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Isobaric Vapor–Liquid Equilibrium for Binary Systems of Toluene + Ethanol and Toluene + Isopropanol at (101.3, 121.3, 161.3, and 201.3) kPa

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ABSTRACT: Vapor–liquid equilibria (VLE) data for the toluene + ethanol and toluene + isopropanol binary systems have been measured at (101.3, 121.3, 161.3, and 201.3) kPa using a VLE recirculating still. The experimental data were checked with the Herington method, which showed thermodynamic consistency. The experimental VLE data were correlated with Wilson, nonrandom two-liquid (NRTL), and universal quasichemical (UNIQUAC) activity coefficient models. The results show that the calculated values of the vapor-phase mole fraction and boiling temperature by the Wilson, NRTL, and UNIQUAC models agree well with the experimental data. Furthermore, azeotropic VLE behaviors can be observed from the experimental data.

INTRODUCTION

Ethanol (with an International Union of Pure and Applied Chemistry (IUPAC) systematic name of ethanol), isopropanol (IUPAC name, propan-2-ol), and toluene (IUPAC name, methylbenzene) are widely used compounds in many industrial applications such as pharmaceutical manufacturing, preparation of pesticide, production of dyestuffs, and cellulose synthesis.[1−3] Also, toluene can be used as an excellent solvent in coating and cleaning agents and plays an important role in organic resins synthesis.[4] Ethanol was found to be an excellent gasoline additive and used extensively in the industry such as balata, plastic, disinfectant, and printing ink.[5,6] Isopropanol was used widely in the fields of perfumery, cosmetics, preservative, antifreeze agents, and sterilizing agents. In view of these considerations, many researchers[7] devote their time to obtaining a high-quality reagent from the mixture, and distillation is a feasible process for such separations. However, the system (toluene + ethanol, toluene + isopropanol) forms an azeotrope, preventing the separation through conventional distillation.[8,9] In the separation of azeotropic mixtures, pressure swing distillation[10−12] is often mentioned as an alternative process. As a result, vapor–liquid equilibrium (VLE) data especially at different pressures are very essential in the design, simulation, operation, and optimization of distillation processes. However, these data are scarce. Until now, Kwak et al.,[13] Zéberg-Mikkelsen et al.,[14] and Kretschmer and Wiebe[15] report the isothermal VLE data of the system of toluene with ethanol, but the isobaric VLE data of this system are small in number. To our knowledge, VLE experimental data of toluene with isopropanol are still not available in the literature.

Isobaric VLE data were measured for toluene + ethanol and toluene + isopropanol binary systems using a VLE equilibrium recirculating apparatus at (101.3, 121.3, 161.3, and 201.3) kPa. The binary VLE systems are both thermodynamically strongly deviating from ideal behavior and show an azeotrope with a minimum boiling azeotrope at testing pressure. The deviation from ideal gas behavior caused by the interaction between two molecules in the vapor phase is described with the Soave–Redich–Kwong (SRK) equation. The nonidealities in the liquid phase are considered by the Wilson model,[22] nonrandom two-liquid model (NRTL),[23] and universal quasi-chemical theory (UNIQUAC) model.[24] The experimental VLE data which had been tested with the Herington method showed good thermodynamic consistency.

Table 1. Physical Properties of the Pure Components

component	ethanol	isopropanol	toluene
$M/\mathrm{g\cdot mol^{-1}}$	46.70^{d}	60.09^{d}	92.13^{d}
T_b/K	351.44^{c}	355.5^{c}	383.78^{c}
T_c/K	514.0^{c}	508.3^{c}	591.80^{c}
P_c/MPa	6.137^{c}	4.764^{c}	4.110^{c}
$V_c/\mathrm{cm^3\cdot mol^{-1}}$	168.0^{c}	222.0^{c}	316.0^{c}
$\rho/\mathrm{g\cdot cm^{-3}}(T = 293\ \mathrm{K})$	0.7893^{d}	0.7863^{d}	0.8669^{d}
r	2.1055^{a}	2.7791^{b}	3.9228^{a}
q	1.9720^{a}	2.5080^{b}	2.9680^{a}

[a] Taken from ref 16. [b] Taken from ref 17. [c] Taken from ref 18. [d] Taken from ref 19.

Table 2. Antoine Constants for the Pure Components[a]

	Antoine constants[b]			
component	A	B	C	temperature range/K
toluene	6.05043	1327.620	−55.525	286 to 420
ethanol	6.84806	1358.124	−71.034	273 to 464
isopropanol	6.40823	1107.303	−103.944	325 to 461

[a] Antoine equation: $\log10(P) = A - B/(T + C)$ with P/kPa and T/K. [b] Taken from ref 20.

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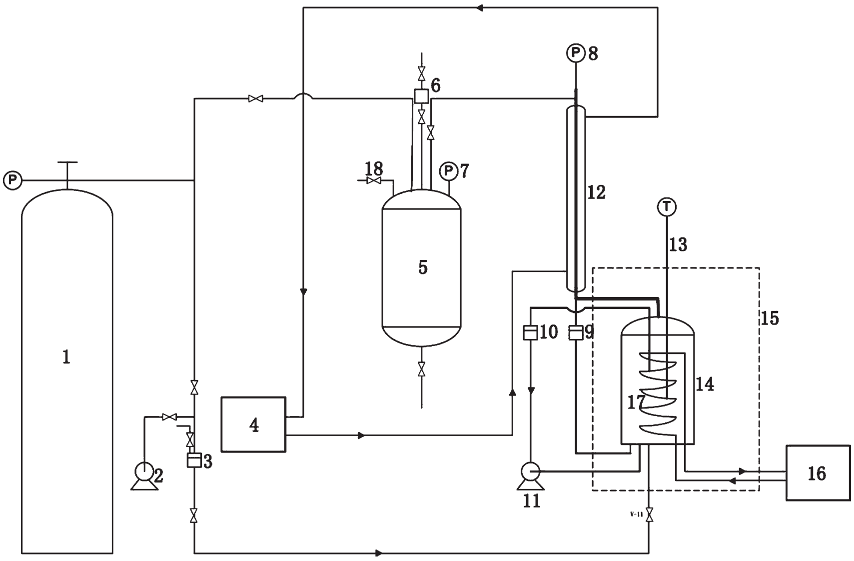

Figure 1. Schematic diagram of the VLE apparatus: 1, N_2 cylinder; 2, vacuum pump; 3, sample inlet; 4, cooling circulating tank; 5, buffer tank; 6, pressure regulator; 7, precision pressure gauge; 8, pressure transducer; 9, vapor-phase sampling port; 10, liquid-phase sampling port; 11, peristaltic pump; 12, condenser pipe; 13, platinum thermometer; 14, equilibrium still; 15, Calorstat oven; 16, constant temperature oil bath; 17, heating coil; 18, gas release valve.

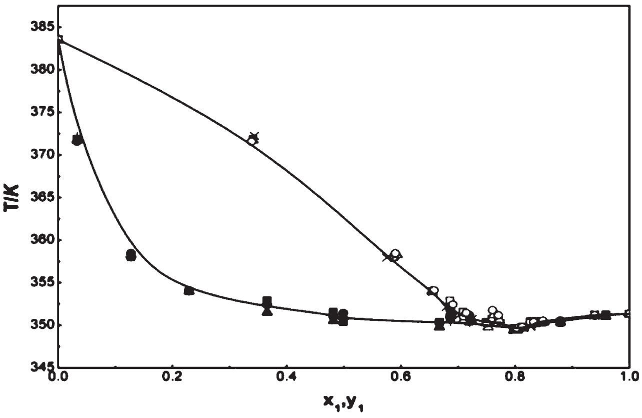

Figure 2. T, x_1, y_1 diagram for the ethanol (1) + toluene (2) system at 101.3 kPa: +, ×, (x_1, y_1) experimental data in this work; ■, □, (x_1, y_1) correlated results by the NRTL model; ▲, △, (x_1, y_1) correlated results by the Wilson model; ●, ○, (x_1, y_1) correlated results by the UNIQUAC model; —, fitted curve by experimental data.

The Wilson, NRTL, and UNIQUAC equations were used to correlate the experimental data. The azeotropes at each pressure were also evaluated for both binary systems.

■ EXPERIMENTAL SECTION

Materials. All of the analytical reagents used were supplied by Tianjin Kewei Reagent Co. with a minimum mass fraction purity of 0.997. The purities of ethanol (analytical reagent grade (AR), 0.997), isopropanol (AR, 0.997), and toluene (AR, 0.997) were checked by gas chromatography (GC-7890A, Agilent Technologies). The GC analysis failed to show any observable impurities for the reagents, so all of the chemicals were used without further purification. Physical properties and Antoine constants of the pure components are shown in Tables 1 and 2.

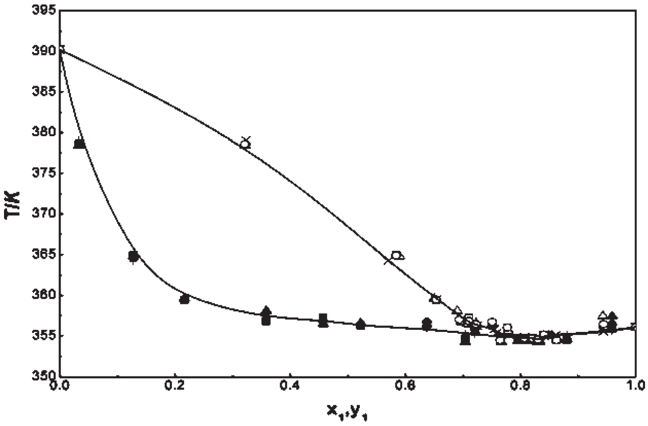

Figure 3. T, x_1, y_1 diagram for the ethanol (1) + toluene (2) system at 121.3 kPa: +, ×, (x_1, y_1) experimental data in this work; ■, □, (x_1, y_1) correlated results bythe NRTL model; ▲, △, (x_1, y_1) correlated results by the Wilson model; ●, ○, (x_1, y_1) correlated results by the UNIQUAC model; —, fitted curve by experimental data.

Apparatus and Procedure.[25] In this work, the VLE measurements were performed in a recirculation VLE still (a modified rose still described by Huang et al.[26]). A schematic diagram of the apparatus is shown in Figure 1. This apparatus is made of stainless steel to adapt to different elevated pressures. The internal volume of the still was about 120 cm^3 of which the liquid occupied about 100 cm^3. Due to the good heat conductivity of stainless steel, the still was not exposed in air but placed in a cuboidal calorstat. A buffer tank (total volume of about 3 L) was used to control the system pressure with high purity nitrogen (0.99999) as the working substance. As an uncondensable and inert gas, nitrogen did not disturb the measurement of the equilibrium components.

During the experiments, when the leakage test for the experimental apparatus had been done, the apparatus was first evacuated

Table 3. Experimental VLE Data for the System Ethanol (1) + Toluene (2)[a]

x_1	y_1^{exp}	T^{exp}/K	$u(x)$	$u(y)$	$u(T)$	x_1	y_1^{exp}	T^{exp}/K	$u(x)$	$u(y)$	$u(T)$
		P = 101.3 kPa						P = 121.3 kPa			
0.0000	0.0000	383.55	0.001	0.001	0.2	0.0000	0.0000	390.26	0.001	0.001	0.2
0.0331	0.3438	372.25	0.001	0.001	0.1	0.0335	0.3240	379.05	0.006	0.010	0.1
0.1276	0.5753	357.95	0.003	0.006	0.2	0.1279	0.5701	364.25	0.008	0.002	0.2
0.2291	0.6557	353.95	0.011	0.001	0.2	0.2166	0.6550	359.55	0.014	0.004	0.1
0.3659	0.6796	352.15	0.006	0.002	0.3	0.3586	0.6995	357.25	0.005	0.003	0.1
0.4819	0.7027	351.25	0.012	0.002	0.3	0.4573	0.7048	356.95	0.002	0.004	0.2
0.4994	0.7248	350.75	0.005	0.003	0.2	0.5228	0.7253	356.25	0.009	0.006	0.2
0.6676	0.7496	350.35	0.003	0.004	0.2	0.6376	0.7550	355.85	0.005	0.003	0.1
0.6870	0.7659	350.35	0.001	0.005	0.2	0.7044	0.7576	355.35	0.006	0.009	0.1
0.7199	0.7738	350.25	0.002	0.005	0.2	0.7212	0.7797	355.15	0.003	0.001	0.1
0.7974	0.8027	349.65	0.002	0.001	0.1	0.7950	0.8070	354.85	0.002	0.002	0.1
0.8142	0.8126	349.75	0.001	0.001	0.1	0.8182	0.8201	354.75	0.001	0.002	0.1
0.8344	0.8274	349.85	0.001	0.003	0.1	0.8337	0.8296	354.45	0.005	0.002	0.1
0.8400	0.8346	350.25	0.001	0.003	0.1	0.8488	0.8410	355.05	0.001	0.002	0.1
0.8792	0.8433	350.45	0.003	0.003	0.1	0.8807	0.8621	355.15	0.001	0.002	0.1
0.9586	0.9392	351.25	0.001	0.001	0.2	0.9589	0.9445	355.55	0.001	0.002	0.1
1.0000	1.0000	351.35	0.001	0.001	0.2	1.0000	1.0000	356.11	0.001	0.001	0.1
		P = 161.3 kPa						P = 201.3 kPa			
0.0000	0.0000	400.75	0.001	0.001	0.2	0.0000	0.0000	409.65	0.001	0.001	0.2
0.0333	0.2796	390.15	0.001	0.003	0.2	0.0293	0.2708	399.25	0.002	0.001	0.1
0.1231	0.5718	374.35	0.001	0.006	0.1	0.1158	0.5904	381.45	0.002	0.004	0.2
0.1943	0.6375	369.75	0.005	0.010	0.2	0.1757	0.6266	377.75	0.005	0.005	0.1
0.3542	0.7046	366.05	0.001	0.002	0.1	0.3479	0.7050	372.95	0.009	0.004	0.2
0.4370	0.7144	364.55	0.002	0.006	0.2	0.4161	0.7136	371.75	0.006	0.004	0.2
0.5337	0.7363	364.15	0.011	0.009	0.2	0.5088	0.7516	370.65	0.007	0.003	0.1
0.6205	0.7502	363.95	0.005	0.004	0.2	0.6128	0.7581	370.35	0.006	0.002	0.2
0.7002	0.7813	363.45	0.001	0.002	0.1	0.6974	0.7780	369.75	0.012	0.002	0.1
0.7215	0.7876	363.45	0.001	0.002	0.1	0.7205	0.7861	369.75	0.002	0.003	0.1
0.7940	0.8138	362.65	0.002	0.002	0.1	0.7899	0.8180	368.25	0.002	0.002	0.1
0.8147	0.8266	362.55	0.004	0.004	0.1	0.8140	0.8310	368.15	0.001	0.004	0.1
0.8326	0.8365	362.35	0.001	0.001	0.2	0.8321	0.8387	368.15	0.002	0.002	0.1
0.8488	0.8481	361.95	0.005	0.002	0.2	0.8513	0.8527	368.05	0.001	0.003	0.2
0.8808	0.8680	362.05	0.002	0.002	0.1	0.8782	0.8730	368.25	0.001	0.001	0.1
0.9599	0.9492	362.85	0.001	0.002	0.1	0.9601	0.9495	368.55	0.001	0.002	0.1
1.0000	1.0000	363.55	0.001	0.001	0.1	1.0000	1.0000	369.55	0.001	0.001	0.1

[a] The deviations between the compositions of the gravimetrically composed samples and temperatures indicated standard uncertainties $u(q)$ in the quantity q as discussed in the text (0.95 level of confidence); the maximum expanded uncertainties of the temperature and composition measurements were assumed to below 0.5 K and 0.02 mole fraction.

to remove the remaining gas and impurity in the equilibrium apparatus and recirculation loop. Then the liquid was injected into the boiling chamber and heated. After the desired pressure was reached, a peristaltic pump (Cole Parmer Co. model 177390-00) was used to recirculate the liquid phase to accelerate the thermodynamic equilibrium process. The vapor was condensed in the condenser and at the same time returned to equilibrium chamber through the vapor phase sampling port. Both liquid and condensed vapor phases are continuously recirculated to provide intimate contact of the phases and ensure the equilibrium can be established rapidly. When the fluctuation of the pressure was maintained at less than ± 0.05 % and constant experimental temperature was obtained in about 1 to 1.5 h, the equilibrium was assumed to be established. Then the temperature in the still was measured. Samples of vapor and liquid phase were immediately taken out for analysis from the sampling ports using a microsyringe. This is done with minor disturbances on the equilibrium since the samples (1 μL) is negligible compared to the volume of the still, 100 cm^3.

The temperature was measured with Pt-100 probes connected to a digital temperature meter with the accuracy of ± 0.1 K according to the calibration certificate. The pressure was measured by a calibrated high accuracy pressure transducer (Foshan Pulian Electronics Co. Pt 500-503) which had an accuracy of ± 0.1 %. Atmospheric pressure was measured by a Fortin-type mercury barometer located adjacent to the experimental apparatus with an accuracy of ± 0.04 kPa. The range of the pressure measurement was from (0 to 600) kPa. The compositions of the

Table 4. Experimental VLE Data for the System Isopropanol (1) + Toluene (2)[a]

x_1	y_1^{exp}	T^{exp}/K	$u(x)$	$u(y)$	$u(T)$	x_1	y_1^{exp}	T^{exp}/K	$u(x)$	$u(y)$	$u(T)$
		P = 101.3 kPa						P = 121.3 kPa			
0.0000	0.0000	383.55	0.001	0.001	0.2	0.0000	0.0000	390.25	0.001	0.001	0.2
0.0745	0.3947	369.15	0.001	0.001	0.1	0.0650	0.3689	376.65	0.002	0.002	0.1
0.1265	0.5052	364.55	0.001	0.001	0.1	0.1197	0.5051	370.35	0.003	0.004	0.2
0.2172	0.5794	360.35	0.005	0.003	0.1	0.2142	0.5855	365.95	0.002	0.001	0.1
0.3061	0.6443	358.25	0.003	0.003	0.1	0.2987	0.6196	364.05	0.004	0.003	0.2
0.3925	0.6516	357.25	0.006	0.007	0.2	0.3802	0.6786	362.35	0.002	0.003	0.1
0.5085	0.6878	356.25	0.002	0.002	0.2	0.5042	0.7002	361.35	0.001	0.001	0.2
0.5958	0.7206	355.15	0.005	0.001	0.1	0.5974	0.7217	360.35	0.002	0.002	0.2
0.6581	0.7338	355.05	0.001	0.002	0.1	0.6553	0.7502	360.25	0.002	0.002	0.1
0.7155	0.7669	354.65	0.003	0.002	0.1	0.7313	0.7686	359.85	0.001	0.003	0.1
0.8038	0.8095	354.35	0.002	0.002	0.1	0.8037	0.8162	359.45	0.002	0.003	0.1
0.8225	0.8232	354.15	0.002	0.002	0.1	0.8248	0.8262	359.35	0.001	0.001	0.1
0.8356	0.8330	354.15	0.002	0.002	0.1	0.8356	0.8378	359.15	0.002	0.001	0.1
0.8484	0.8423	354.25	0.001	0.002	0.1	0.8517	0.8483	359.05	0.001	0.002	0.1
0.8761	0.8641	354.45	0.002	0.002	0.1	0.8757	0.8680	359.15	0.002	0.001	0.1
0.9367	0.9220	354.55	0.001	0.002	0.1	0.9373	0.9273	359.55	0.001	0.001	0.1
1.0000	1.0000	355.35	0.001	0.001	0.1	1.0000	1.0000	359.95	0.001	0.001	0.1
		P = 161.3 kPa						P = 201.3 kPa			
0.0000	0.0000	400.75	0.001	0.001	0.2	0.0000	0.0000	409.65	0.001	0.001	0.2
0.0598	0.3491	387.65	0.002	0.002	0.1	0.0566	0.3166	396.55	0.002	0.003	0.2
0.1129	0.4771	381.25	0.001	0.006	0.1	0.1054	0.4846	389.05	0.001	0.004	0.2
0.2061	0.5800	376.05	0.003	0.002	0.2	0.1945	0.5772	383.35	0.003	0.005	0.1
0.2987	0.6296	373.45	0.004	0.003	0.2	0.2741	0.6193	380.85	0.003	0.001	0.2
0.3790	0.6922	371.35	0.011	0.004	0.2	0.3696	0.6921	377.75	0.009	0.002	0.2
0.4948	0.7215	370.15	0.002	0.001	0.1	0.4940	0.7258	376.45	0.010	0.003	0.1
0.5943	0.7382	369.45	0.006	0.007	0.1	0.5943	0.7415	375.25	0.006	0.002	0.2
0.6545	0.7513	369.05	0.003	0.003	0.1	0.6522	0.7551	374.55	0.002	0.003	0.2
0.7306	0.7830	367.45	0.001	0.001	0.1	0.7285	0.7844	374.15	0.002	0.001	0.1
0.8113	0.8197	367.35	0.002	0.003	0.1	0.8025	0.8306	373.35	0.002	0.002	0.1
0.8222	0.8336	367.25	0.001	0.001	0.1	0.8200	0.8391	373.25	0.001	0.002	0.1
0.8385	0.8442	366.85	0.001	0.003	0.1	0.8472	0.8601	373.05	0.002	0.001	0.1
0.8476	0.8549	366.75	0.002	0.002	0.1	0.8752	0.8798	372.95	0.002	0.002	0.1
0.8757	0.8739	366.65	0.002	0.001	0.1	0.9059	0.9047	372.95	0.001	0.001	0.1
0.9372	0.9296	366.85	0.001	0.001	0.1	0.9378	0.9325	373.15	0.001	0.001	0.1
1.0000	1.0000	367.65	0.001	0.001	0.1	1.0000	1.0000	373.65	0.001	0.001	0.1

[a] The deviations between the compositions of the gravimetrically composed samples and temperatures indicated standard uncertainties $u(q)$ in the quantity q as discussed in the text (0.95 level of confidence); the maximum expanded uncertainties of the temperature and composition measurements were assumed to below 0.5 K and 0.02 mole fraction.

liquid and vapor phases were analyzed by a gas chromatograph GC-7890A supplied by Agilent Technologies Co. The gas chromatography was calibrated with standard solutions that were prepared gravimetrically by an electronic balance (uncertainty of ± 0.0001 g). The deviations between the compositions of the gravimetrically composed samples indicated a standard uncertainties 0.001 of mole fraction x_i, y_i. The flame ionization detector (FID) was used together with a DB-1701 capillary column (30 m × 0.32 μm × 0.25 μm). Nitrogen was used as the carrier gas at a constant flow rate of 3 mL·min^{-1}. The injector, detector, and oven temperatures were kept at (523.15, 523.15, and 348.15) K, respectively. At least three analyses were made for each sample. If the difference of the measuring value among the three samples was less than 0.5 %, the average value was recorded.

■ RESULTS AND DISCUSSION

The isobaric VLE data, calculated activity coefficients, and correlation results for the binary systems of ethanol (1) + toluene (2) and isopropanol (1) + toluene (2) at (101.3, 121.3, 161.3, and 201.3) kPa are listed in Tables 3 to 6. The general equilibrium relationship for VLE can be expressed by the following equation[27]

$$y_i \hat{\varphi}_i^{V} P = x_i \gamma_i \varphi_i^{s} \exp\left\{\frac{V_i^{L}(p - p_i^{s})}{RT}\right\} \qquad (1)$$

where P and T are the total pressure and the temperature in the equilibrium system, respectively; P_i^s is the saturation vapor

Table 5. Correlation Results for the Ethanol (1) + Toluene (2) System

experimental data			calculated data											
			NRTL				Wilson				UNIQUAC			
x_1	γ_1^{exp}	γ_2^{exp}	y_1^{cal}	T^{cal}/K	γ_1^{cal}	γ_2^{cal}	y_1^{cal}	T^{cal}/K	γ_1^{cal}	γ_2^{cal}	y_1^{cal}	T^{cal}/K	γ_1^{cal}	γ_2^{cal}
P = 101.3 kPa														
0.0000		1.008	0.0000	383.57		1.000	0.0000	383.57		1.000	0.0000	383.57		1.000
0.0331	4.835	0.955	0.3411	371.87	4.828	1.005	0.3415	371.72	4.984	1.003	0.3385	371.57	4.906	1.003
0.1276	3.511	1.082	0.5887	358.00	3.644	1.048	0.5938	358.27	3.687	1.048	0.5902	358.46	3.618	1.042
0.2291	2.597	1.137	0.6560	354.02	2.590	1.131	0.6543	353.99	2.589	1.141	0.6581	354.11	2.605	1.127
0.3659	1.808	1.369	0.6862	352.93	1.831	1.312	0.6874	351.52	1.827	1.327	0.6911	352.44	1.835	1.314
0.4819	1.470	1.604	0.7085	351.59	1.477	1.542	0.7089	350.51	1.479	1.554	0.7096	351.02	1.474	1.551
0.4994	1.493	1.564	0.7190	350.39	1.443	1.582	0.7161	351.01	1.441	1.597	0.7143	351.43	1.436	1.596
0.6676	1.173	2.173	0.7520	350.40	1.168	2.132	0.7526	349.76	1.175	2.127	0.7503	350.22	1.165	2.145
0.6870	1.165	2.157	0.7596	350.76	1.147	2.215	0.7621	351.21	1.155	2.208	0.7603	351.78	1.144	2.227
0.7199	1.128	2.338	0.7707	350.76	1.116	2.369	0.7723	350.62	1.123	2.360	0.7708	351.18	1.113	2.379
0.7974	1.081	2.879	0.8029	349.64	1.060	2.817	0.8037	349.40	1.064	2.804	0.8028	349.68	1.057	2.814
0.8142	1.068	2.972	0.8126	349.83	1.050	2.925	0.8131	349.62	1.054	2.916	0.8126	349.81	1.048	2.918
0.8344	1.057	3.060	0.8266	350.47	1.039	3.063	0.8264	350.29	1.043	3.062	0.8266	350.38	1.038	3.051
0.8400	1.042	2.992	0.8332	350.47	1.036	3.085	0.8319	350.35	1.040	3.098	0.8328	350.40	1.035	3.077
0.8792	0.998	3.729	0.8477	350.30	1.020	3.371	0.8504	350.37	1.023	3.424	0.8485	350.56	1.020	3.361
0.9586	0.988	4.104	0.9394	351.27	1.002	3.996	0.9386	351.03	1.003	4.276	0.9396	351.21	1.002	4.032
1.0000	1.004		1.0000	351.36	1.000		1.0000	351.36	1.000		1.0000	351.36	1.000	
P = 121.3 kPa														
0.0000		1.001	0.0000	390.26		1.000	0.0000	390.26		1.000	0.0000	390.26		1.000
0.0335	4.289	0.961	0.3222	378.51	4.396	1.003	0.3221	378.45	4.384	1.003	0.3219	378.58	4.399	1.003
0.1279	3.294	1.067	0.5843	365.00	3.439	1.041	0.5897	364.83	3.524	1.046	0.5843	364.92	3.433	1.041
0.2166	2.656	1.111	0.6538	359.42	2.636	1.110	0.6503	359.59	2.630	1.125	0.6537	359.44	2.638	1.111
0.3586	1.868	1.276	0.6951	356.78	1.844	1.291	0.6903	358.09	1.826	1.312	0.6942	357.03	1.844	1.294
0.4573	1.493	1.497	0.7107	357.29	1.520	1.477	0.7082	356.49	1.518	1.491	0.7107	356.83	1.521	1.480
0.5228	1.380	1.622	0.7233	356.23	1.376	1.635	0.7231	356.58	1.377	1.643	0.7231	356.40	1.376	1.638
0.6376	1.196	1.931	0.7501	356.50	1.195	1.995	0.7520	356.45	1.202	1.987	0.7506	356.71	1.196	1.996
0.7044	1.107	2.382	0.7653	354.68	1.124	2.272	0.7665	354.25	1.131	2.254	0.7644	354.46	1.125	2.272
0.7212	1.122	2.311	0.7769	356.01	1.110	2.353	0.7782	355.55	1.116	2.332	0.7772	356.03	1.111	2.353
0.7950	1.065	2.782	0.8072	354.75	1.058	2.752	0.8084	354.37	1.062	2.729	0.8073	354.71	1.058	2.751
0.8182	1.056	2.934	0.8202	354.72	1.045	2.899	0.8211	354.38	1.049	2.878	0.8203	354.68	1.045	2.897
0.8337	1.060	3.069	0.8295	354.59	1.038	3.014	0.8302	354.24	1.041	2.989	0.8296	354.54	1.038	3.010
0.8488	1.032	3.086	0.8409	355.16	1.030	3.092	0.8411	355.00	1.034	3.088	0.8409	355.14	1.031	3.092
0.8807	1.015	3.381	0.8627	354.48	1.019	3.320	0.8631	354.58	1.021	3.340	0.8628	354.47	1.019	3.323
0.9589	1.006	3.896	0.9444	356.13	1.002	3.961	0.9434	357.44	1.003	4.116	0.9442	356.44	1.002	3.993
1.0000	1.000		1.0000	356.11	1.000		1.0000	356.11	1.000		1.0000	356.11	1.000	
P = 161.3 kPa														
0.0000		1.007	0.0000	400.77		1.000	0.0000	400.77		1.000	0.0000	400.77		1.000
0.0333	3.478	0.995	0.2796	390.14	3.481	1.002	0.2790	389.87	3.471	1.002	0.2796	390.14	3.505	1.002
0.1231	3.204	1.026	0.5683	374.15	3.166	1.032	0.5746	374.47	3.278	1.036	0.5682	374.13	3.168	1.033
0.1943	2.651	1.088	0.6391	369.92	2.654	1.080	0.6397	369.81	2.686	1.091	0.6389	369.91	2.654	1.081
0.3542	1.832	1.243	0.7002	365.94	1.822	1.265	0.6966	366.71	1.811	1.284	0.6997	365.90	1.821	1.267
0.4370	1.589	1.446	0.7162	364.54	1.566	1.411	0.7131	364.77	1.556	1.428	0.7158	364.55	1.565	1.414
0.5337	1.360	1.633	0.7348	364.34	1.347	1.631	0.7346	364.48	1.348	1.639	0.7348	364.35	1.348	1.633
0.6205	1.201	1.913	0.7531	363.37	1.212	1.888	0.7537	363.16	1.218	1.885	0.7531	363.32	1.213	1.888
0.7002	1.129	2.154	0.7793	364.11	1.125	2.194	0.7803	363.72	1.132	2.180	0.7795	364.07	1.127	2.193
0.7215	1.104	2.252	0.7865	363.85	1.106	2.286	0.7875	363.45	1.113	2.271	0.7867	363.80	1.108	2.285
0.7940	1.067	2.739	0.8147	362.19	1.057	2.671	0.8160	361.83	1.061	2.651	0.8148	362.13	1.058	2.671
0.8147	1.061	2.845	0.8268	362.47	1.046	2.796	0.8276	362.13	1.050	2.777	0.8268	362.43	1.047	2.796

Table 5. Continued

experimental data			calculated data											
			NRTL				Wilson				UNIQUAC			
x_1	γ_1^{exp}	γ_2^{exp}	y_1^{cal}	T^{cal}/K	γ_1^{cal}	γ_2^{cal}	y_1^{cal}	T^{cal}/K	γ_1^{cal}	γ_2^{cal}	y_1^{cal}	T^{cal}/K	γ_1^{cal}	γ_2^{cal}
0.8326	1.058	2.989	0.8368	362.21	1.037	2.914	0.8375	361.91	1.041	2.896	0.8368	362.19	1.038	2.916
0.8488	1.068	3.114	0.8477	362.34	1.030	3.038	0.8481	362.04	1.033	3.016	0.8477	362.35	1.031	3.040
0.8808	1.049	3.422	0.8686	361.54	1.019	3.263	0.8691	361.41	1.021	3.258	0.8686	361.54	1.019	3.269
0.9599	1.022	3.814	0.9489	362.93	1.002	3.879	0.9481	363.56	1.002	3.993	0.9488	363.31	1.002	3.914
1.0000	1.008		1.0000	363.58	1.000		1.0000	363.58	1.000		1.0000	363.58	1.000	
P = 201.3 kPa														
0.0000		1.005	0.0000	409.66		1.000	0.0000	409.66		1.000	0.0000	409.66		1.000
0.0293	3.639	0.982	0.2709	399.23	3.717	1.002	0.2708	400.05	3.703	1.002	0.2709	399.23	3.716	1.002
0.1158	3.468	0.985	0.5720	380.85	3.320	1.027	0.5748	382.29	3.417	1.032	0.5726	380.83	3.331	1.027
0.1757	2.739	1.073	0.6350	378.17	2.827	1.062	0.6342	378.79	2.848	1.074	0.6349	378.16	2.829	1.064
0.3479	1.830	1.238	0.7065	372.87	1.861	1.249	0.7016	373.77	1.839	1.270	0.7056	372.89	1.857	1.252
0.4161	1.614	1.392	0.7193	371.39	1.629	1.363	0.7145	371.28	1.615	1.383	0.7185	371.39	1.627	1.366
0.5088	1.444	1.485	0.7395	371.28	1.400	1.561	0.7393	371.84	1.396	1.574	0.7395	371.34	1.399	1.564
0.6128	1.222	1.851	0.7581	370.34	1.224	1.855	0.7586	370.24	1.229	1.854	0.7582	370.32	1.225	1.855
0.6974	1.125	2.215	0.7804	369.11	1.129	2.173	0.7816	368.85	1.135	2.161	0.7806	369.04	1.130	2.171
0.7205	1.100	2.310	0.7885	369.05	1.108	2.273	0.7897	368.78	1.115	2.260	0.7886	368.98	1.110	2.270
0.7899	1.101	2.740	0.8179	368.39	1.059	2.642	0.8189	368.07	1.064	2.625	0.8181	368.33	1.061	2.640
0.8140	1.089	2.883	0.8307	368.39	1.046	2.784	0.8314	368.12	1.050	2.769	0.8308	368.35	1.047	2.783
0.8321	1.075	3.048	0.8397	367.73	1.037	2.896	0.8404	367.59	1.041	2.886	0.8398	367.70	1.038	2.896
0.8513	1.072	3.153	0.8528	368.11	1.029	3.024	0.8531	368.01	1.032	3.021	0.8528	368.10	1.030	3.025
0.8782	1.057	3.298	0.8727	368.60	1.019	3.209	0.8724	368.64	1.022	3.223	0.8726	368.62	1.020	3.214
0.9601	1.040	3.966	0.9493	368.66	1.002	3.883	0.9486	369.51	1.002	4.002	0.9491	368.91	1.002	3.913
1.0000	1.016		1.0000	369.60	1.000		1.0000	369.60	1.000		1.0000	369.60	1.000	

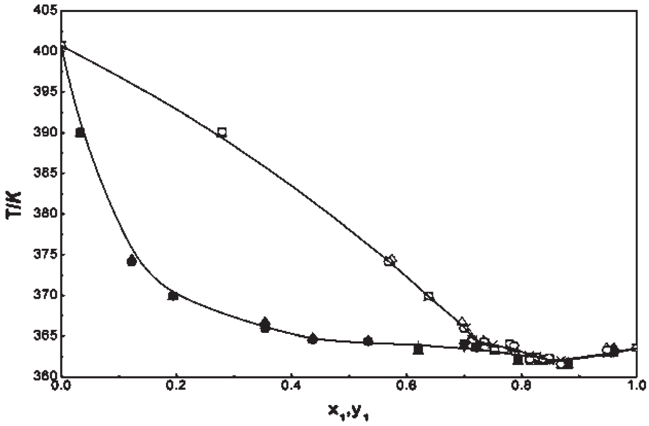

Figure 4. T, x_1, y_1 diagram for the ethanol (1) + toluene (2) system at 161.3 kPa: +, ×, (x_1, y_1) experimental data in this work; ■, □, (x_1, y_1) correlated results by the NRTL model; ▲, △, (x_1, y_1) correlated results by the Wilson model; ●, ○, (x_1, y_1) correlated results by the UNIQUAC model; —, fitted curve by experimental data.

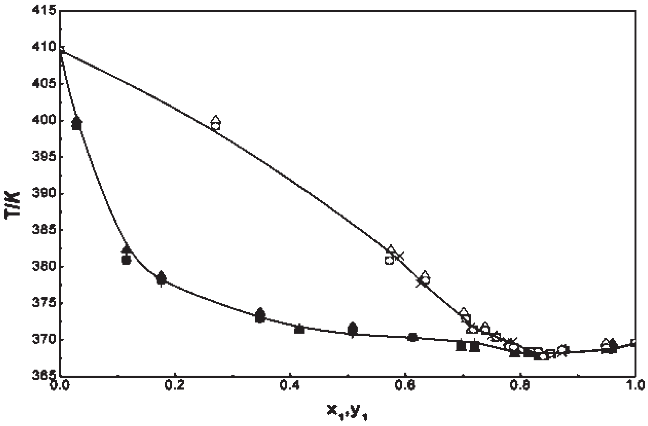

Figure 5. T, x_1, y_1 diagram for the ethanol (1) + toluene (2) system at 201.3 kPa: +, ×, (x_1, y_1) experimental data in this work; ■, □, (x_1, y_1) correlated results by the NRTL model; ▲, △, (x_1, y_1) correlated results by the Wilson model; ●, ○, (x_1, y_1) correlated results by the UNIQUAC model; —, fitted curve by experimental data.

pressure of pure component i which can be obtained from the Antoine equation; y_i is the mole fraction of component i in the vapor phase; x_i is the mole fraction of component i in the liquid phase; R is the gas constant; V_i^L is the liquid mole volume of pure liquid i, calculated from the modified Rackett equation.[28] $\hat{\varphi}_i^V$ and φ_i^s are the fugacity coefficients of component i in the mixture vapor phase and in the pure state, and γ_i is the activity coefficient of component i.

At low pressure, the exponential term in eq 1 is approximately equal to 1, thus eq 1 can be simplified to

$$y_i\hat{\varphi}_i^V P = x_i\gamma_i\varphi_i^s \qquad (2)$$

Table 6. Correlation Results for the Isopropanol (1) + Toluene (2) System

			calculated data											
experimental data			NRTL				Wilson				UNIQUAC			
x_1	γ_1^{exp}	γ_2^{exp}	y_1^{cal}	T^{cal}/K	γ_1^{cal}	γ_2^{cal}	y_1^{cal}	T^{cal}/K	γ_1^{cal}	γ_2^{cal}	y_1^{cal}	T^{cal}/K	γ_1^{cal}	γ_2^{cal}
P = 101.3 kPa														
0.0000		1.008	0.0000	383.57		1.000	0.0000	383.57		1.000	0.0000	383.57		1.000
0.0745	3.167	1.012	0.3942	369.10	3.146	1.009	0.3953	369.24	3.175	1.011	0.3957	369.24	3.178	1.010
0.1265	2.824	1.014	0.5046	364.49	2.854	1.028	0.5025	364.38	2.839	1.033	0.5026	364.43	2.833	1.030
0.2172	2.209	1.103	0.5920	360.20	2.300	1.086	0.5854	360.30	2.255	1.097	0.5885	360.36	2.270	1.089
0.3061	1.890	1.128	0.6354	358.96	1.880	1.175	0.6296	359.26	1.845	1.187	0.6325	358.70	1.861	1.176
0.3925	1.550	1.305	0.6577	356.40	1.589	1.290	0.6547	356.88	1.571	1.299	0.6574	356.76	1.580	1.290
0.5085	1.313	1.495	0.6894	355.92	1.331	1.496	0.6892	355.98	1.329	1.497	0.6897	355.95	1.329	1.493
0.5958	1.226	1.688	0.7179	355.81	1.203	1.701	0.7188	355.58	1.208	1.694	0.7183	355.66	1.204	1.696
0.6581	1.135	1.908	0.7362	354.47	1.137	1.871	0.7375	354.15	1.143	1.859	0.7368	354.34	1.139	1.865
0.7155	1.108	2.036	0.7645	355.38	1.090	2.053	0.7656	355.06	1.096	2.041	0.7650	355.28	1.092	2.049
0.8038	1.054	2.437	0.8103	354.12	1.040	2.382	0.8105	353.96	1.045	2.383	0.8102	354.07	1.042	2.384
0.8225	1.056	2.518	0.8233	354.20	1.032	2.461	0.8233	354.16	1.036	2.469	0.8232	354.23	1.034	2.468
0.8356	1.052	2.568	0.8328	354.30	1.028	2.517	0.8327	354.34	1.031	2.530	0.8327	354.37	1.029	2.526
0.8484	1.043	2.620	0.8423	354.33	1.023	2.574	0.8420	354.44	1.026	2.591	0.8421	354.41	1.024	2.583
0.8761	1.028	2.744	0.8643	354.40	1.015	2.702	0.8638	354.65	1.018	2.732	0.8641	354.49	1.016	2.713
0.9367	1.022	3.072	0.9221	354.57	1.004	3.014	0.9214	355.32	1.005	3.092	0.9219	354.80	1.004	3.039
1.0000	1.006		1.0000	355.37	1.000		1.0000	355.37	1.000		1.0000	355.37	1.000	
P = 121.3 kPa														
0.0000		1.001	0.0000	390.25		1.000	0.0000	390.25		1.000	0.0000	390.25		1.000
0.0650	3.124	0.996	0.3695	376.67	3.172	1.008	0.3691	376.65	3.164	1.008	0.3695	376.67	3.171	1.008
0.1197	2.893	1.004	0.4957	370.02	2.832	1.026	0.4975	369.98	2.861	1.029	0.4960	370.02	2.835	1.026
0.2142	2.198	1.081	0.5907	365.96	2.252	1.083	0.5888	365.89	2.251	1.092	0.5908	365.95	2.255	1.084
0.2987	1.789	1.181	0.6328	363.88	1.871	1.161	0.6290	363.46	1.861	1.173	0.6327	363.77	1.872	1.162
0.3802	1.641	1.193	0.6642	362.55	1.610	1.263	0.6628	363.59	1.599	1.276	0.6643	362.72	1.610	1.264
0.5042	1.326	1.438	0.6979	361.57	1.336	1.470	0.6972	361.81	1.334	1.479	0.6979	361.60	1.336	1.471
0.5974	1.198	1.698	0.7234	360.06	1.204	1.681	0.7232	360.04	1.205	1.684	0.7233	360.05	1.204	1.682
0.6553	1.140	1.786	0.7472	360.91	1.142	1.837	0.7478	360.82	1.145	1.835	0.7474	360.91	1.142	1.837
0.7313	1.062	2.151	0.7733	359.67	1.082	2.082	0.7740	359.24	1.085	2.075	0.7733	359.34	1.082	2.081
0.8037	1.042	2.370	0.8163	359.40	1.042	2.365	0.8167	359.25	1.044	2.359	0.8164	359.38	1.042	2.364
0.8248	1.032	2.519	0.8277	358.56	1.033	2.458	0.8282	358.48	1.035	2.453	0.8278	358.53	1.033	2.456
0.8356	1.041	2.522	0.8374	359.39	1.029	2.511	0.8376	359.27	1.031	2.506	0.8375	359.36	1.029	2.509
0.8517	1.038	2.624	0.8483	359.09	1.023	2.588	0.8485	359.01	1.025	2.585	0.8484	359.06	1.024	2.586
0.8757	1.029	2.715	0.8677	359.44	1.016	2.703	0.8676	359.43	1.018	2.707	0.8677	359.42	1.016	2.702
0.9373	1.012	2.925	0.9265	359.92	1.004	3.028	0.9259	360.22	1.004	3.064	0.9264	359.96	1.004	3.030
1.0000	1.007		1.0000	359.97	1.000		1.0000	359.97	1.000		1.0000	359.97	1.000	
P = 161.3 kPa														
0.0000		1.007	0.0000	400.77		1.000	0.0000	400.77		1.000	0.0000	400.77		1.000
0.0598	2.974	0.990	0.3458	387.32	2.959	1.006	0.3457	387.15	2.950	1.006	0.3459	387.31	2.961	1.006
0.1129	2.649	1.011	0.4784	381.27	2.692	1.021	0.4799	381.36	2.716	1.022	0.4779	381.26	2.688	1.021
0.2061	2.102	1.057	0.5887	376.10	2.210	1.069	0.5884	376.00	2.217	1.074	0.5881	376.12	2.206	1.069
0.2987	1.723	1.141	0.6422	373.49	1.840	1.145	0.6401	372.98	1.836	1.153	0.6419	373.56	1.838	1.145
0.3790	1.607	1.141	0.6772	371.58	1.606	1.237	0.6760	372.67	1.599	1.248	0.6771	371.51	1.606	1.237
0.4948	1.339	1.317	0.7124	370.81	1.358	1.417	0.7124	371.41	1.356	1.425	0.7125	370.79	1.359	1.416
0.5943	1.170	1.576	0.7386	369.29	1.214	1.628	0.7385	369.29	1.215	1.631	0.7387	369.27	1.214	1.627
0.6545	1.096	1.780	0.7563	367.93	1.149	1.788	0.7563	367.78	1.152	1.787	0.7564	367.90	1.150	1.787
0.7306	1.085	2.094	0.7854	366.70	1.089	2.048	0.7859	366.55	1.091	2.040	0.7854	366.68	1.089	2.048
0.8113	1.026	2.491	0.8237	367.32	1.042	2.375	0.8246	367.34	1.044	2.365	0.8236	367.34	1.042	2.377
0.8222	1.034	2.448	0.8343	366.86	1.037	2.427	0.8347	366.70	1.039	2.417	0.8342	366.88	1.037	2.429

Table 6. Continued

			calculated data											
experimental data			NRTL				Wilson				UNIQUAC			
x_1	γ_1^{exp}	γ_2^{exp}	y_1^{cal}	T^{cal}/K	γ_1^{cal}	γ_2^{cal}	y_1^{cal}	T^{cal}/K	γ_1^{cal}	γ_2^{cal}	y_1^{cal}	T^{cal}/K	γ_1^{cal}	γ_2^{cal}
0.8385	1.041	2.555	0.8445	366.68	1.031	2.514	0.8449	366.50	1.032	2.502	0.8445	366.71	1.031	2.517
0.8476	1.047	2.530	0.8535	366.82	1.027	2.562	0.8535	366.59	1.029	2.550	0.8534	366.85	1.027	2.565
0.8757	1.040	2.704	0.8730	367.50	1.018	2.713	0.8730	367.34	1.019	2.705	0.8730	367.55	1.018	2.718
0.9372	1.026	2.969	0.9286	366.80	1.005	3.080	0.9282	366.89	1.005	3.093	0.9286	366.87	1.005	3.087
1.0000	1.005		1.0000	367.67	1.000		1.0000	367.67	1.000		1.0000	367.67	1.000	
P = 201.3 kPa														
0.0000		1.005	0.0000	409.66		1.000	0.0000	409.66		1.000	0.0000	409.66		1.000
0.0566	2.703	1.016	0.3178	396.84	2.699	1.003	0.3188	397.07	2.726	1.004	0.3199	397.09	2.742	1.004
0.1054	2.797	0.989	0.4711	388.14	2.674	1.015	0.4688	387.89	2.650	1.018	0.4664	388.01	2.622	1.017
0.1945	2.167	1.057	0.5891	383.34	2.285	1.057	0.5814	383.37	2.223	1.065	0.5817	383.40	2.215	1.059
0.2741	1.791	1.135	0.6383	380.69	1.944	1.118	0.6312	380.51	1.888	1.129	0.6335	380.81	1.894	1.119
0.3696	1.647	1.157	0.6812	378.29	1.630	1.228	0.6758	378.28	1.599	1.237	0.6777	377.60	1.608	1.224
0.4940	1.351	1.335	0.7180	377.11	1.349	1.422	0.7164	377.00	1.339	1.423	0.7171	376.63	1.343	1.413
0.5943	1.196	1.626	0.7415	375.24	1.202	1.635	0.7420	375.13	1.203	1.627	0.7424	375.06	1.203	1.622
0.6522	1.137	1.836	0.7585	373.72	1.141	1.785	0.7595	373.46	1.144	1.774	0.7596	373.45	1.144	1.773
0.7285	1.072	2.095	0.7891	373.96	1.081	2.014	0.7897	373.50	1.085	2.001	0.7892	373.54	1.084	2.005
0.8025	1.059	2.318	0.8306	373.42	1.040	2.279	0.8308	373.31	1.044	2.279	0.8305	373.43	1.043	2.286
0.8200	1.051	2.424	0.8403	373.01	1.033	2.348	0.8401	372.82	1.037	2.354	0.8398	372.92	1.035	2.360
0.8472	1.050	2.497	0.8594	373.32	1.023	2.460	0.8593	373.55	1.026	2.477	0.8592	373.66	1.025	2.483
0.8752	1.043	2.635	0.8794	373.14	1.015	2.584	0.8790	373.54	1.017	2.615	0.8791	373.61	1.017	2.617
0.9059	1.037	2.771	0.9041	373.18	1.009	2.728	0.9037	373.89	1.010	2.778	0.9039	373.89	1.009	2.774
0.9378	1.025	2.951	0.9325	373.22	1.004	2.892	0.9319	373.95	1.004	2.963	0.9321	373.81	1.004	2.947
1.0000	1.013		1.0000	373.69	1.000		1.0000	373.69	1.000		1.0000	373.69	1.000	

Table 7. Interpolated Azeotropic Composition and Temperature for the Binary System at Different Pressures

	ethanol(1) + toluene (2)			isopropanol (1) + toluene (2)	
P/kPa	x_1^{azo} (y_1^{azo})	T^{azo}/K	P/kPa	x_1^{azo} (y_1^{azo})	T^{azo}/K
101.3	0.8122	349.74	101.3	0.8253	354.22
121.3	0.8234	354.65	121.3	0.8374	359.14
161.3	0.8457	362.02	161.3	0.8809	366.67
201.3	0.8573	368.10	201.3	0.9015	372.92
12.31[a]	0.6960	303.15	101.3[b]	0.8500	354.48
51.04[a]	0.7620	333.15	73.3[b]	0.8000	346.28

[a] Interpolated azeotropic data by Van Ness et al.[32] [b] Interpolated azeotropic data by Rao and Basu.[33]

The fugacity coefficients,[21] φ_i^s and $\hat{\varphi}_i^V$, were calculated by using the Soave−Redich−Kwong (SRK)[29] equation.

$$\ln \hat{\varphi}_i^V = \frac{b_i}{b}(z-1) - \ln\frac{P(V-b)}{RT} + \frac{a}{bRT}\left(\frac{b_i}{b} - \frac{2}{a}\sum_{j=1}^{n} y_j a_{ij}\right)\ln\left(1+\frac{b}{V}\right) \quad (3)$$

with

$$a_i = \frac{0.42748R^2T_{c,i}^{2.5}}{P_{c,i}} \quad (4)$$

$$b_i = \frac{0.08664RT_{c,i}}{P_{c,i}} \quad (5)$$

$$a_{ij} = (a_i a_j)^{0.5}(1-k_{ij}) \quad (6)$$

$$a = \sum_i \sum_j y_i y_j a_{ij} \quad (7)$$

$$b = \sum y_i b_i \quad (8)$$

where V is the molar volume of the mixture; Z is the molar compressibility factor; a_{ii}, a_{jj}, b_i, and b_j are the SRK equation constants of component i, j, respectively; a_{ij} is the SRK equation cross coupling constant; k_{ij} is the binary interaction parameters (as recommended by Zéberg-Mikkelsen et al.,[14] k_{ij} was set as 0.027 for toluene-alcohol systems).

The activity coefficient of component i, γ_i, can be determined based on these equations. $\gamma_i$was also calculated by the solution models for the excess Gibbs energy, such as the Wilson, NRTL, and UNIQUAC models, and the relationship is

$$\ln \gamma_i = \left(\frac{\partial(nG^E/RT)}{\partial n_i}\right)_{T,P,n_{j\neq i}} \quad (9)$$

Experimental errors may cause deviation of the activity coefficients drawn from the experimental VLE data from the

Gibbs–Duhem[27] equation. Therefore, the Herington[30] method was used to check the thermodynamic consistency.

$$D = 100 \cdot \frac{\int_{x_1=0}^{x_1=1} \ln \frac{\gamma_1}{\gamma_2}\, dx_1}{\int_{x_1=0}^{x_1=1} \left| \ln \frac{\gamma_1}{\gamma_2} \right| dx_1} \qquad (10)$$

$$J = 150 \cdot \frac{T_{\max} - T_{\min}}{T_{\min}} \qquad (11)$$

where $T_{\max}$ and $T_{\min}$ are the maximum and minimum boiling temperatures in the studied systems, respectively. Herington suggested that if $(D - J) < 10$, then the experimental points are considered to be thermodynamically consistent. The check results for the systems of ethanol (1) + toluene (2) at (101.3, 121.3, 161.3, and 201.3) kPa were −10.68, −9.76, −7.86, and −10.39. The check results for the systems of isopropanol (1) + toluene (2) at (101.3, 121.3, 161.3, and 201.3) kPa were −8.59, −7.87, −5.91, and −8.60; this indicates that the experimental data were thermodynamically consistent.

The results reported in these tables indicate that all of the systems exhibit a positive deviation from ideal behavior.

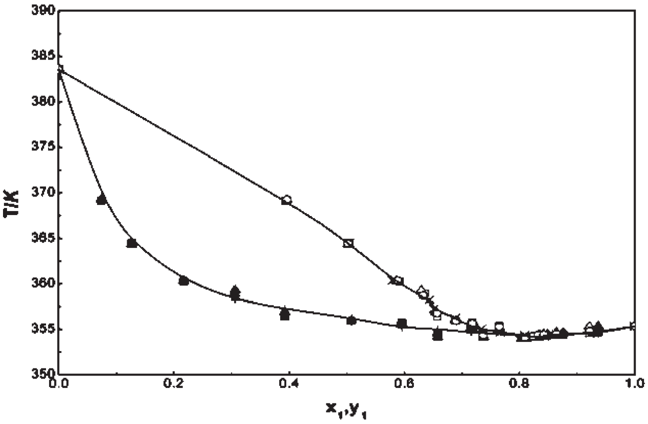

Figure 6. T, x_1, y_1 diagram for the isopropanol (1) + toluene (2) system at 101.3 kPa: +, ×, (x_1, y_1) experimental data in this work; ■, □, (x_1, y_1) correlated results by the NRTL model; ▲, △, (x_1, y_1) correlated results by the Wilson model; ●, ○, (x_1, y_1) correlated results by the UNIQUAC model; —, fitted curve by experimental data.

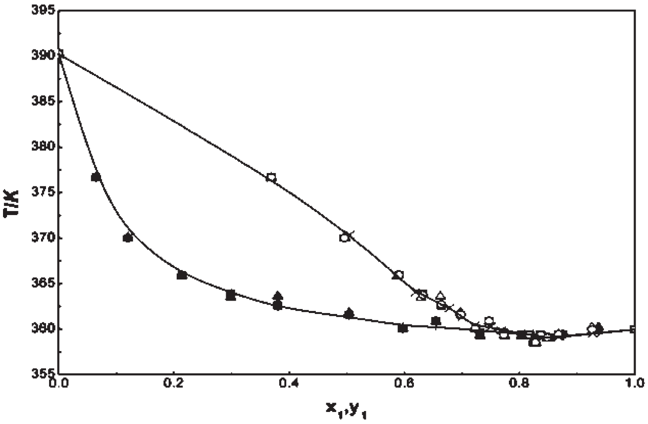

Figure 7. T, x_1, y_1 diagram for the isopropanol (1) + toluene (2) system at 121.3 kPa: +, ×, (x_1, y_1) experimental data in this work; ■, □, (x_1, y_1) correlated results by the NRTL model; ▲, △, (x_1, y_1) correlated results by the Wilson model; ●, ○, (x_1, y_1) correlated results by the UNIQUAC model; —, fitted curve by experimental data.

Table 8. Correlated Binary Interaction Parameters and Root-Mean-Square Deviations Between Experimental and Calculated Values for the Binary System with Different Models

ethanol (1) + toluene (2)						isopropanol (1) + toluene (2)					
model	A_{12}[a]/K	A_{21}[a]/K	α	σT[b]/K	σy_1[b]	model	A_{12}[a]/K	A_{21}[a]/K	α	σT[b]/K	σy_1[b]
P = 101.3 kPa											
NRTL	8034.25	−8607.46	0.3	0.3343	0.0047	NRTL	−1443.16	3578.53	0.3	0.4019	0.0042
Wilson	2224.95	445.79		0.4178	0.0060	Wilson	3177.61	−28.72		0.4401	0.0041
UNIQUAC	919.15	−675.92		0.5201	0.0060	UNIQUAC	−7.76	826.12		0.3384	0.0041
P = 121.3 kPa											
NRTL	4655.47	−3162.72	0.3	0.4624	0.0046	NRTL	1341.85	448.98	0.3	0.3154	0.0056
Wilson	2862.68	433.37		0.6762	0.0060	Wilson	2886.36	−29.12		0.5072	0.0052
UNIQUAC	1039.98	−675.92		05055	0.0045	UNIQUAC	253.44	375.13		0.3544	0.0056
P = 161.3 kPa											
NRTL	3079.08	−399.56	0.3	0.3175	0.0018	NRTL	1977.99	−201.70	0.3	0.4447	0.0060
Wilson	3478.31	436.04		0.4442	0.0025	Wilson	2132.11	396.96		0.6504	0.0060
UNIQUAC	808.28	119.07		0.3417	0.0018	UNIQUAC	948.82	−611.17		0.4534	0.0059
P = 201.3 kPa											
NRTL	868.98	1225.63	0.3	0.3739	0.0060	NRTL	−2633.39	4533.29	0.3	0.3926	0.0073
Wilson	2989.00	43.75		0.6819	0.0054	Wilson	3026.19	−32.20		0.6062	0.0069
UNIQUAC	172.02	813.41		0.4048	0.0058	UNIQUAC	22.38	826.12		0.5576	0.0072

[a] The interaction parameters for various models are as follows: Wilson, $A_{ij} = (\lambda_{ij} - \lambda_{ii})/R$; NRTL, $A_{ij} = (g_{ij} - g_{ii})/R$; UNIQUAC, $A_{ij} = (U_{ij} - U_{ii})/R$. [b] $\sigma T = (\Sigma_{i=1}{}^{n}(T_i^{\text{cal}} - T_i^{\text{exp}})^2/n)^{1/2}$; $\sigma y_1 = (\Sigma_{i=1}{}^{n}(y_{1,i}^{\text{cal}} - y_{1,\text{i}}^{\text{exp}})^2/n)^{1/2}$.

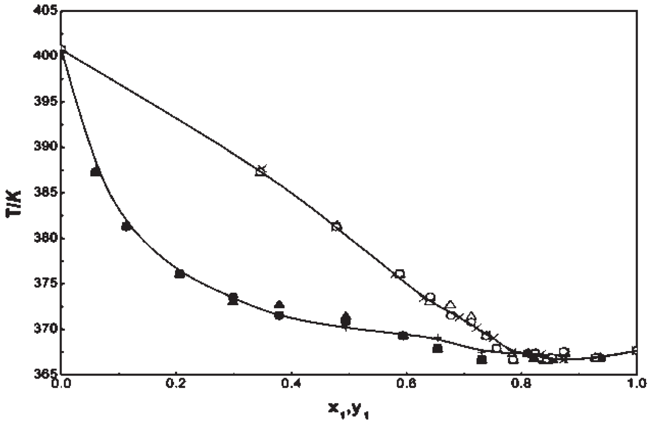

Figure 8. T, x_1, y_1 diagram for the isopropanol (1) + toluene (2) system at 161.3 kPa: +, ×, (x_1, y_1) experimental data in this work; ■, □, (x_1, y_1) correlated results by the NRTL model; ▲, △, (x_1, y_1) correlated results by the Wilson model; ●, ○, (x_1, y_1) correlated results by the UNIQUAC model; —, fitted curve by experimental data.

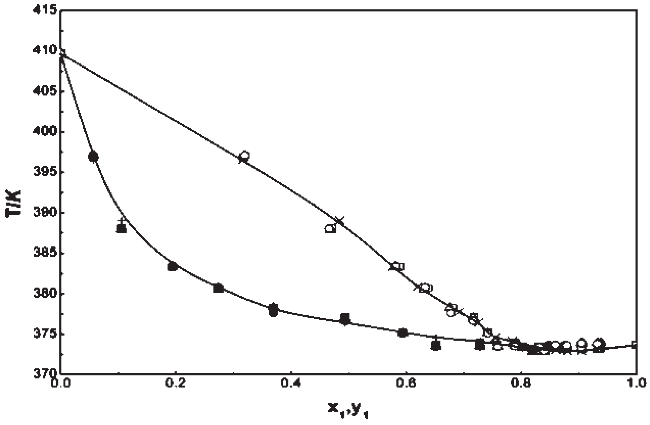

Figure 9. T, x_1, y_1 diagram for the isopropanol (1) + toluene (2) system at 201.3 kPa: +, ×, (x_1, y_1) experimental data in this work; ■, □, (x_1, y_1) correlated results by the NRTL model; ▲, △, (x_1, y_1) correlated results by the Wilson model; ●, ○, (x_1, y_1) correlated results by the UNIQUAC model; —, fitted curve by experimental data.

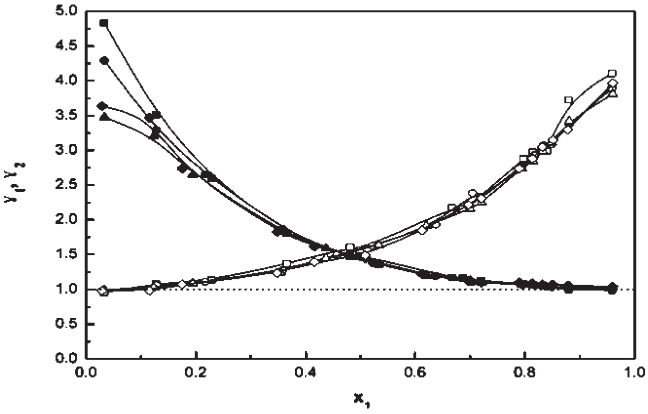

Figure 10. Activity coefficient diagram for the ethanol (1) + toluene (2) system at 101.3 kPa, ■, γ_1; □, γ_2; at 121.3 kPa, ●, γ_1; ○, γ_2; at 161.3 kPa, ▲, γ_1; △, γ_2; at 201.3 kPa, ♦, γ_1; ◇, γ_2; —, fitted curve.

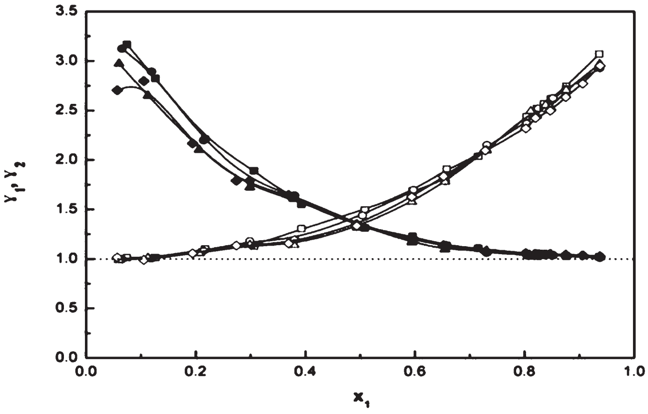

Figure 11. Activity coefficient diagram for the isopropanol (1) + toluene (2) system at 101.3 kPa, ■, γ_1; □, γ_2; at 121.3 kPa, ●, γ_1; ○, γ_2; at 161.3 kPa, ▲, γ_1; △, γ_2; at 201.3 kPa, ♦, γ_1; ◇, γ_2; —, fitted curve.

Both binary systems at testing pressure exhibit a minimum boiling azeotrope. Azeotropic compositions were obtained by determining the x_1 values so as to make the function $(x_1 - y_1) = f(x_1)$ equal to zero. A polynomial equation $T = f(x_1)$ was obtained by fitting the experimental results around the azeotropic point, from which we can compute the corresponding azeotropic temperatures by using the x_1 values previously determined. The azeotropic composition and boiling temperature for the binary mixtures are listed in Table 7. More azeotropic data available in the literature are also listed in Table 7 as a reference. As can be seen in this table, azeotropic positions were shifted substantially while changing system pressure for both binary mixtures.

The experimental data were correlated with the Wilson, NRTL, and UNIQUAC models by minimizing the objective function F[31]

$$F = \sum_{k=1}^{n} \sum_{i=1}^{2} \left(\frac{\gamma_i^{\text{exp}} - \gamma_i^{\text{cal}}}{\gamma_i^{\text{exp}}} \right)^2 \qquad (12)$$

where n is the number of experimental data. As recommended by Renon and Prausnitz,[23] the parameter α which is taken into account the nonrandomness of the solution in the NRTL equation was set as 0.3. The interaction parameters for the Wilson, NRTL, and UNIQUAC and the root-mean-squared deviations (rmsd) of the vapor mole fraction and bubble-point temperature between the experimental and the calculated values are listed in Table 8.

It can be seen from Tables 5, 6, and 8 and Figures 2 to 11 that the differences among the vapor phase mole fraction and boiling temperature calculated by the Wilson, NRTL, and UNIQUAC models are indistinct. The rmsd's of the vapor mole fraction and bubble-point temperature calculated by using the correlated parameters are no more than 0.0073 and 0.6819 K, respectively. The NRTL model represents better calculation results. The lines calculated by the Wilson and UNIQUAC models are almost overlapped and have the same deviations for some system. Generally the largest deviation is occurred around the azeotropic composition. From the view of industrial applications, the Wilson, NRTL, and UNIQUAC models can be used to calculate the VLE of the two binary systems.

■ CONCLUSIONS

The isobaric VLE data of the binary systems ethanol + toluene and isopropanol + toluene were determined at (101.3, 121.3, 161.3, and 201.3) kPa. The experimental data were checked with the Herington method, which showed good thermodynamic consistency. The Wilson, NRTL, and UNIQUAC activity coefficient models are used to correlate the experimental data. The results show that all of the models agree well with the experimental data, while the NRTL equation gives a slightly better agreement. Furthermore, there is azeotropic behavior in the two binary systems ethanol + toluene and isopropanol + toluene at testing pressure.

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