Vapor−Liquid Equilibria for Binary and Ternary Mixtures of 1,3-Dioxolane, 2-Propanol, and 2,2,4-Trimethylpentane at 101.3 kPa

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Vapor−liquid equilibrium (VLE) at 101.3 kPa have been determined for a ternary system (1,3-dioxolane + 2-propanol + 2,2,4-trimethylpentane) and its constituent binary systems (1,3-dioxolane + 2-propanol, 1,3-dioxolane + 2,2,4-trimethylpentane, and 2-propanol + 2,2,4-trimethylpentane). Minimum boiling azeotropes were observed for all of the three binary systems. No azeotropic behavior was found for the ternary system. The activity coefficients of liquid mixtures were obtained from a modified Raoult's law and were used to calculate the reduced excess molar Gibbs free energy g^E/RT. Thermodynamic consistency tests were performed for all VLE data. The VLE data of the binary mixtures were correlated using the Wilson, NRTL, and UNIQUAC activity coefficient models. The models with their best-fitted interaction parameters of the binary systems were used to predict the ternary vapor−liquid equilibrium.

Introduction

Certain oxygenated compounds are usually added to gasoline to improve the octane number and reduce pollution. This work has been carried out as part of the project to study the thermophysical behavior of liquid mixtures including oxygenated compounds and hydrocarbon liquids. The present paper is concerned with an experimental determination of vapor−liquid equilibrium (VLE) for the system formed by the oxygenated compounds of the type {cyclic ether or aliphatic alcohol} with a hydrocarbon liquid. Such data of oxygenated mixtures are important for predicting the vapor-phase composition that would be in equilibrium with different hydrocarbon liquids.

For these reasons, we measured VLE data for a ternary system (1,3-dioxolane + 2-propanol + 2,2,4-trimethylpentane) and three binary systems (1,3-dioxolane + 2-propanol, 1,3-dioxolane + 2,2,4-trimethylpentane, and 2-propanol + 2,2,4-trimethylpentane) at 101.3 kPa. The oxygenated compounds, such as 1,3-dioxolane and 2-propanol, were chosen for the present study because they are two potential candidates as blending agents for reformulated gasoline. The third added compound, 2,2,4-trimethylpentane, represents the hydrocarbon in gasoline. In the past, experimental VLE data were measured at 298.15 K for 1,3-dioxolane + 2,2,4-trimethylpentane.[1] Experimental VLE data were reported at 101.3 kPa for 2-propanol + 2,2,4-trimethylpentane.[2,3] However, we are not aware of any other data in the literature for the systems presented in this study.

Experimental Section

Chemicals. The source and mass purities of the chemicals employed are as follows: 1,3-dioxolane (Merck, > 0.995 mass fraction), 2-propanol (Tedia, > 0.995 mass fraction), and 2,2,4-trimethylpentane (Merck, > 0.997 mass fraction). All chemicals were used without further purification after gas chromatography failed to show any significant impurities. Before measurements, the liquids were dried over molecular sieves (Merck, type 0.3 nm pellets). The purity of each component was further ascertained by comparing its boiling point, density, and refractive index with the corresponding literature values as shown in Table 1. The density ρ was measured at (298.15 ± 0.01) K using a DMA-5000 vibrating-tube densimeter (Anton-Paar; Graz, Austria) with an uncertainty of ± 0.01 $kg \cdot m^{-3}$. The refractive index n_D was measured at (298.15 ± 0.05) K using an automatic Anton Paar RXA-156 refractometer, with an uncertainty of ± 0.00002.

Apparatus and Procedure. The VLE measurements were carried out by circulation for both vapor and liquid in an all-glass equilibrium still (NGW, Wertheim, Germany) of the Hunsmann type[9] connected to a manostat as used by Fowler and Hunt.[10] The boiling temperature was measured with a precision thermometer (Hart Scientific, model 1560/2560) with a platinum RTD probe to within ± 0.01 K, the uncertainty of the measurement being estimated at ± 0.05 K. Constant pressure was maintained by the manostat within ± 0.1 kPa. The equilibrium pressures were determined comparatively via the boiling temperature of pure water, measured in a Świętosławski type ebulliometer[11] connected to the system. The equilibrium still was insulated by an oil jacket, and its temperature was maintained at a temperature of approximately 6 K above the boiling point of the mixture in the boiling chamber to ensure that no phase composition change occurred.

Equilibrium compositions of sampled liquid and condensed vapor phases were analyzed with a Perkin-Elmer Autosystem gas chromatograph (GC). A flame ionization detector (FID) was used along with a capillary column packed (60 m long, 0.25 mm i.d., 0.5 μm film) with Petrocol DH (SUPELCO, PA/USA). Helium was used as the carrier gas with a flow rate of 10 $mL \cdot min^{-1}$. The FID was kept at 473 K. The column of the GC was kept between (333 and 388) K by using a temperature program (initial temperature 333 K, temperature ramp 10 $K \cdot min^{-1}$ to 388 K; temperature maintained at 388 K for 4 min, giving a total run time of 9.5 min). The GC response peaks were integrated by using Perkin-Elmer Turbochrom software. Calibration analyses using gravimetrically prepared standard solutions were carried out to convert the peak area ratios to mole fractions of the sample. The uncertainty of equilibrium

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10.1021/je900327x CCC: $40.75

Table 1. Comparison of Measured Boiling Points T at 101.3 kPa and Densities ρ and Refractive Indices n_D at 298.15 K with Literature Values

	T/K		ρ/kg·m^{-3}		n_D	
compounds	exptl	lit.	exptl	lit.	exptl	lit.
1,3-dioxolane	348.59	348.57[a] 348.60[b]	1058.87	1058.6[a] 1058.593[c]	1.39779	1.3980[b] 1.3984[c]
2-propanol	355.39	355.42[d] 355.392[e]	781.01	780.86[d] 781.26[e]	1.37509	1.3752[e] 1.37512[f]
2,2,4-trimethylpentane	372.37	372.40[d] 372.388[e]	687.73	687.64[d] 687.67[g]	1.38887	1.3890[g]

[a] Kurihara et al., 2003.[4] [b] Wisniak et al., 1997.[5] [c] Francesconi et al., 1984.[1] [d] Hiaki et al., 1994.[3] [e] Riddick et al., 1986.[6] [f] Nagata et al., 2000.[7] [g] Martinez-Soria et al., 1999.[8]

Table 2. VLE Data for the System of 1,3-Dioxolane (1) + 2-Propanol (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2	g^E/RT
355.39	0.000	0.000		1.000	0.000
352.83	0.074	0.173	2.040	0.991	0.044
351.25	0.127	0.260	1.879	1.004	0.083
349.98	0.182	0.332	1.745	1.019	0.117
349.39	0.213	0.366	1.676	1.031	0.134
348.32	0.279	0.428	1.549	1.062	0.166
347.72	0.332	0.470	1.458	1.089	0.182
347.23	0.384	0.505	1.377	1.127	0.196
346.92	0.423	0.530	1.326	1.157	0.203
346.56	0.480	0.565	1.260	1.207	0.209
346.34	0.521	0.596	1.234	1.228	0.208
346.19	0.558	0.606	1.177	1.306	0.209
346.05	0.606	0.630	1.132	1.385	0.204
345.97	0.655	0.660	1.100	1.458	0.193
345.96	0.694	0.692	1.089	1.490	0.181
346.00	0.739	0.710	1.048	1.642	0.164
346.12	0.782	0.755	1.049	1.652	0.147
346.36	0.828	0.794	1.034	1.743	0.123
346.75	0.879	0.832	1.007	1.987	0.089
347.50	0.932	0.893	0.994	2.181	0.048
348.59	1.000	1.000	1.000		0.000

Table 3. VLE Data for the System of 1,3-Dioxolane (1) + 2,2,4-Trimethylpentane (3) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_3	g^E/RT
372.37	0.000	0.000		1.000	0.000
366.59	0.030	0.171	3.276	1.009	0.044
361.81	0.064	0.300	3.100	1.018	0.089
358.60	0.094	0.380	2.946	1.027	0.126
355.13	0.137	0.462	2.736	1.043	0.174
352.04	0.194	0.536	2.473	1.063	0.225
349.71	0.256	0.588	2.216	1.103	0.277
348.61	0.299	0.614	2.054	1.135	0.304
348.02	0.326	0.628	1.965	1.160	0.321
346.83	0.405	0.659	1.727	1.256	0.357
346.35	0.445	0.675	1.636	1.304	0.366
345.89	0.498	0.690	1.517	1.396	0.375
345.32	0.599	0.706	1.316	1.690	0.375
345.17	0.645	0.717	1.247	1.847	0.360
345.08	0.671	0.724	1.214	1.949	0.350
345.02	0.708	0.736	1.172	2.105	0.330
344.99	0.786	0.771	1.107	2.494	0.276
345.10	0.828	0.794	1.078	2.781	0.238
345.40	0.877	0.824	1.046	3.289	0.186
346.07	0.926	0.864	1.016	4.130	0.119
348.59	1.000	1.000	1.000		0.000

Table 4. VLE Data for the System of 2-Propanol (2) + 2,2,4-Trimethylpentane (3) at 101.3 kPa

T/K	x_2	y_2	γ_2	γ_3	g^E/RT
372.37	0.000	0.000		1.000	0.000
360.65	0.058	0.319	4.460	1.019	0.104
358.30	0.081	0.382	4.195	1.019	0.133
356.27	0.105	0.423	3.886	1.040	0.178
354.65	0.132	0.457	3.566	1.063	0.220
353.44	0.167	0.485	3.142	1.091	0.264
352.14	0.232	0.527	2.592	1.133	0.317
350.80	0.353	0.565	1.931	1.292	0.398
350.27	0.412	0.580	1.736	1.397	0.424
350.06	0.514	0.606	1.467	1.596	0.424
349.99	0.523	0.612	1.460	1.605	0.424
349.94	0.545	0.614	1.409	1.677	0.422
349.47	0.613	0.628	1.307	1.930	0.418
349.67	0.637	0.639	1.269	1.983	0.400
349.73	0.684	0.653	1.204	2.186	0.374
349.82	0.728	0.660	1.139	2.481	0.342
350.00	0.780	0.682	1.091	2.852	0.298
350.31	0.816	0.702	1.059	3.163	0.259
351.36	0.894	0.794	1.047	3.668	0.179
352.94	0.946	0.878	1.025	4.052	0.099
355.39	1.000	1.000	1.000		0.000

Table 5. Parameters of Vapor Pressure, of Liquid Molar Volume, and of UNIQUAC Equation for the Pure Components in This Study

parameters	1,3-dioxolane	2-propanol	2,2,4-trimethylpentane
$P°$/Pa			
A	71.018	73.032	120.81
B	−6400.8	−7215.9	−7550.0
C	−7.0388	−7.1145	−16.111
D	$6.02 \cdot 10^{-7}$	$4.62 \cdot 10^{-6}$	$1.71 \cdot 10^{-2}$
E	2.0	2.0	1.0
v^L/(m^3·kmol^{-1})			
a	1.3878	1.18	0.5886
b	0.2741	0.26475	0.27373
c	553.78	508.31	543.96
d	0.2857	0.243	0.2846
UNIQUAC q	2.6400	2.5078	5.0079
UNIQUAC r	3.1854	2.7790	5.8463

composition measurements was estimated to be within ± 0.003 units of mole fraction.

Results and Discussion

The VLE data for the binary systems of 1,3-dioxolane + 2-propanol, 1,3-dioxolane + 2,2,4-trimethylpentane, and 2-propanol + 2,2,4-trimethylpentane at the pressure of 101.3 kPa are presented in Tables 2 to 4, respectively. The activity coefficients of pure liquid γ_i were calculated from the equality of component fugacity in both liquid and vapor phases under the assumption of an ideal behavior of the vapor phase, i.e.

$$\gamma_i = \frac{y_i P}{x_i P_i^\circ} \tag{1}$$

where x_i and y_i are the liquid and vapor mole fractions at equilibrium for pure component; P_i° is the vapor pressure for pure component i; and P is the total pressure. Equation 1 is also known as the modified Raoult's law. The temperature dependence of the pure component vapor pressure ($P°$) was calculated from

$$\ln P^\circ\ (\mathrm{Pa}) = A + \frac{B}{T} + C \ln T + DT^E \tag{2}$$

where A, B, C, D, and E are the component specific coefficients for vapor pressure and T is the equilibrium temperature in Kelvin. The constants A, B, C, D, and E for 1,3-dioxolane and

Table 6. Results of the Thermodynamic Consistency Test for Binary VLE Data

	consistency test		Margules[e]	
systems $i + j$	rmsd[a]	index	A_{ij}	A_{ji}
$1 + 2$[b]	0.029	2	273.307	305.142
$1 + 3$[c]	0.052	3	479.037	580.423
$2 + 3$[d]	0.059	3	641.448	584.774

[a]

$$\mathrm{rmsd}\delta\ \ln\left(\frac{\gamma_i}{\gamma_j}\right) = \sqrt{\frac{\sum_{k=1}^{n}\left[\left(\ln\frac{\gamma_i}{\gamma_j}\right)_k^{\mathrm{exptl}} - \left(\ln\frac{\gamma_i}{\gamma_j}\right)_k^{\mathrm{calcd}}\right]^2}{n}}$$

[b] 1 + 2: 1,3-dioxolane (1) + 2-propanol (2). [c] 1 + 3: 1,3-dioxolane (1) + 2,2,4-trimethylpentane (3). [d] 2 + 3: 2-propanol (2) + 2,2,4-trimethylpentane (3). [e] Margules equation:

$$\frac{g^{\mathrm{E}}}{RT} = x_i x_j (A'_{ji} x_i + A'_{ij} x_j);$$

$$A'_{ij} = \frac{A_{ij}}{T},\ A'_{ji} = \frac{A_{ji}}{T}$$

Table 7. VLE Data Reduction for Binary Systems with the Wilson, the NRTL, and the UNIQUAC Models

	system				rmsd[b]	
models	$i + j$	A_{ij}[a]	A_{ji}[a]	α	δT/K	δy_i
Wilson	1 + 2	347.48	293.57		0.11	0.006
	1 + 3	1056.20	276.47		0.31	0.006
	2 + 3	1373.60	199.15		0.39	0.009
NRTL	1 + 2	75.76	82.53	0.262	0.14	0.004
	1 + 3	225.76	68.67	0.271	0.39	0.005
	2 + 3	146.45	192.80	0.277	0.40	0.008
UNIQUAC	1 + 2	59.55	51.84		0.14	0.005
	1 + 3	−42.17	238.02		0.24	0.006
	2 + 3	−98.65	387.21		0.34	0.008

[a] The binary adjustable parameters for Wilson: $A_{ij} = (\lambda_{ij} - \lambda_{ii})/R$, $A_{ji} = (\lambda_{ji} - \lambda_{jj})/R$. NRTL: $A_{ij} = (g_{ij} - g_{jj})/R$, $A_{ji} = (g_{ji} - g_{ii})/R$. UNIQUAC: $A_{ij} = (U_{ij} - U_{jj})/R$, $A_{ji} = (U_{ji} - U_{ii})/R$. [b] rmsd: root-mean-square deviation, defined as:

$$\mathrm{rmsd}\ \delta T = \sqrt{\frac{\sum_{j=1}^{n}(T_j^{\mathrm{exptl}} - T_j^{\mathrm{calcd}})^2}{n}};$$

$$\mathrm{rmsd}\ \delta y_i = \sqrt{\frac{\sum_{j=1}^{n}(y_{i,j}^{\mathrm{exptl}} - y_{i,j}^{\mathrm{calcd}})^2}{n}}$$

[c] 1 + 2: 1,3-dioxolane (1) + 2-propanol (2). [d] 1 + 3: 1,3-dioxolane (1) + 2,2,4-trimethylpentane (3). [e] 2 + 3: 2-propanol (2) + 2,2,4-trimethylpentane (3).

2-propanol were obtained after fitting the experimental vapor pressure data from the literature.[12,13] The corresponding parameters for 2,2,4-trimethylpentane were obtained directly from the CHEMCAD Data Bank.[14] Table 5 lists the values of these constants A, B, C, D, and E. The reduced excess molar Gibbs energy (g^{E}/RT) was calculated according to the definition

$$\frac{g^{\mathrm{E}}}{RT} = \sum_{i=1}^{N} x_i \ln \gamma_i \tag{3}$$

where N is the number of components.

The thermodynamic consistency for the VLE data of three binary systems was treated using the direct test proposed by Van Ness.[15] In the direct test, a proposed consistency index associated with the test characterizes the degree of departure of a data set from consistency. The consistency index starts at 1 for highly consistent data and goes to 10 for data of very poor quality based on an appropriate measure in the rmsd (root-mean-square deviation) value of $\delta\ \ln(\gamma_i/\gamma_j)$. The residual in the logarithms of the activity coefficient ratio $\delta\ \ln(\gamma_i/\gamma_j)$ is calculated between two sets of activity coefficients coming from the experimental data and from the correlation.

For this test, the values of g^{E}/RT in this study were calculated from experimental activity coefficients and were correlated with the three-suffix Margules equation[16] with a temperature dependence assumed for each parameter. With constants from this fit, the rmsd values of $\delta\ \ln(\gamma_i/\gamma_j)$ were determined. Table 6 shows the results for the thermodynamic consistency test. The consistency index values for 1,3-dioxolane + 2-propanol, 1,3-dioxolane + 2,2,4-trimethylpentane, and 2-propanol + 2,2,4-trimethylpentane systems were found to be 2, 3, and 3, respectively, suggesting that all binary VLE data are of acceptable quality. The values of $\delta\ \ln(\gamma_i/\gamma_j)$ for these three binary systems were illustrated in

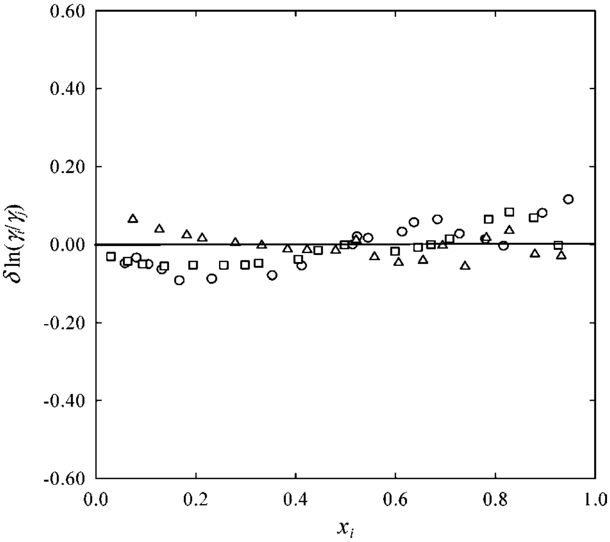

Figure 1. Results of $\delta\ \ln(\gamma_i/\gamma_j)$ in the direct test of consistency for three binary systems: Δ, 1,3-dioxolane (1) + 2-propanol (2), $x_i = x_1$; □, 1,3-dioxolane (1) + 2,2,4-trimethylpentane (3), $x_i = x_1$; ○, 2-propanol (2) + 2,2,4-trimethylpentane (3).

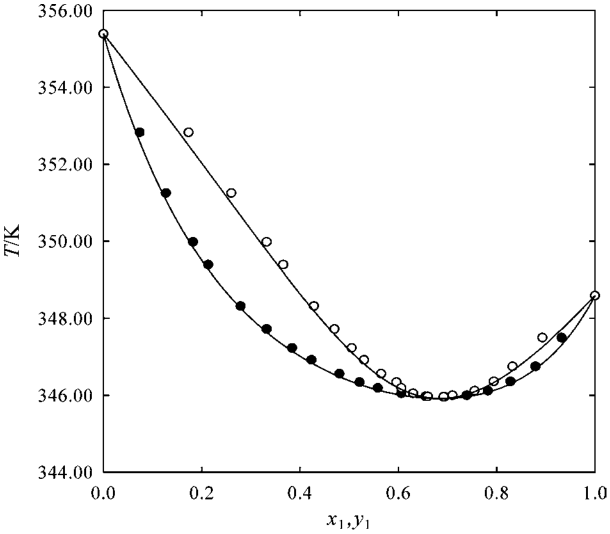

Figure 2. Experimental $T-x_1-y_1$ diagram of 1,3-dioxolane (1) + 2-propanol (2) at 101.3 kPa: ●,○, this work; —, Wilson equation. Full symbols refer to liquid phase compositions. and open symbols refer to vapor phase compositions.

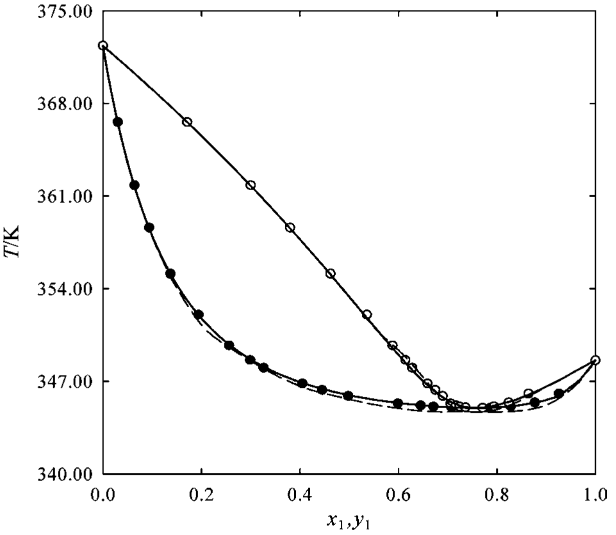

Figure 3. Experimental $T-x_1-y_1$ diagram of 1,3-dioxolane (1) + 2,2,4-trimethylpentane (3) at 101.3 kPa: ●,○, this work; - -, calculated from Francesconi et al.;[1] —, Wilson equation. Full symbols refer to liquid phase compositions, and open symbols refer to vapor phase compositions.

Figure 1. The residuals of three binaries are small and seen to scatter fairly about zero.

The VLE experimental data of the three binary systems were then calculated with the various activity coefficient models, including the Wilson,[17] the NRTL,[18] and the UNIQUAC[19] models by a bubble temperature calculation procedure.[20] Estimation of energy parameters of all the models studied was based on the minimization between the predicted and experimental γ values as the following objective function

$$\mathrm{OF} = \sum_{k=1}^{n} \sum_{i=1}^{N} \left[\left(\frac{\gamma_i^{\mathrm{exptl}} - \gamma_i^{\mathrm{calcd}}}{\gamma_i^{\mathrm{exptl}}} \right)^2 \right]_k \tag{4}$$

where n is the number of data points and N is the number of components. The liquid molar volume (v^{L}) of pure component for the Wilson equation was evaluated from

$$v^{\mathrm{L}}\,(\mathrm{m^3 \cdot kmol^{-1}}) = \frac{b^{\left[1+\left(1-\frac{T}{c}\right)^d\right]}}{a} \tag{5}$$

where a, b, c, and d are the component-specific coefficients for liquid molar volume and T is the temperature in Kelvin. The values of the constants a, b, c, and d for the liquid molar volume together with the parameters required for the UNIQUAC equation were also shown in Table 5. All the activity coefficient models gave satisfactory representations for the investigated binary systems, as shown in Table 7.

Figures 2 to 4 are the temperature−composition diagrams for the binary systems of 1,3-dioxolane (1) + 2-propanol (2), 1,3-dioxolane (1) + 2,2,4-trimethylpentane (3), and 2-propanol (2) + 2,2,4-trimethylpentane (3), respectively. All these three systems show the azeotropes with a minimum boiling temperature. The azeotropic composition was obtained by determining the x_i value that makes the function $((x_i - y_i) = f(x_i))$ zero. The corresponding azeotropic temperature was computed from the experimental results around the azeotropic point, using the x_i values previously determined. The azeotropic points determined from the experimental VLE data for the three binary systems are summarized in Table 8 together with those from the literature and those from the Wilson, the NRTL, and the UNIQUAC models.

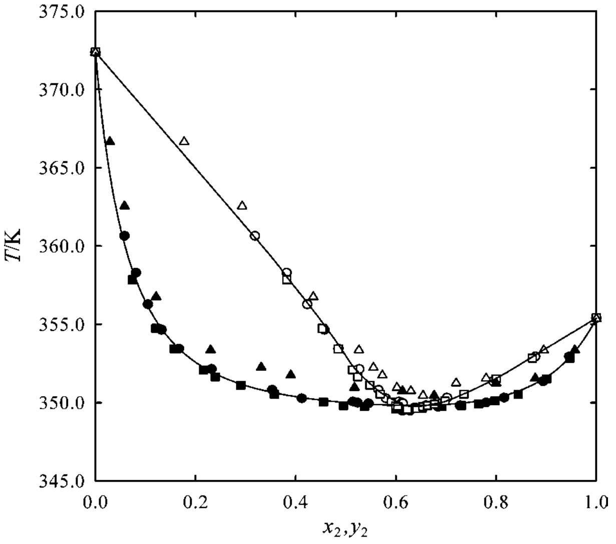

Figure 4. Experimental $T-x_1-y_1$ diagram of 2-propanol (2) + 2,2,4-trimethylpentane (3) at 101.3 kPa: ●,○, this work; ▲,△, Bures et al.;[2] ■,□, Hiaki et al.;[3] —, Wilson equation. Full symbols refer to liquid phase compositions, and open symbols refer to vapor phase compositions.

Table 8. Comparison of Azeotropic Points for Binary Systems at 101.3 kPa

source	T^{az}/K	x_i^{az}
1,3-Dioxolane (1) +2-Propanol (2)		
this work	345.95	0.668
Wilson	346.06	0.690
NRTL	345.94	0.667
UNIQUAC	346.11	0.679
1,3-Dioxolane (1) + 2,2,4-Trimethylpentane (3)		
this work	344.94	0.757
Wilson	345.21	0.765
NRTL	345.33	0.760
UNIQUAC	345.22	0.755
2-Propanol (2) + 2,2,4-Trimethylpentane (3)		
this work	349.66	0.642
Hiaki et al.[3]	349.58	0.635
Wilson	350.14	0.644
NRTL	350.13	0.634
UNIQUAC	350.08	0.629

Figures 3 and 4 contain a comparison of our experimental $T-x-y$ values with those from the literature for 1,3-dioxolane + 2,2,4-trimethylpentane and 2-propanol + 2,2,4-trimethylpentane. A reasonable agreement between our experimental and the literature results is obtained except for those from Bures et al.[2] for 2-propanol + 2,2,4-trimethylpentane, which show higher values in equilibrium temperature. Figure 5 plots the reduced excess molar Gibbs energy (g^{E}/RT) as a function of liquid composition for these three binary systems. The g^{E}/RT values of these three binary systems are all positive over the entire composition range.

The equilibrium phase compositions were also measured for the ternary system of 1,3-dioxolane (1) + 2-propanol (2) + 2,2,4-trimethylpentane (3) at 101.3 kPa, and the results are presented in Table 9. Similarly, eq 1 was applied to calculate the activity coefficients for each component, and eq 3 was used to obtain g^{E}/RT for the ternary mixtures. The g^{E}/RT values for the ternary mixtures are all positive. As shown in this table, no ternary azeotrope was found for the system. Figure 6 shows the experimental tie-lines between the saturated vapor and liquid phases, indicating the absence of a ternary azeotrope. The residue curve map using the Wilson equation for the ternary system is presented in Figure 7.

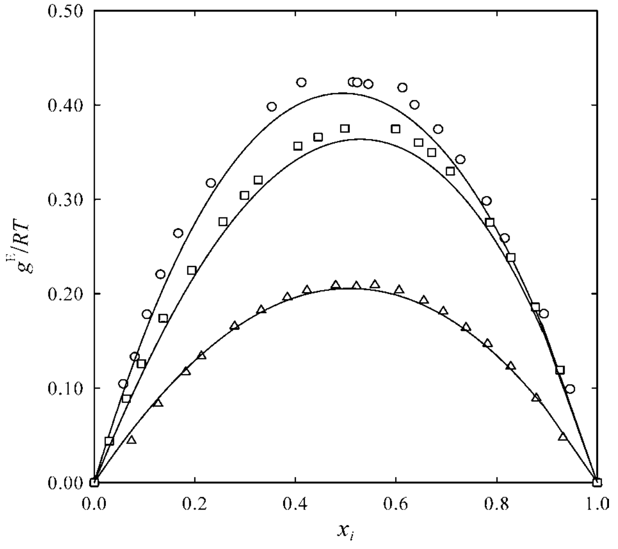

Figure 5. Experimental g^E/RT vs x_i diagram at 101.3 kPa for the systems: Δ, 1,3-dioxolane (1) + 2-propanol (2), $x_i = x_1$; □, 1,3-dioxolane (1) + 2,2,4-trimethylpentane (3), $x_i = x_1$; ○, 2-propanol (2) + 2,2,4-trimethylpentane (3), $x_i = x_2$; —, Wilson equation.

Table 9. VLE Data for the Ternary System of 1,3-Dioxolane (1) + 2-Propanol (2) + 2,2,4-Trimethylpentane (3) at 101.3 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	g^E/RT
343.00	0.601	0.157	0.611	0.177	1.228	1.897	2.185	0.413
343.02	0.595	0.258	0.581	0.253	1.179	1.649	2.814	0.379
343.23	0.506	0.153	0.560	0.185	1.326	2.014	1.850	0.460
343.38	0.704	0.154	0.655	0.171	1.109	1.838	3.016	0.324
343.50	0.537	0.259	0.550	0.246	1.194	1.627	2.452	0.404
343.55	0.434	0.161	0.517	0.216	1.412	2.204	1.614	0.471
343.78	0.498	0.354	0.534	0.305	1.261	1.401	2.642	0.379
343.83	0.399	0.260	0.462	0.281	1.359	1.754	1.827	0.474
343.90	0.400	0.374	0.464	0.335	1.359	1.449	2.151	0.434
344.10	0.348	0.270	0.431	0.294	1.441	1.747	1.729	0.487
344.37	0.299	0.439	0.375	0.388	1.446	1.401	2.153	0.459
344.37	0.378	0.463	0.461	0.361	1.406	1.236	2.664	0.383
344.50	0.332	0.206	0.448	0.238	1.549	1.821	1.610	0.489
344.71	0.608	0.049	0.677	0.062	1.269	1.977	1.790	0.378
344.89	0.704	0.047	0.704	0.063	1.133	2.078	2.188	0.317
345.04	0.299	0.549	0.382	0.430	1.440	1.206	2.878	0.373
345.09	0.800	0.047	0.759	0.064	1.067	2.092	2.687	0.238
345.42	0.698	0.255	0.666	0.257	1.061	1.527	3.763	0.212
345.45	0.598	0.354	0.598	0.326	1.111	1.393	3.633	0.242
345.57	0.388	0.043	0.568	0.090	1.620	3.150	1.374	0.417
345.59	0.180	0.435	0.276	0.428	1.696	1.480	1.756	0.482
345.61	0.195	0.546	0.276	0.456	1.565	1.255	2.362	0.434
345.69	0.807	0.146	0.749	0.169	1.023	1.733	3.971	0.164
345.81	0.176	0.323	0.286	0.389	1.784	1.794	1.471	0.484
346.09	0.927	0.037	0.882	0.047	1.035	1.870	4.429	0.109
346.14	0.195	0.648	0.286	0.505	1.593	1.145	2.984	0.350
346.43	0.171	0.217	0.304	0.345	1.912	2.306	1.273	0.440
346.64	0.092	0.545	0.162	0.519	1.880	1.369	1.937	0.469
346.65	0.383	0.587	0.472	0.440	1.316	1.077	6.465	0.205
346.73	0.095	0.451	0.156	0.479	1.748	1.521	1.767	0.501
347.06	0.091	0.361	0.173	0.448	2.002	1.752	1.504	0.489
347.27	0.179	0.123	0.355	0.261	2.074	2.970	1.188	0.384
347.50	0.312	0.043	0.528	0.108	1.756	3.481	1.209	0.352
347.87	0.101	0.755	0.176	0.613	1.786	1.108	3.101	0.299
348.23	0.072	0.658	0.132	0.560	1.857	1.144	2.385	0.368
348.39	0.087	0.221	0.189	0.396	2.189	2.392	1.247	0.414
348.60	0.046	0.395	0.094	0.517	2.045	1.731	1.437	0.453
348.67	0.043	0.640	0.085	0.585	1.974	1.206	2.145	0.391
348.69	0.193	0.761	0.307	0.619	1.587	1.072	3.313	0.197
348.85	0.056	0.284	0.124	0.470	2.198	2.166	1.260	0.416
348.95	0.043	0.421	0.090	0.528	2.071	1.635	1.455	0.439
351.15	0.085	0.876	0.165	0.736	1.788	0.999	4.824	0.110
351.30	0.176	0.037	0.435	0.113	2.265	3.609	1.086	0.256
351.40	0.037	0.863	0.072	0.754	1.778	1.028	3.280	0.164
351.78	0.079	0.113	0.214	0.305	2.445	3.127	1.108	0.283
352.26	0.039	0.148	0.121	0.385	2.757	2.954	1.114	0.288
354.48	0.059	0.073	0.187	0.248	2.625	3.523	1.112	0.241
355.91	0.078	0.039	0.263	0.156	2.670	3.915	1.074	0.193

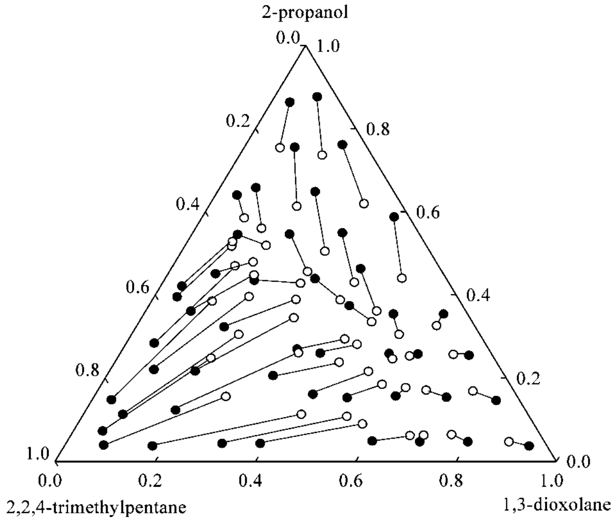

Figure 6. Tie-lines for the ternary system of 1,3-dioxolane (1) + 2-propanol (2) + 2,2,4-trimethylpentane (3) at 101.3 kPa: ●, liquid phase; ○, vapor phase.

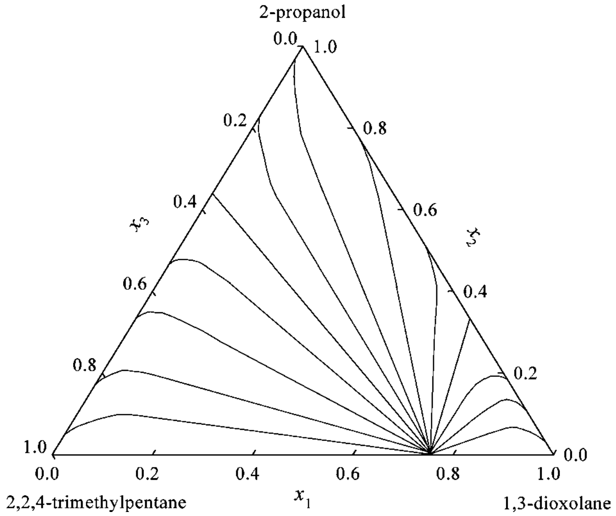

Figure 7. Residue curve map using the Wilson equation for the ternary system of 1,3-dioxolane (1) + 2-propanol (2) + 2,2,4-trimethylpentane (3) at 101.3 kPa.

The ternary system was found to be thermodynamically consistent as tested by the McDermott−Ellis method modified by Wisniak and Tamir.[21,22] According to this method, two experimental points *a* and *b* are considered to be thermodynamically consistent if $D < D_{\max}$ where D is a local deviation and $D_{\max}$ is a maximum deviation, both related to the equilibrium data *a* and *b*. The errors in the present measurements as $\delta P = \pm 0.1$ kPa, $\delta T = \pm 0.05$ K, and $\delta x = \pm 0.003$ mol fraction units were used for the consistency method. The calculated $D_{\max} - D$ values were greater than zero for all experimental points with a mean value of 0.101, which indicates that the system is thermodynamically consistent according to the method.

The experimental VLE data of the ternary system of 1,3-dioxolane + 2-propanol + 2,2,4-trimethylpentane have been predicted using the Wilson, the NRTL, and the UNIQUAC models for the activity coefficients of the components with the binary interaction parameters from Table 7. The average deviations of the predicted bubble temperatures and saturated vapor compositions for the ternary mixtures are summarized in Table 10. As can be seen, there are no significant differences in the prediction results among these models.

Table 10. VLE Prediction for the Ternary System of 1,3-Dioxolane (1) + 2-Propanol (2) + 2,2,4-Trimethylpentane (3) from the Determined Binary Parameters in Table 7

	rmsd[a]			
models	δT/K	δy_1	δy_2	δy_3
Wilson	0.50	0.012	0.014	0.017
NRTL	0.60	0.012	0.013	0.016
UNIQUAC	0.68	0.012	0.013	0.016

[a] rmsd as defined in Table 7.

Conclusions

Isobaric VLE data were determined experimentally for a ternary system (1,3-dioxolane + 2-propanol + 2,2,4-trimethylpentane) and its constituent binary systems (1,3-dioxolane + 2-propanol, 1,3-dioxolane + 2,2,4-trimethylpentane, and 2-propanol + 2,2,4-trimethylpentane) at 101.3 kPa. Comparison between experimental and literature data has been made for the binary systems of 1,3-dioxolane + 2,2,4-trimethylpentane and 2-propanol + 2,2,4-trimethylpentane. A reasonable agreement between our experimental and the literature results is obtained. All of the binary systems show the azeotropes with a minimum boiling temperature. No azeotropic behavior was found for the ternary system. The activity coefficients of pure liquid were obtained from the modified Raoult's law. The g^E/RT values for binary and ternary mixtures are all positive.

The thermodynamic consistency of the VLE data was tested for the three binary systems using the Van Ness direct test. All the binary VLE data were shown to be acceptable by the test. Using the test of McDermott−Ellis as modified by Wisniak and Tamir for ternary VLE data, the ternary system adequately fulfilled the criterion of thermodynamic consistency. Reduction of the binary VLE data using the Wilson, the NRTL, and the UNIQUAC models showed that all three models gave satisfactory correlations. On the basis of the information of the constituent binaries, the experimental ternary VLE data have been predicted using these three liquid activity coefficient models. No significant difference in the prediction was found from these models.

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Received for review April 3, 2009. Accepted May 21, 2009. The authors wish to extend their deep gratitude for the support by the National Science Council of Republic of China under grant NSC 95-2221-E-126-010-MY3.

JE900327X