.[7] [b] Inglese et al.[8] [c] Wu and Sandler.[9]

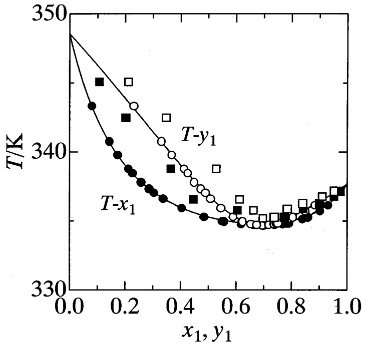

Figure 1. Temperature–composition diagram for the methanol (1) + 1,3-dioxolane (2) system: (●, ○) experimental liquid and vapor phase mole fractions; (■, □) literature liquid and vapor phase mole fractions;[10] (—) Wilson equation; (···) NRTL equation.

99.9 mol %. In Table 2, some measured properties of the purified chemicals are shown together with the literature values for these properties. As shown in Table 2, the experimental results in the present study approximately agree with the literature values.[7–9]

Experimental Results

Because we have not found the second virial coefficient data that are required for the calculation of the vapor phase fugacity coefficients of 1,3-dioxolane, the activity coefficients γ_i of component i were calculated using the following equation, which assumes ideal gas behavior.

$$Py_i = x_i \gamma_i P_i^S \tag{2}$$

The vapor pressures of the pure components, P_i^S, were calculated from the Antoine equation constant shown in Table 1. The Antoine constants were determined from the vapor pressure data of the pure components measured in the present study. The average absolute percent deviations between the values calculated by the Antoine equation and the experimental values are less than about 0.5% in all cases.

Binary Systems. Binary VLE data for both methanol + 1,3-dioxolane and 1,3-dioxolane + water are reported in Table 3 and Figures 1–4 along with the activity coefficients calculated by eq 2. These figures also show a comparison of published VLE data[10,11] and our results.

The experimental binary VLE data were tested for thermodynamic consistency using the point test of Fredenslund et al.[12] and the area test of Herington.[13] These point and area tests have been described by Gmehling and Onken.[14] In addition, we performed the infinite dilution test proposed by Kojima et al.[15,16] for both systems. The results of all three tests indicate that the reported data for the two systems are thermodynamically consistent. However, not all literature data[10,11] shown in Figures 1–4 are reliable, as determined by three tests mentioned above.

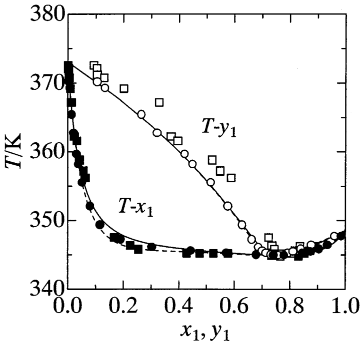

Figure 2. Temperature–composition diagram for the 1,3-dioxolane (1) + water (2) system: (●, ○) experimental liquid and vapor phase mole fractions; (■, □) literature liquid and vapor phase mole fractions;[11] (—) Wilson equation; (···) NRTL equation.

Table 3. Isobaric Binary Vapor–Liquid Equilibrium Data, Bubble Point Temperature, T, Liquid Phase, x_1, and Vapor Phase, y_1, Mole Fractions, and Activity Coefficients, γ_i, at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
		Methanol (1) + 1,3-Dioxolane (2)		
343.29	0.082	0.233	2.293	0.998
340.74	0.145	0.331	2.029	1.021
339.77	0.175	0.369	1.945	1.032
338.76	0.213	0.414	1.864	1.041
338.44	0.228	0.426	1.815	1.052
337.78	0.259	0.451	1.735	1.073
337.31	0.288	0.474	1.670	1.088
337.00	0.305	0.493	1.661	1.086
337.02	0.306	0.491	1.647	1.091
336.60	0.338	0.509	1.572	1.120
336.58	0.339	0.510	1.571	1.121
335.92	0.406	0.547	1.444	1.181
335.27	0.486	0.590	1.336	1.264
334.95	0.552	0.623	1.258	1.349
334.92	0.559	0.624	1.245	1.369
334.74	0.619	0.655	1.189	1.463
334.68	0.663	0.676	1.148	1.557
334.64	0.702	0.696	1.118	1.654
334.69	0.740	0.719	1.094	1.750
334.75	0.769	0.737	1.076	1.839
334.81	0.784	0.747	1.068	1.888
334.83	0.792	0.752	1.063	1.918
335.11	0.840	0.788	1.038	2.114
335.25	0.860	0.807	1.033	2.194
335.70	0.903	0.850	1.018	2.416
336.12	0.932	0.885	1.010	2.603
		1,3-Dioxolane (1) + Water (2)		
370.14	0.005	0.106	10.923	0.999
369.26	0.008	0.134	8.851	1.002
365.38	0.015	0.266	10.492	0.985
362.67	0.022	0.323	9.416	1.013
359.66	0.033	0.422	8.986	0.982
358.12	0.040	0.450	8.289	0.999
355.53	0.052	0.516	7.927	0.986
352.09	0.082	0.578	6.284	1.021
349.31	0.117	0.630	5.255	1.044
347.21	0.192	0.664	3.618	1.133
346.12	0.304	0.688	2.456	1.279
345.59	0.444	0.702	1.746	1.565
345.23	0.573	0.715	1.395	1.980
345.01	0.680	0.732	1.213	2.508
344.95	0.742	0.746	1.135	2.956
344.96	0.779	0.759	1.099	3.273
345.19	0.846	0.793	1.049	3.994
345.45	0.876	0.813	1.030	4.431
345.84	0.906	0.841	1.017	4.886
346.42	0.937	0.879	1.008	5.411
347.69	0.985	0.962	1.006	6.761

The methanol + 1,3-dioxolane and 1,3-dioxolane + water systems both form a minimum boiling azeotrope.

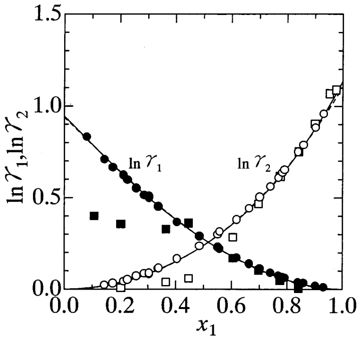

Figure 3. Activity coefficient−liquid composition for the methanol (1) + 1,3-dioxolane (2) system: (●, ○) experimental liquid and vapor phase mole fractions; (■, □) literature liquid and vapor phase mole fractions;[10] (—) Wilson equation; (···) NRTL equation.

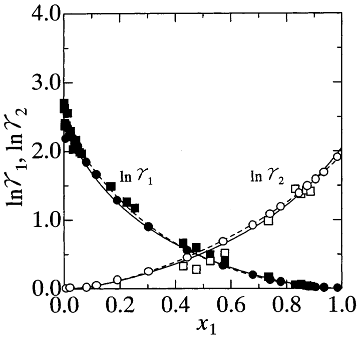

Figure 4. Activity coefficient−liquid composition for the 1,3-dioxolane (1) + water (2) system: (●, ○) experimental liquid and vapor phase mole fractions; (■, □) literature liquid and vapor phase mole fractions;[11] (—) Wilson equation; (···) NRTL equation.

Table 4. Azeotropic Composition $x_{1(\mathrm{az})}$ in Mole Fraction and Temperature $T_{(\mathrm{az})}$ for the Two Binary Systems

$T_{(\mathrm{az})}$/K	$x_{1(\mathrm{az})}$	P/kPa
	Methanol (1) + 1,3-Dioxolane (2)	
334.66	0.691	101.3[a]
335.15	0.6981	101.3[b]
	1,3-Dioxolane (1) + Water (2)	
344.95	0.748	101.3[a]
344.85	0.7185	101.3[c]

[a] This work. [b] Chubarov et al.[10] [c] Petrenkova et al.[11]

These binary azeotropic points were determined using a graphical method[17] on the basis of experimental VLE data. The evaluated binary azeotropic compositions and temperatures are shown in Table 4 together with the literature data.

Ternary System. Table 5 and Figure 5 show the experimental VLE data for the ternary system of methanol + 1,3-dioxolane + water at 101.3 kPa. The tails of the solid arrows in Figure 5 represent experimental liquid compositions while the heads of the arrows show experimental vapor compositions on the same tie line. As Figure 5 indicates, this ternary system has a valley from the binary minimum boiling azeotrope of methanol + 1,3-dioxolane to that of 1,3-dioxolane + water. The vapor−liquid tie lines of this system near the valley turn toward the valley.

Table 5. Isobaric Ternary Vapor−Liquid Equilibrium Data, Bubble Point Temperature, *T*, Liquid Phase, x_i, and Vapor Phase, y_i, Mole Fractions, and Activity Coefficients, γ_i, for Methanol (1) + 1,3-Dioxolane (2) + Water (3) at 101.3 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
339.80	0.227	0.592	0.339	0.540	1.376	1.230	2.522
341.11	0.193	0.505	0.281	0.551	1.276	1.405	1.979
341.96	0.169	0.443	0.248	0.557	1.245	1.572	1.721
342.89	0.146	0.379	0.217	0.564	1.218	1.802	1.515
343.22	0.136	0.350	0.205	0.562	1.220	1.923	1.468
352.62	0.101	0.044	0.290	0.308	1.651	6.135	1.022
350.63	0.199	0.034	0.465	0.189	1.442	5.196	1.064
349.07	0.285	0.025	0.588	0.127	1.346	4.997	1.040
348.50	0.342	0.018	0.646	0.077	1.258	4.288	1.116
347.52	0.405	0.013	0.700	0.054	1.193	4.301	1.136
344.16	0.596	0.009	0.806	0.027	1.056	3.478	1.314
342.70	0.074	0.768	0.148	0.683	1.650	1.084	3.544
339.31	0.232	0.634	0.354	0.544	1.433	1.177	2.937
337.08	0.407	0.488	0.504	0.437	1.268	1.330	2.402
336.21	0.520	0.394	0.582	0.378	1.186	1.470	2.070
335.61	0.658	0.282	0.665	0.308	1.097	1.710	2.060
335.56	0.784	0.177	0.750	0.233	1.040	2.065	2.000
335.93	0.868	0.106	0.826	0.165	1.020	2.409	1.561
343.70	0.047	0.856	0.113	0.751	1.911	1.033	4.446
341.31	0.139	0.680	0.235	0.613	1.470	1.153	2.960
340.44	0.222	0.508	0.315	0.530	1.276	1.375	2.104
340.27	0.296	0.374	0.382	0.470	1.168	1.667	1.657
340.40	0.324	0.316	0.406	0.436	1.128	1.822	1.612
339.70	0.420	0.252	0.495	0.369	1.090	1.981	1.572
339.33	0.507	0.192	0.575	0.304	1.064	2.170	1.550
346.48	0.059	0.176	0.114	0.579	1.385	3.527	1.128
345.75	0.055	0.228	0.098	0.606	1.312	2.920	1.197
345.03	0.045	0.338	0.076	0.640	1.277	2.132	1.377
344.71	0.037	0.441	0.061	0.662	1.262	1.708	1.610
344.62	0.029	0.522	0.050	0.678	1.324	1.483	1.845
344.58	0.025	0.574	0.043	0.689	1.323	1.372	2.039
346.65	0.166	0.107	0.313	0.399	1.343	3.975	1.105
344.61	0.176	0.172	0.288	0.457	1.257	3.034	1.192
344.94	0.166	0.165	0.277	0.461	1.266	3.155	1.176
344.87	0.162	0.169	0.271	0.467	1.273	3.128	1.180
344.88	0.162	0.170	0.272	0.468	1.277	3.115	1.172
345.38	0.155	0.155	0.268	0.465	1.291	3.337	1.140
356.74	0.099	0.018	0.350	0.170	1.762	7.264	1.001
341.14	0.184	0.568	0.274	0.562	1.303	1.273	2.349
340.22	0.263	0.464	0.349	0.506	1.203	1.449	1.966
336.13	0.803	0.139	0.774	0.204	1.025	2.255	1.695
335.78	0.759	0.186	0.734	0.243	1.043	2.033	1.899
338.71	0.707	0.096	0.752	0.172	1.022	2.510	1.530
338.94	0.552	0.179	0.606	0.283	1.046	2.197	1.619
339.58	0.425	0.233	0.516	0.357	1.128	2.082	1.415
341.43	0.348	0.213	0.452	0.381	1.124	2.278	1.334

Correlation and Prediction

The activity coefficients derived from the experimental binary VLE data were correlated by the Wilson[18] and NRTL equations.[19] The following objective function was minimized during optimization of the parameters in each of the two equations. The parameters for the methanol + water system were determined from the VLE data at 101.3 kPa presented in our previous work.[1]

$$\mathrm{OF} = \sum_{k=1}^{\mathrm{NDP}}\left[\left(\frac{\gamma_{1,\mathrm{calc}} - \gamma_{1,\mathrm{expt}}}{\gamma_{1,\mathrm{expt}}}\right)_k^2 + \left(\frac{\gamma_{2,\mathrm{calc}} - \gamma_{2,\mathrm{expt}}}{\gamma_{2,\mathrm{expt}}}\right)_k^2\right] \tag{3}$$

where NDP is the number of data points. Table 6 lists the estimated parameters for the three binary systems and the deviations between experimental and calculated vapor phase compositions and bubble point temperatures. The solid and dotted lines in Figures 1−4 also show the correlated results by the Wilson and NRTL equations, respectively. The liquid molar volumes v_i^{L} in the Wilson equation are the constant values shown in Table 1. In accordance with Walas,[20] the mixture nonrandomness parameter, α_{12}, in the NRTL equation was set to 0.3 for nonaqueous mixtures and to 0.4 for aqueous mixtures. The results for the NRTL equation were better than those for the Wilson equation for the two binary systems containing water. For

Table 6. Parameters and Deviations between the Calculated and Experimental Vapor Phase Mole Fractions, Δy_i, and Temperatures, ΔT, for the Wilson and NRTL Equations[a]

	methanol (1) + 1,3-dioxolane (2)	1,3-dioxolane (1) + water (2)	methanol (1) + water (2)	methanol (1) + 1,3-dioxolane (2) + water (3)
Wilson parameters				
$\lambda_{12} - \lambda_{11}$[b]	2746.114	1179.818	1011.344	no ternary parameters
$\lambda_{21} - \lambda_{22}$[b]	673.816	7454.402	1809.072	
deviations				
ΔT/K	0.09	0.35	0.14	0.20
Δy_1	0.002	0.010	0.007	0.008
Δy_2				0.007
NRTL parameters				
α_{12}	0.3	0.4	0.4	no ternary parameters
$g_{12} - g_{22}$[b]	2255.746	3094.316	−768.266	
$g_{21} - g_{11}$[b]	935.446	5123.820	3537.764	
deviations				
ΔT/K	0.09	0.22	0.09	0.27
Δy_1	0.002	0.006	0.006	0.004
Δy_2				0.005

[a] $\Delta y_i = \sum_k |y_{i,\mathrm{expt}} - y_{i,\mathrm{calc}}|_k/N$, $\Delta T = \sum_k |(T_{\mathrm{expt}} - T_{\mathrm{calc}})|_k/N$, N = number of data points. [b] J·mol^{-1}.

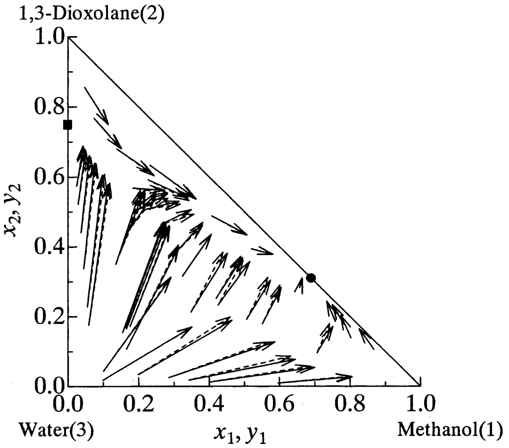

Figure 5. Vapor−liquid equilibrium tie lines (tails of arrows represent liquid phase mole fractions x_1 and x_2, and heads of arrows represent vapor phase mole fractions y_1 and y_2) for methanol (1) + 1,3-dioxolane (2) + water (3) at 101.3 kPa: (●) azeotropic point of methanol (1) + 1,3-dioxolane (2); (■) azeotropic point of 1,3-dioxolane (2) + water (3); (→) experimental values; (·····>) NRTL equation.

the methanol + 1,3-dioxolane system, both equations gave similar results.

The predictions of the VLE of the ternary system methanol + 1,3-dioxolane + water using the binary Wilson and NRTL parameters are shown in Table 6. The results are also summarized in this table. Table 6 shows that the NRTL equation gave lower deviations of vapor phase mole fraction for this ternary system. The result given by the NRTL equation is illustrated by the broken arrows in Figure 5.

Conclusions

Isobaric VLE data were measured for three binary systems and one ternary system containing methanol, 1,3-dioxolane, and water at 101.3 kPa. For both the methanol + 1,3-dioxolane and 1,3-dioxolane + water systems, the experimental data show the existence of a minimum boiling azeotrope. From the behavior of the experimental vapor−liquid tie lines for this ternary system, the valley that connects the two binary minimum boiling azeotropes was also observed. The binary experimental VLE data were correlated by the Wilson and NRTL equations, and the ternary experimental data were compared with those predicted using the binary Wilson and NRTL parameters. The NRTL equation seems to provide a better prediction for vapor phase composition than the Wilson equation for this ternary system.

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