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Isothermal Vapor−Liquid Equilibrium for Methanol and 2,3-Dimethyl-1-butene at 343.06 K, 353.27 K, 363.19 K, and 372.90 K

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ABSTRACT: Isothermal vapor−liquid equilibrium (VLE) data of the methanol and 2,3-dimethyl-1-butene binary system were measured at 343.06 K, 353.27 K, 363.19 K, and 372.90 K. These measurements were made with novel recirculation equilibrium stainless steel equipment. Gas chromatography was used to analyze compositions of the samples from the vapor−liquid equilibrium systems. The binary VLE data were correlated with various activity coefficient models including Wilson, NRTL, and UNIIQUAC, as well as the Soave−Redlich−Kwong equation of state.

INTRODUCTION

Simulation of the processes is the first step in the design or optimization of any stage of the plant. The process simulation needs accurate thermodynamic data, especially vapor−liquid equilibrium data. Reactive distillation is an energy-saving process. This is a process of combining the chemical reaction with product separation simultaneously in a unit. There are some advantages of reactive distillation over the conventional process: (1) reduced downstream process; (2) utilization of heat of reaction for evaporation of the liquid phase; (3) changed chemical equilibrium by removing products. So, some thermodynamic data especially vapor−liquid equilibrium data are very important. Because of the environmental restrictions, ethers, as blending agents, can enhance the octane number and modify the refinery planning. MTBE was banned in California on December 31, 2002, due to the groundwater pollution problems (because of the high water solubility).[1] Higher carbon ethers are attracting much more attention. The temperature of the reaction of the higher carbon olefins and methanol is almost 333 K to 373 K.[2−4] In this paper, the isothermal vapor−liquid equilibrium data were measured for the methanol and 2,3-dimethyl-1-butene system at 343.06 K, 353.27 K, 363.19 K, and 372.90 K. No VLE data have been reported previously for the systems measured.

EXPERIMENTAL SECTION

Materials for Vapor−Liquid Equilibrium (VLE) Measurements. Methanol ($w > 0.994$), benzene ($w > 0.995$), and cyclohexane ($w > 0.998$) were provided by Tianjin GuangFu company. 2,3-Dimethyl-1-butene ($w > 0.995$) was purchased from Dalian Chemphy Fine Chemical Co. Ltd. The purity of all chemical reactants was provided by the supplier. No significant amount of water was detected in the reactants. The reactants were used without further purification except for drying over molecular sieves (Nankai University 3A) for 24 h. Density and refractive index for the materials were measured with a densimeter (Beijin Yingkesaide company, EX510A) and an Abbe refractometer (Shanghai Jingke Company, 2WAJ), respectively. The data of measurement and literature[5] were presented in Table 1.

ASSEMBLY FOR VLE MEASUREMENTS

The vapor−liquid equilibrium data were measured using a new equilibrium still which was designed following the general Othmer-type still.[6−8] It was made of stainless steel, and the total volume of mixture needed for the measurements was approximately 120 mL. The basic flow sheet of the apparatus is shown in Figure 1. Temperature was measured with a SME-700W-J (Yuyao Shimai Electron company) temperature meter equipped with a Pt-100 resistant temperature probe, which was located in the liquid phase. The uncertainty of temperature is estimated to 0.09 K. According to the data provided by the manufacturers of the pressure measurement devices, the uncertainty of the pressure measurement was 0.5 kPa. The thermometers and the pressure meter (Beijin Weisite company, CYB-20S) were calibrated at the Bureau of Quality and Technical Supervision of Tianjin. To determine the reliability of this new vapor−liquid equilibrium still, we measured the isothermal vapor−liquid equilibrium data for the binary system of benzene (1) and cyclohexane (2) at 403.15 K and compared them with the data of the literature.[9] The VLE data of experiment and literature[9] were presented in Table 2, and the pressure−composition plots were shown in Figure 2. The VLE data lines of the experiment and the literature[9] coincided approximately. This proved that the data measured by the equilibrium still were reliable.

Analysis and GC Calibration. The condensed vapor phase and liquid phase were analyzed with a FULI9790 gas chromatograph with a capillary column (SGE, dimethyl polysiloxane, length 60 m, column inner diameter 0.22 mm, film thickness 0.25 μm) and a flame ionization detector. Nitrogen, 99.999 % pure, was used as a carrier gas. The temperatures of the injector and detector were both at 493.15 K. The oven was operated at a programmed temperature, from 353.15 K to 433.15 K at a rate of 10 K·min^{-1}, and then stayed for 5 min at a temperature of 433.15 K. Calibration curves were obtained by a set of solutions of known composition. Standard samples were made with an electronic

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Table 1. Density and Refractive Index Data of the Measurement and of the Literature[5] for Methanol, Benzene, Cyclohexane, and 2,3-Dimethyl-1-butene[a]

component CAS No.		methanol 67-56-1	benzene 71-43-2	cyclohexane 110-82-7	2,3-dimethyl-1-butene 563-78-
density/ρ	measurement	0.792	0.874	0.778	0.678
	literature[5]	0.7914	0.8737	0.7785	0.6783
	$\Delta\rho$	0.0006	0.0003	0.0005	0.0003
refractive index/n_D	measurement	1.3289	1.5123	1.4261	1.3903
	literature[5]	1.3285	1.5118	1.4263	1.3905
	Δn_D	0.0004	0.0005	0.0002	0.0002

[a] $\Delta\rho=|\rho_m-\rho_l|$, $\Delta n_D=|n_{Dm}-n_{Dl}|$.

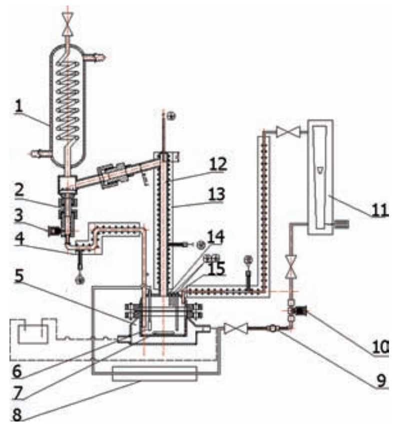

Figure 1. Schematic diagram of the equilibrium still: (1) condensation, (2) observing tube of vapor condensate, (3) septum for vapor sample, (4) electric heating tapes for preheating the condensate and backflow of the liquid phase, (5) oil bath, (6) equilibrium still, (7) magnetic stirrer, (8) cooling, (9) piston pump, (10) septum for liquid sample, (11) flow meter, (12) vapor rising space, (13) electric heating tapes for heating the vapor space, (14) pressure transducer, and (15) thermocouple.

Table 2. Isothermal VLE Data at 403.15 K for the Benzene (1) and Cyclohexane (2) Binary System

p/kPa	x_1	y_1	p/kPa	x_1	y_1
	literature[9] data			experimental data	
387.6	0.8770	0.8670	379.3	1.0000	1.0000
395.4	0.7228	0.7137	388.8	0.8537	0.8441
396.4	0.6307	0.6291	394.5	0.7382	0.7276
396.4	0.5917	0.5866	396.5	0.6048	0.6017
396.3	0.5774	0.5791	396.1	0.5552	0.5619
395.8	0.5332	0.5441	395.0	0.4986	0.5083
393.9	0.4533	0.4704	393.5	0.4408	0.456
391.2	0.3785	0.3998	391.9	0.3948	0.4213
387.3	0.3091	0.3348	389.0	0.3402	0.3645
382.2	0.2266	0.2541	385.1	0.2715	0.3005
372.1	0.0991	0.1178	381.2	0.2184	0.2426
			377.6	0.1676	0.1943
			372.8	0.1107	0.1301
			362.8	0.0000	0.0000

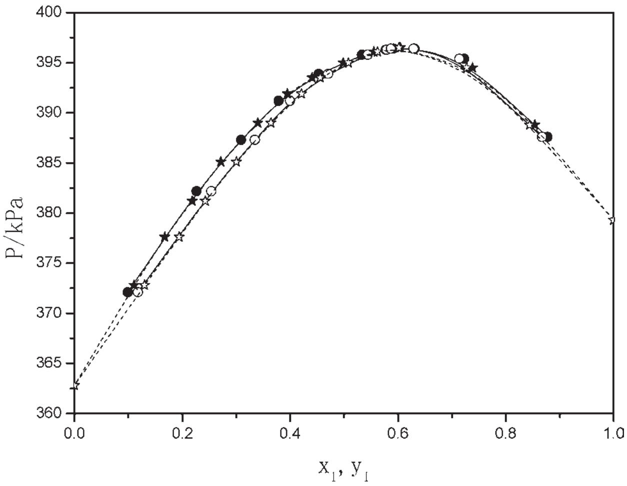

Figure 2. Pressure−composition plots for the benzene (1) + cyclohexane (2) system at 403.15 K: ●, x_1 liquid mole fraction from the literature;[9] ○, y_1 vapor mole fraction from the literature;[9] ★, x_1 liquid mole fraction from this work; ☆, y_1 vapor mole fraction from this work; —, x_1, y_1 calculated from the literature; - - -, x_1, y_1 calculated from this work.

balance (Sartorius, resolution 0.0001 g). The same sample was taken 3 times for GC analysis. The amplitude of areas of peaks of GC was less than 0.001. The accuracy of the analysis of the compositions was estimated to be 0.003 in mole fraction.

Procedure of the VLE Measurement. Pure component 1 was introduced to the recirculation still. The still was vacuumed with a vacuum pump to remove the noncondensable air from the system, and its vapor pressure was measured. After the vapor pressure measurements, component 2 was added to the equilibrium still. In the isothermal runs, the temperature was adjusted to the desired value by adjusting the temperature of the oil bath. The temperature fluctuation of the oil bath was 0.03 K. It took about 50 min to achieve constant temperature, and the temperature was held constant for 30 min to enhance the steady-state condition before sampling. Samples of the liquid and the vapor condensate were taken manually with a cooled syringe after the steady-state condition was achieved. Every sample was analyzed 3 times, and the amplitude of areas of peaks of GC was less than 0.002.

RESULTS AND DISCUSSION

The measured data and calculated activity coefficients are reported in Tables 3 to 6 and Figures 3 to 7. Azeotropic behavior was observed for the methanol + 2,3-dimethyl-1-butene system. Azeotropic data are presented in Table 7. Azeotropic data were determined graphically from the measured values. The data sets measured passed the integral[10] test. The results of the integral

Table 3. VLE Data, Measured Liquid-Phase Mole Fractions x_1, and Measured Vapor-Phase Mole Fractions y_1, for the Methanol (1) + 2,3-Dimethyl-1-butene (2) System at 372.90 K

p/kPa	x_1	y_1	γ_1	γ_2
350.9	1.0000	1.0000		
354.6	0.9997	0.9968	1.01	10.87
425.3	0.9738	0.8205	1.01	8.22
489.1	0.9406	0.7018	1.02	6.81
538.7	0.8932	0.6225	1.05	5.21
591.2	0.7821	0.5531	1.16	3.27
606.9	0.7223	0.5391	1.26	2.71
610.9	0.6596	0.5235	1.35	2.30
615.1	0.5824	0.5049	1.48	1.95
618.2	0.5064	0.5013	1.70	1.67
618.6	0.4727	0.4989	1.81	1.57
614.0	0.4282	0.4969	1.98	1.45
610.1	0.3793	0.4854	2.17	1.36
600.1	0.2846	0.4659	2.73	1.20
575.5	0.1769	0.4165	3.78	1.10
550.1	0.1327	0.3979	4.62	1.04
530.1	0.1053	0.3615	5.11	1.03
491.1	0.0651	0.2997	6.39	1.01
460.8	0.0535	0.2678	6.54	0.99
351.5	0.0000	0.0000		

Table 4. VLE Data, Measured Liquid-Phase Mole Fractions x_1, and Measured Vapor-Phase Mole Fractions y_1, for the Methanol (1) + 2,3-Dimethyl-1-butene (2) System at 363.19 K

p/kPa	x_1	y_1	γ_1	γ_2
255.9	1.0000	1.0000		
263.4	0.9972	0.9689	1.00	10.74
325.1	0.9707	0.7817	1.01	8.74
388.2	0.9178	0.6348	1.03	6.11
443.2	0.818	0.5439	1.13	3.88
456.7	0.7262	0.5089	1.22	2.85
463.6	0.6557	0.5028	1.36	2.32
466.3	0.5833	0.4916	1.50	1.97
467.0	0.499	0.4845	1.73	1.67
466.3	0.4318	0.4706	1.94	1.51
465.6	0.3871	0.4657	2.14	1.41
461.2	0.3101	0.4571	2.60	1.26
452.3	0.2429	0.4378	3.12	1.17
442.7	0.1858	0.4197	3.83	1.10
422.0	0.1184	0.379	5.19	1.04
386.5	0.0679	0.3137	6.90	1.00
331.4	0.0295	0.1895	8.30	0.99
275.3	0.0000	0.0000		

Table 5. VLE Data, Measured Liquid-Phase Mole Fractions x_1, and Measured Vapor-Phase Mole Fractions y_1, for the Methanol (1) + 2,3-Dimethyl-1-butene (2) System at 353.27 K

p/kPa	x_1	y_1	γ_1	γ_2
181.8	1.0000	1.0000		
207.9	0.9865	0.8691	1.00	9.59
224.6	0.9788	0.8121	1.02	9.43
268.3	0.9437	0.6682	1.03	7.39
314.2	0.8543	0.5425	1.08	4.55
325.8	0.8076	0.5113	1.12	3.80
335.3	0.7645	0.4945	1.17	3.30
342.6	0.6439	0.4739	1.36	2.31
345.3	0.5467	0.4597	1.57	1.88
346.9	0.4376	0.4491	1.92	1.55
346.2	0.3716	0.4415	2.22	1.40
344.6	0.2780	0.4315	2.89	1.24
335.5	0.1769	0.4091	4.19	1.10
325.8	0.1380	0.3782	4.84	1.08
299.9	0.0689	0.3208	7.59	1.01
211.4	0.0000	0.0000		

Table 6. VLE Data, Measured Liquid-Phase Mole Fractions x_1, and Measured Vapor-Phase Mole Fractions y_1, for the Methanol (1) + 2,3-Dimethyl-1-butene (2) System at 343.06 K

p/kPa	x_1	y_1	γ_1	γ_2
124.8	1.0000	1.0000		
154.9	0.9788	0.7927	1.00	9.61
193.1	0.9321	0.6285	1.03	6.62
211.0	0.8932	0.5592	1.05	5.43
231.2	0.8115	0.4957	1.12	3.83
241.0	0.7336	0.4633	1.20	3.00
246.3	0.6439	0.4527	1.36	2.33
248.1	0.5933	0.4368	1.43	2.13
248.6	0.5505	0.4358	1.55	1.92
248.7	0.4961	0.4315	1.70	1.73
248.3	0.4067	0.4206	2.02	1.49
247.8	0.3015	0.4100	2.66	1.29
245.0	0.2081	0.3941	3.66	1.15
231.6	0.1068	0.3458	5.93	1.05
223.6	0.0805	0.3139	6.90	1.03
158.3	0.0000	0.0000		

test are also presented in Table 7. The activity coefficients for species i, γ_i, were calculated from eq 1

$$\gamma_i = \frac{p y_i \Phi_i^{\mathrm{v}}}{p_i^{\mathrm{s}} \Phi_i^{\mathrm{s}} x_i \exp\left[\dfrac{V_i^{\mathrm{l}}(p - p_i^{\mathrm{s}})}{RT}\right]} \qquad (1)$$

where y_1 is the molar fraction of component i in the vapor phase; p is the system total pressure; Φ_i^{v} is the fugacity coefficient of component i in the vapor phase; x_i is the molar fraction of component i in the liquid phase; p_i^{s} is the vapor pressure of pure component i at the system temperature; Φ_i^{s} is the pure component saturated liquid fugacity coefficient at the system temperature; V_i^{l} is the component i liquid-phase molar volume at the system temperature; T is the temperature in Kelvin; and R is the universal gas constant (8.314 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$). The Soave−Redlich−Kwong equation of state with quadratic mixing rules in the attractive parameter and linear mixing rules in the covolume

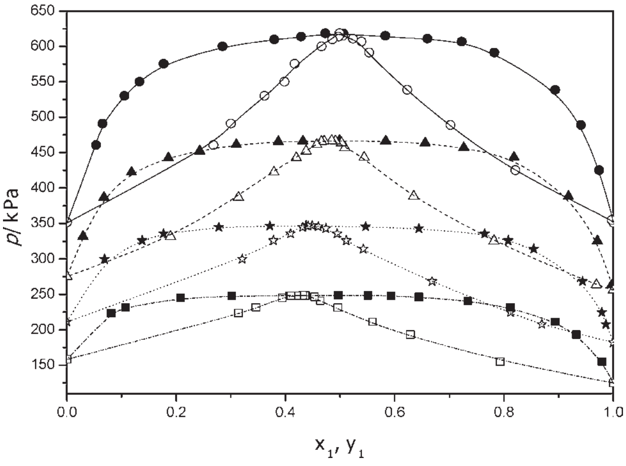

Figure 3. Pressure—composition diagram for the methanol (1) + 2,3-dimethyl-1-butene (2) system at 343.06 K, 353.27 K, 363.19 K, and 372.90 K: ●, x_1 liquid mole fraction measured at 372.90 K; ○, y_1 vapor mole fraction measured at 372.90 K; ▲, x_1 liquid mole fraction measured at 363.19 K; □, y_1 vapor mole fraction measured at 363.19 K; □, x_1 liquid mole fraction measured at 353.27 K; □, y_1 vapor mole fraction measured at 353.27 K; ■, x_1 liquid mole fraction measured at 343.06 K; □, y_1 vapor mole fraction measured at 343.06K; —, x_1, y_1 calculated at 372.90 K; ---, x_1, y_1 calculated at 363.19 K; ······, x_1, y_1 calculated at 353.27 K; — · —, x_1, y_1 calculated at 343.06 K.

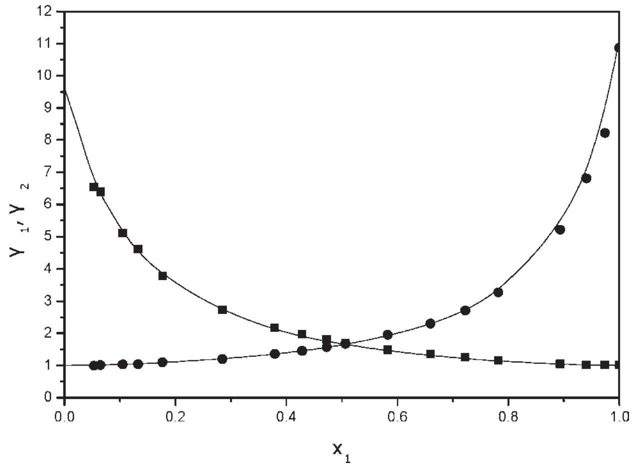

Figure 4. Activity coefficient—composition diagram for the methanol (1) + 2,3-dimethyl-1-butene (2) system at 372.90 K: ■, γ_1 calculated from measurements; ●, γ_2 calculated from measurements; —, γ_1 predicted by the model; —, γ_2 predicted by the model.

was used for vapor-phase calculation. The binary interaction parameter in the quadratic mixing rule was set to zero. The liquid phase was modeled with the Wilson, NRTL, and UNIQUAC equation. The equation for the Wilson model[11] is eq 2.

$$\ln \gamma_i = 1 - \ln\left(\sum_j A_{ij} x_j\right) - \sum_j \frac{A_{ji} x_j}{\sum_k A_{jk} x_k} \tag{2}$$

where $A_{ij} = \exp(b_{ij}/T)$, and b_{ij} can be determined from VLE data regression by using least-squares.

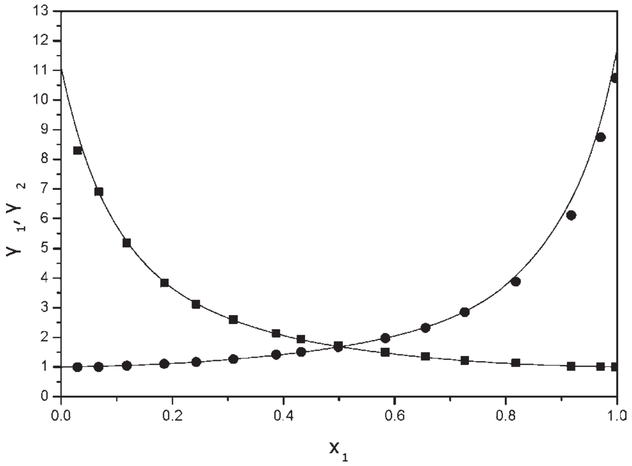

Figure 5. Activity coefficient—composition diagram for the methanol (1) + 2,3-dimethyl-1-butene (2) system at 363.19 K: ■, γ_1 calculated from measurements; ●, γ_2 calculated from measurements; —, γ_1 predicted by the model; —, γ_2 predicted by the model.

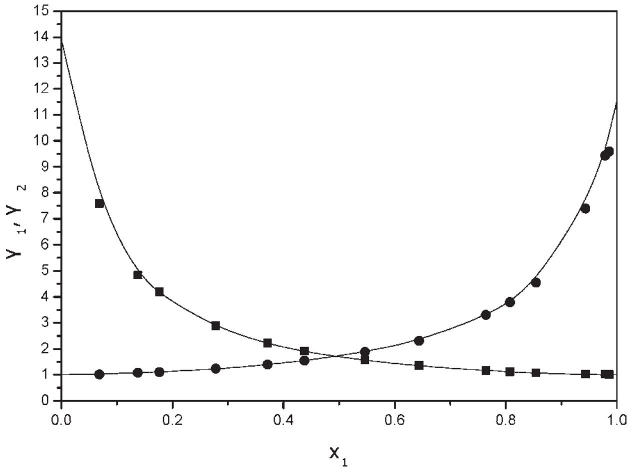

Figure 6. Activity coefficient—composition diagram for the methanol (1) + 2,3-dimethyl-1-butene (2) system at 353.27 K: ■, γ_1 calculated from measurements; ●, γ_2 calculated from measurements; —, γ_1 predicted by the model; —, γ_2 predicted by the model.

The equation for the NRTL model[12] is eq 3

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_x G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right) \tag{3}$$

where $G_{ij} = \exp(-_{ij}\tau_{ij})$, $\tau_{ij} = (g_{ij} - g_{jj})/RT$, and $\alpha_{ij} = \alpha_{ji}$ The parameters $g_{ij} - g_{jj}$ can be determined from VLE data regression by using least-squares. $\alpha_{ij} = \alpha_{ji} = 0.3$ for this system of methanol and 2,3-dimethyl-1-butene.

The equation for the UNIQUAC model[13] is eq 4.

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \left(\frac{Z}{2}\right) q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j - q_i \ln\left(\sum_j \theta_j \tau_{ji}\right)$$

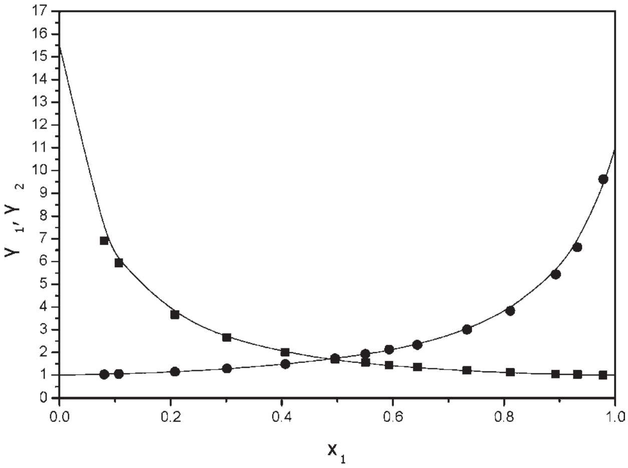

Figure 7. Activity coefficient−composition diagram for the methanol (1) + 2,3-dimethyl-1-butene (2) system at 343.06 K: ■, γ_1 calculated from measurements; ●, γ_2 calculated from measurements; —, γ_1 predicted by the model; —, γ_2 predicted by the model.

Table 7. Binary Interaction Parameters b_{12} and b_{21} of the Wilson Model, Binary Interaction Parameters $g_{12} - g_{22}$ and $g_{21} - g_{11}$ of the NRTL and UNIQUAC Model, Averages of Relative Pressure Residuals $\triangle p$, Averages of the Absolute Vapor Fraction Residuals $\triangle y$ of the Wilson, NRTL, and UNIQUAC Fit, Azeotropic Data, and Results of the Integral Test D[a]

temperature		372.90 K	363.19 K	353.27 K	343.06 K
Wilson	b_{12}	−543.790	−579.448	−647.930	−670.122
	b_{21}	−612.846	−604.330	−568.020	−527.941
	Δp	0.0084	0.0070	0.0054	0.0055
	Δy	0.0038	0.0030	0.0030	0.0033
NRTL	$g_{12} - g_{22}$	4239.508	4074.467	3903.340	3537.965
	$g_{21} - g_{11}$	3550.560	3758.402	3962.743	4150.332
	Δp	0.0089	0.0109	0.0146	0.0114
	Δy	0.0084	0.0116	0.0136	0.0112
UNIQUAC	$g_{12} - g_{22}$	−142.261	−154.349	−171.119	−238.346
	$g_{21} - g_{11}$	5453.178	5538.920	5629.983	5696.661
	Δp	0.0076	0.0091	0.0128	0.0097
	Δy	0.00717	0.0102	0.0118	0.0098
Aze. data	x_{az}	0.501	0.484	0.447	0.426
	p/kPa	620.3	467.6	347.0	248.9
D/%		0.55	0.59	0.51	0.50

[a] The criterion for passing the test is $D < 10$ %.[10]

$$+ q_i - q_i \sum_j \frac{\theta_j \tau_{ij}}{\sum\limits_k \theta_k \tau_{kj}} \tag{4}$$

where $l_i = (Z/2)(r_i - q_i) - (r_i - 1)$, $\theta_i = (q_i x_i)/(\Sigma_j q_j x_j)$, $\Phi_i = (r_i x_i)/(\Sigma_j r_j x_j)$, and $\tau_{ij} = \exp(-(g_{ij} - g_{jj})/RT)$. The parameters $g_{ij} - g_{jj}$ can be determined from VLE data regression by using least-squares. The parameter values of Wilson, NRTL, and UNIQUAC are also presented in Table 7. The average values of the absolute vapor fraction residuals Δy and the averages value of relative pressure residuals Δp for the Wilson, NRTL, and UNIQUAC fit are also presented in Table 7. Values of Δp were calculated from eq 5, values of Δy were calculated from eq 6.

Table 8. Critical Temperatures[5] T_c, Critical Pressures[5] p_c, Critical Molar Volumes[5] V_c, Acentric Factors[5] ω, Critical Compressibility Factors[5] Z_c, Pure-Component Vapor Pressure Equation Parameters A, B, and C Correlated from the Data Measured Regression for the Antoine Equation, and Recommended Temperature Ranges of the Vapor Pressure Correlation $T_{\min}$ and $T_{\max}$

component	methanol	2,3-dimethyl-1-butene
T_c/K	512.58	500.00
P_c/kPa	8090	3220
V_c/cm^3·mol^{-1}	117.8	349.0
ω	0.566	0.227
Z_c	0.244	0.270
A	9.6002	7.288
B	3591.792	2846.140
C	−35.5678	−31.356
$T_{\min}$/K	333.42	341.87
$T_{\max}$/K	375.89	377.37

$$\Delta p = \frac{\sum\limits_i^{NP} |(p_{iexp} - p_{ical})/p_{iexp} \cdot 100\ \%|}{NP} \tag{5}$$

$$\Delta y = \frac{\sum\limits_i^{NP} |(y_{iexp} - y_{ical})|}{NP} \tag{6}$$

The critical temperatures, critical pressures, critical volumes, acentric factors, and critical compressibility factor used in the calculations are presented in Table 8. The vapor pressures of the pure component were calculated from the Antoine equation, eq 7.

$$\ln p = A - \frac{B}{T + C} \tag{7}$$

here p is the vapor pressure in MPa and T is the temperature in K. Antoine constants determined from experimental vapor pressure data are also presented in Table 8. Tables 9 and 10 show the experimental vapor pressure data for methanol and 2,3-dimethyl-1-butene. If calculated with Antoine constants from the literature,[14,5] vapor pressure values of methanol[14] and 2,3-dimethyl-1-butene[5] are compared with the measured values at 333.42 K and 345.85 K, respectively, and the relative pressure residuals between measured and calculated are 0.2 % and 0.7 %, respectively, which can indicate the measured values are close to those from the literature.[14,5] The results shown in Figure 8 were fitted to the Antoine equation, eq 7. There is a Bancroft point at 372.2 K for methanol and 2,3-dimethyl-1-butene. The reason is that methanol is a lower molecular weight and strong polarity component, and 2,3-dimethyl-1-butene is a nonpolarity component. Their boiling temperatures are reasonably close, and the slopes of their vapor pressure curves are different. The liquid molar volumes can be calculated from the Rackett[15] equation, eq 8

$$V_i^l = V_c Z_c^{(1 - T_r)^{2/7}} \tag{8}$$

where $T_r = T/T_c$; T_c is the critical temperature of component i; V_c is the critical molar volume of component i; and Z_c is the critical

Table 9. Pure Component Vapor Pressures of Methanol

T/K	p/kPa	T/K	p/kPa
333.42	85.4	358.91	221.3
334.56	89.5	361.45	241.4
337.65	101.3	363.85	261.6
342.17	120.9	366.88	288.9
346.64	142.6	370.13	321.3
350.25	163.2	372.04	341.2
353.17	181.0	375.89	385.4
356.35	202.7		

Table 10. Pure Component Vapor Pressures of 2,3-Dimethyl-1-butene

T/K	p/kPa	T/K	p/kPa	T/K	p/kPa
341.87	153.7	358.73	244.9	371.12	336.4
343.95	162.3	361.30	262.1	372.21	346.1
345.83	171.3	362.89	273.7	373.70	358.8
347.12	178.2	364.38	284.9	374.59	366.7
348.71	186.4	365.57	292.7	375.19	372.1
350.49	196.3	366.96	303.8	375.78	377.4
352.78	208.6	368.24	313.9	376.87	386.8
354.06	216.3	369.04	319.7	377.37	391.7
356.15	228.9	370.13	328.6		

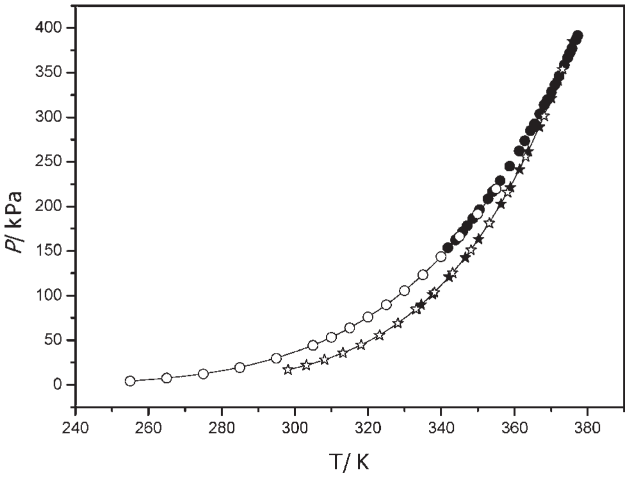

Figure 8. Vapor pressure: ●, 2,3-dimethyl-1-butene, this work; -○-, 2,3-dimethyl-1-butene, the literature;[5] ★, methanol, this work; -☆-, methanol, the literature.[14].

compressibility factor of component i. The objective function,[16] OF, used to fit the Wilson, NRTL, and UNIQUAC equation parameters is presented in eq 9.

$$\mathrm{OF} = \sum_{i=1}^{\mathrm{NP}} \left[\left(\frac{P_{i\mathrm{exp}} - P_{i\mathrm{cal}}}{P_{i\mathrm{exp}}} \right)^2 + \left(\frac{y_{i\mathrm{exp}} - y_{i\mathrm{cal}}}{y_{i\mathrm{exp}}} \right)^2 \right] \qquad (9)$$

where NP is the number of points used in the fit.

CONCLUSIONS

1. The binary interaction parameters of Wilson, NRTL, and UNIQUAC equations for the system of methanol and 2,3-dimethyl-1-butene were determined from VLE data measured in this paper.
2. The isothermal binary VLE data of methanol and 2,3-dimethyl-1-butene correlated by using the Wilson equation with temperature-dependent parameters are better than those by using NRTL and UNIQUAC equations.
3. The system of methanol and 2,3-dimethyl-1-butene has azeotropic behavior, and the azeotropic composition increases with increasing temperature. The amplitude of variation is small. The increasing range of the azeotropic composition is from 0.017 to 0.038 when the temperature is raised 10 K at the range of 343.06 K to 372.90 K.

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REFERENCES

(1) *Commission Findings: Timetable for the Phaseout of MTBE from California's Gasoline Supply: DocketNo.99-GEO-1*, California Energy Commission: Sacram-cram, CA, 1999.

(2) Snelling, J.; Christine, W. C.; YoonKook, P. Synthesis of higher carbon ethers from olefins and alcohols I. Reactions with methanol. *Fuel Process. Technol.* **2003**, *83*, 219–234.

(3) Shaobin, W.; James, A. G. Catalytic activity of silica supported sulfated zirconia catalysts for liquid phase etherification of C_6 olefins with alcohols. *Fuel Process. Technol.* **2003**, *84*, 135–146.

(4) Sergey, P. V. Thermochemistry of Branched Ethers: Experimental Study of Chemical Equilibrium in the Reacting System of tert-Amyl Alkyl Ether Synthesis. *J. Chem. Eng. Data* **2004**, *49*, 576–581.

(5) Yaws, C. L. *Chemical Properties Handbook*; McGraw-Hill: New York, 1999

(6) Maria, C. I.; Fernand, C. T. Vapor-liquid equilibrium for the acetone−methanol−inorganic salt system. *Fluid Phase Equilib.* **1995**, *103*, 257–284.

(7) Thomas, E. S.; Robert, F. B. Vapor-liquid Equilibrium Still for Partially Miscible Liquids. *Ind. Eng. Chem.* **1949**, *41*, 2867–2871.

(8) Fu-Ming, L.; Robert, H. P. Solvent Screening Study and Conceptual Extractive Distillation Process To Produce Anhydrous Ethanol from Fermentation Broth. *Ind. Eng. Chem. Process Des. Dev.* **1985**, *24*, 168–172.

(9) Wisniewska, B.; Gregorowicz, J.; Malanowski, S. Development of a vapor-liquid equilibrium apparatus to work at pressures up to 3 MPa. *Fluid Phase Equilib.* **1993**, *86*, 173–186.

(10) Gmehling, J.; Onken, U. *Vapor-Liquid Equilibrium Data Collection*; DECHEMA Chemistry Data Series; DECHEMA: Frankfurt/Main, Germany, 1977; Vol 1, Part 1.

(11) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.

(12) Renon, H.; Prausnitz, J. M. Local compositions in Thermodynamic Excess Function for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135–144.

(13) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or completely Miscible Systems. *AIChE J.* **1975**, *21*, 116.

(14) Uusi-Kyyny, P.; Pokki, J. P.; Aittamaa, J.; Liukkonen, S. Vapor-Liquid Equilibrium for the Binary Systems of Methanol + 2,4,4-Trimethyl-1-pentene at 331 K and 101 kPa and Methanol + 2-Methoxy-2,4,4-trimethyl-1-pentane at 333 K. *J. Chem. Eng. Data* **2001**, *46*, 1244–1248.

(15) Rackett, H. G. Equation of state for saturated liquids. *J. Chem. Eng. Data* **1970**, *15*, 514.

(16) Barker, J. A. Determination of Activity Coefficients from Total Pressure Measurements. *Aust. J. Chem.* **1953**, *6*, 207–210.