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Isothermal Vapor Liquid Equilibrium for Binary 2-Methylpropene + Methanol to Butanol Systems

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Vapor−liquid equilibria measured with a static apparatus are reported for binary mixtures of 2-methylpropene and the following C1−C4 alcohols at the corresponding temperatures: methanol (323.15 K), ethanol (323.15 K), 2-propanol (323.15 K), 2-butanol (323.15 K), and 2-methyl-2-propanol (313.15 K and 322.77 K). Measured *pTz* (pressure−temperature−total composition) data were reduced to liquid- and vapor-phase compositions using Barker's method. Binary interaction parameters were optimized for the Legendre polynomial, Wilson, UNIQUAC, and nonrandom two-liquid methods. An error analysis for all measured results was performed. All systems indicated a positive deviation from Raoult's law. Azeotropic behavior was observed for 2-methyl propene + methanol binary.

Introduction

Isooctane can be used to replace methyl-*tert*-butyl ether as a fuel additive. It can be hydrogenated from isooctene, which is produced by dimerizing isobutene (2-methylpropene). Oil refinery feed for the dimerization process is a mixture of C_4−alkene isomers. The feed originates either from gas fields or from the fluid catalytic cracking (FCC) process, where long hydrocarbons of oil are cracked into shorter ones. The C4 alkane coming from the gas fields is mainly *n*-butane, which first has to be isomerized to isobutane and then further dehydrogenated into 2-methylpropene. Prepared this way, the feed consists of around 50% 2-methylpropene and 50% isobutane, with small amounts of other short alkanes and alkenes. The FCC produces a mixture of short hydrocarbons containing 15−20% 2-methylpropene.[1]

In dimerization, two 2-methylpropene molecules react on an ion-exchange resin catalyst to produce isooctene isomers (2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene). The presence of 2-methyl-2-propanol (TBA) improves reaction selectivity. Trimers and tetramers are formed as side products. Water and alkenes have reaction equilibrium with corresponding alcohols, and therefore also short-chained alcohols other than TBA exist in the process.

These measurements are part of a measurement project for which the earlier measurements were made with a manual version of the apparatus used.[2,3]

Total pressure−temperature−total composition (pTz) measurements were carried out for the following binary pairs: 2-methylpropene + methanol at 323.15 K; 2-methylpropene + ethanol at 323.15 K; 2-methylpropene + 2-propanol at 323.15 K; 2-methylpropene + 2-butanol at 323.15 K; 2-methylpropene + 2-methyl-2-propanol at 313.15 K and 322.77 K.

Of the systems studied, earlier vapor−liquid equilibria (VLE) studies for 2-methylpropene with methanol and ethanol were found in the literature. Verrazzi and Kikic measured isothermal VLE data for the 2-methylpropene−ethanol binary system at 323.8 K and 374.6 K.[4] Fischer et al.[5] measured isothermal VLE data for the 2-methylpropene−methanol binary system at 363 K, and Miyano et al.[6] measured Henry's constants and infinite dilution activity coefficients for the same binary at (255 to 320) K.

Table 1. Materials, Suppliers, and Purities

compound	company	purity
2-methylpropene	Messer Finland Oy	>99.8 mass %
methanol	Merck	99.8 mass %
ethanol	Primalco Oy	99.5 mass %
2-propanol	Riedel-de Haen	99.8 mass %
2-butanol	Fluka	>99.8 mass %
2-methyl-2-propanol	Fluka	>99.7 mass %

Experimental Section

Materials. The materials, their suppliers, and purities are listed in Table 1. Before degassing, the alcohols were dried with a molecular sieve (Merck3A) for at least 24 h. Alcohol degassing was done in a round-bottomed flask, which was placed in an ultrasonic bath. The degassing procedure for alcohols is discussed in more detail by Laakkonen et al.[3] The schematic figure of the degassing apparatus for the alcohols is presented by Uusi-Kyyny et al.[7]

2-Methylpropene was degassed by first filling a steel cylinder with pressurized 2-methylpropene. The cylinder, equipped with separate inlet and outlet connections with manual valves, was then immersed in a carbon dioxide ice bath and connected to a vacuum pump. The outlet valve was opened with 10-min. intervals to let the gases exit the cylinder. The degassing procedure lasted for at least 3 h. Success of the degassing procedure was checked for both alcohols and 2-methylpropene by measuring the pure-component vapor pressure and comparing it with values from the literature. Table 2 shows the measured pure component vapor pressures and values calculated from literature correlations.

Apparatus. Uusi-Kyyny et al.[7] previously described the static apparatus used in more detail. The experimental setup is presented in Figure 1. Temperature was measured with a temperature meter (Thermolyzer S2541, (Frontek)),

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Table 2. Measured Vapor Pressures and Values Calculated from Literature Correlations

		vapor pressure/kPa			
compound	T/K	a	b	c	d
2-methylpropene	323.11	608.94	605.37	614.81	607.57
	313.12	469.75	464.89	472.75	467.20
	323.14	609.14	605.84	615.28	608.04
		608.84			
	323.15	611.04	605.99	615.43	608.19
	322.79	605.14	600.44	609.82	602.64
Methanol	323.14	55.57	55.61	55.46	55.60
Ethanol	323.17	29.27	29.55	29.43	29.64
2-propanol	323.16	23.47	23.77	24.06	24.03
2-butanol	323.11	10.57	10.65	10.99	11.10
2-methyl-2-propanol	322.78	23.07	23.19	23.08	23.31
	313.13	13.77	13.81	13.74	13.86

[a] This work. [b] Reid et al.[20] [c] Yaws.[21] [d] Perry et al.[15]

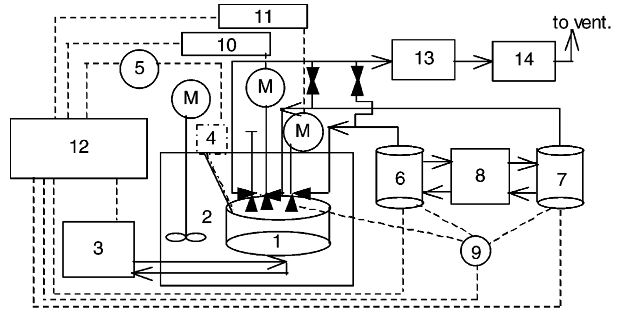

Figure 1. Schematic figure of the automated apparatus: 1, equilibrium cell with a magnetic stirrer; 2, 70-dm^3 water bath; 3, circulator thermostat; 4, electrically traced pressure transducer connected to the equilibrium cell with electrically traced $^1/_{16}$ in. tubing; 5, pressure display; 6 and 7, syringe pumps; 8, circulator thermostat; 9, temperature display; 10 and 11, stepper motor interface card; 12, PC with a SmartIO C168H card at PCI bus; 13, liquid nitrogen trap; 14, vacuum pump.

which was equipped with Pt-100 probes; its resolution was 0.005 K. The equilibrium cell temperature was measured with a probe located in contact with the cell wall. The uncertainty of the temperature measurement was ±0.03 K. The temperature meter was calibrated according to ITS-90.

The pressure was measured with a pressure transducer (Digiquartz 2100A-101-CE (0−689 kPa, compensated temperature range 219−380 K)) equipped with a Digiquartz 740 intelligent display unit. The uncertainty of the pressure measurement was ±0.169 kPa, according to the manufacturer.

The components were injected with syringe pumps (Isco 260D and Isco 100DM). Both the temperature and the pressure of the pump barrels were controlled. The temperature probes were located in contact with the pump barrels, and the pressures of the barrels were controlled with built-in strain gauge pressure meters in the pumps. The injection volumes of the pumps were calibrated gravimetrically with distilled water prior to the measurements.

The equilibrium cell was immersed in a water bath with a volume of approximately 70 dm^3. The water bath was equipped with a water-filled heating coil that maintained the temperature constant. The temperature stability of the bath was ±0.02 K as discussed earlier by Uusi-Kyyny et al.[7] Total volume of the equilibrium cell was 113.66 cm^3. The estimated uncertainty of the cell volume is ±0.05 cm^3.

Procedure. For each six measured systems, an identical measuring procedure was followed. The composition range was measured in two parts; from both ends of pure components to an approximately equimolar mixture. Injection volumes were optimized so that the equilibrium cell became nearly filled with mixture in both parts of the measurement. This was done to improve the measurement accuracy of overall compositions in the equilibrium cell. The syringe pumps were operated in constant pressure mode (900 kPa) to ensure the accuracy of the volume measurement, to prevent the contamination of degassed components, and to keep isobutene in the liquid phase. The Hankinson-Brobst-Thomson model[8] was used to take into account the pressure effects on the liquid densities in the syringe pumps. The temperatures of the syringe pumps were measured. The cell content and the bath were mixed continuously during the measurements.

Pure-component vapor pressures and 23−24 equilibrium points were measured in each run. At first, component 1 was introduced into the cell and its vapor pressure was measured. The unchanged pressure after a second addition of the first component into the cell indicated the success of the degassing. The vapor pressure would rise due to incomplete degassing of the component as a result of dissolved gases in the equilibrium cell. After the vapor pressure measurement of component 1 was taken, a predetermined volume of component 2 was added to the equilibrium cell. The cell content was mixed with a magnetic mixer, and the cell was let to equilibrate for approximately 30 min. The additions of component 2 were continued until the target composition was reached and the cell became nearly filled with the mixture. The emptying and the evacuation of the equilibrium cell ended the first part of the measurement. Measuring the other side of the isotherm was started by injecting the pure component 2 and checking its vapor pressure. The additions of component 1 were continued to the target composition. The success of the run could be verified by comparing the coincidence of the cell pressures as a function of total composition when the different sides of the isotherm meet at the mole fraction of approximately 0.5.

The data transfer between water bath, temperature and pressure meters, stepping motors and syringe pumps, and the PC was operated via a SmartIO C168H/8 ports card at a PCI bus. The actual run was planned in a spreadsheet program. The plan was typed in to Wonderware InTouch program. Once the program was started, the proceeding of measurements could be followed with trend plots. Data written into file as a function of time allowed detailed analysis of the measurements and further calculation of final results.

Data Reduction. The method proposed by Barker[9] was used to convert the total amount of moles fed into the cell into mole fractions in both the vapor and liquid phase. The method of Barker data reduction assumes that there is an activity coefficient model that can predict the bubble point pressure in higher accuracy than the experimental error of the measured total pressure. Barker's method is an iterative method, which needs vapor-phase fugacities and liquid-phase activities to be calculated. The method for calculating fugacity coefficients was chosen to be the Soave modification of Redlich−Kwong cubic equation of state with quadratic mixing rule.[10] Liquid-phase activity coefficients were obtained using the Legendre polynomial,[11] which due to its flexible nature is suitable for accurately predicting nonideal behavior of the liquid phase.

The scheme for data reduction is reported in several publications,[9,12−14] and the scheme used here is reported by Uusi-Kyyny et al.[7] The critical properties needed for

Table 3. Critical Temperature T_c, Critical Pressure p_c, Acentric Factor ω, Liquid Molar Volume v_i, UNIQUAC Volume Parameter R_{UNIQ}, UNIQUAC Area Parameter Q_{UNIQ}

	component					
	2-methylpropene	methanol	ethanol	2-propanol	2-butanol	2-methyl-2-propanol
T_c (K)[a]	417.9 ± 4.18	512.58 ± 5.13	516.25 ± 5.16	508.31 ± 5.08	536.01 ± 5.36	506.2 ± 5.06
p_c (MPa)[a]	3.999 ± 0.12	8.0959 ± 0.24	6.3835 ± 0.19	4.7643 ± 0.14	4.1938 ± 0.13	3.9719 ± 0.12
ω[a]	0.1893	0.5656	0.6371	0.6689	0.5711	0.6158
v_i(cm^3/mol)[a]	94.46 ± 0.94	40.702 ± 0.41	58.515 ± 0.59	76.784 ± 0.15	92.118 ± 0.92	94.861 ± 2.85
R_{UNIQ}[b]	2.920	1.4311	2.2668	3.2491	3.9235	3.9228
Q_{UNIQ}[b]	2.684	1.4320	2.3283	3.1240	3.6640	3.7440

[a] Daubert and Danner.[22] [b] Poling et al.[8]

Table 4. VLE Data for the 2-Methylpropene (1) + Methanol (2) System at 323.15 K[a]

				P/kPa					
T/K	n_1	n_2	z_1	exp	calc	x_1	y_1	γ_1	γ_2
323.14 ± 0.03	0.0000 ± 0.0	0.9571 ± 0.0102	0.0000 ± 0.0	55.57 ± 0.17	55.57	0.0000	0.0000	8.71	1.00
323.13 ± 0.03	0.0339 ± 0.0006	0.9571 ± 0.0102	0.0342 ± 0.0009	180.06 ± 0.17	180.57	0.0309	0.6928	7.36	1.00
323.14 ± 0.03	0.0556 ± 0.0008	0.9571 ± 0.0102	0.0549 ± 0.0013	242.86 ± 0.17	242.86	0.0503	0.7721	6.68	1.01
323.15 ± 0.03	0.1104 ± 0.0013	0.9571 ± 0.0102	0.1034 ± 0.0021	357.26 ± 0.17	356.38	0.0971	0.8460	5.42	1.02
323.15 ± 0.03	0.1713 ± 0.0020	0.9571 ± 0.0102	0.1518 ± 0.0029	435.95 ± 0.17	435.20	0.1452	0.8752	4.49	1.05
323.16 ± 0.03	0.2416 ± 0.0027	0.9571 ± 0.0102	0.2015 ± 0.0035	490.75 ± 0.17	490.75	0.1956	0.8907	3.78	1.09
323.15 ± 0.03	0.3218 ± 0.0035	0.9571 ± 0.0102	0.2516 ± 0.0041	527.85 ± 0.17	528.39	0.2469	0.8998	3.23	1.14
323.15 ± 0.03	0.4129 ± 0.0045	0.9571 ± 0.0102	0.3014 ± 0.0045	552.64 ± 0.17	553.30	0.2981	0.9053	2.80	1.20
323.15 ± 0.03	0.5182 ± 0.0055	0.9571 ± 0.0102	0.3512 ± 0.0049	569.84 ± 0.17	570.01	0.3493	0.9090	2.46	1.28
323.14 ± 0.03	0.6413 ± 0.0068	0.9571 ± 0.0102	0.4012 ± 0.0051	581.94 ± 0.17	581.48	0.4005	0.9116	2.19	1.37
323.13 ± 0.03	0.5929 ± 0.0063	0.8752 ± 0.0094	0.4039 ± 0.0052	581.74 ± 0.17	581.74	0.4024	0.9117	2.18	1.37
323.13 ± 0.03	0.5929 ± 0.0063	0.7140 ± 0.0077	0.4537 ± 0.0053	590.04 ± 0.17	589.67	0.4515	0.9136	1.97	1.48
323.13 ± 0.03	0.5929 ± 0.0063	0.5847 ± 0.0064	0.5035 ± 0.0054	596.34 ± 0.17	595.98	0.5008	0.9152	1.79	1.61
323.13 ± 0.03	0.5929 ± 0.0063	0.4791 ± 0.0054	0.5531 ± 0.0054	601.34 ± 0.17	601.34	0.5501	0.9167	1.65	1.77
323.13 ± 0.03	0.5929 ± 0.0063	0.3909 ± 0.0045	0.6027 ± 0.0053	605.34 ± 0.17	606.04	0.5995	0.9182	1.53	1.96
323.14 ± 0.03	0.5929 ± 0.0063	0.3164 ± 0.0037	0.6520 ± 0.0051	608.84 ± 0.17	610.11	0.6488	0.9197	1.42	2.21
323.14 ± 0.03	0.5929 ± 0.0063	0.2526 ± 0.0031	0.7012 ± 0.0047	612.04 ± 0.17	613.46	0.6982	0.9211	1.33	2.54
323.13 ± 0.03	0.5929 ± 0.0063	0.1963 ± 0.0025	0.7512 ± 0.0043	615.04 ± 0.17	616.07	0.7485	0.9224	1.24	3.01
323.13 ± 0.03	0.5929 ± 0.0063	0.1485 ± 0.0020	0.7997 ± 0.0038	618.04 ± 0.17	618.04	0.7975	0.9236	1.17	3.69
323.14 ± 0.03	0.5929 ± 0.0063	0.1057 ± 0.0016	0.8488 ± 0.0033	621.04 ± 0.17	619.96	0.8473	0.9252	1.11	4.80
323.14 ± 0.03	0.5929 ± 0.0063	0.0678 ± 0.0012	0.8974 ± 0.0026	623.94 ± 0.17	622.36	0.8967	0.9294	1.06	6.73
323.14 ± 0.03	0.5929 ± 0.0063	0.0334 ± 0.0008	0.9467 ± 0.0018	625.94 ± 0.17	623.96	0.9468	0.9432	1.02	10.52
323.15 ± 0.03	0.5929 ± 0.0063	0.0090 ± 0.0006	0.9851 ± 0.0011	619.44 ± 0.17	617.45	0.9853	0.9755	1.00	16.33
323.14 ± 0.03	0.5929 ± 0.0063	0.0000 ± 0.0	1.0000 ± 0.0000	608.84 ± 0.17	608.84	1.0000	1.0000	1.00	19.82

[a] Key: Experimental temperature, T; moles of components in the equilibrium cell, n_1 and n_2; total composition, z_1; experimental pressure, P_{exp}; pressure calculated from the Legendre polynomial fit P_{calc}; calculated liquid- and vapor-phase mole fractions x_1 and y_1; activity coefficients, γ_i.

data reduction by Barker's method are presented in Table 3.

Error Analysis. Error estimates were obtained for all measured variables. Obtained errors are shown in Tables 4−9 with the measured results. For cell volume, temperature, and pressure, absolute errors reported earlier in this article were used. For total mole fractions z_i, the following analysis was done to find out error margins.

The uncertainty on vapor and liquid mole fractions depends on many quantities, such as uncertainties on the measurement of cell temperature, pressure, overall composition of the mixture in the cell, and the total volume of the cell. The uncertainty of the overall composition of the mixture in the cell depends on the uncertainty of injections. The uncertainty of injection volumes $\Delta V_1 = \pm 0.02$ cm^3 was obtained from the calibration experiments with distilled water. The estimated inaccuracies of temperature and pressure measurement in the pumps are $\Delta T = \pm 0.1$ K and $\Delta p = \pm 20$ kPa. Densities of components were calculated from the correlations in ref 15. Uncertainties of density correlations were for 2-methylpropene, methanol, ethanol, 2-propanol, and 2-methyl-2-propanol < 1.0% ($\Delta\rho_1 = \pm 0.01\rho_1$) and for 2-butanol < 3.0% ($\Delta\rho_1 = \pm 0.03\rho_1$).[16]

To estimate the uncertainty of overall composition of the mixture in the cell, theoretical maximum error for an injection is derived below. By differentiating the injected amount of moles n_1 we obtain

$$\mathrm{d}n_1 = \mathrm{d}\left(\frac{\rho_1(T,p)V_1}{M_1}\right) \tag{1}$$

which results as equation for the theoretical maximum error

$$\Delta n_1 = \frac{V_1}{M_1}\Delta\rho_1 + \frac{V_1}{M_1}\left(\left|\frac{\mathrm{d}\rho_1}{\mathrm{d}T}\right|\Delta T + \frac{\mathrm{d}\rho_1}{\mathrm{d}p}\Delta p\right) + \frac{\rho_1}{M_1}\Delta V_1 \tag{2}$$

The modification of the pressure derivative of density gives

$$\Delta n_1 = \frac{V_1}{M_1}\Delta\rho_1 + \frac{V_1}{M_1}\left(\left|\frac{\mathrm{d}\rho_1}{\mathrm{d}T}\right|\Delta T + \left(-\frac{m_1}{{V_1}^2}\frac{\mathrm{d}V_1}{\mathrm{d}p}\Delta p\right)\right) + \frac{\rho_1}{M_1}\Delta V_1 \tag{3}$$

By taking term $\rho_1 V_1/M_1 = n_1$ as multiplier

$$\Delta n_1 = n_1\left(\frac{\Delta\rho_1}{\rho_1} + \frac{1}{\rho_1}\left|\frac{\mathrm{d}\rho_1}{\mathrm{d}T}\right|\Delta T + \left(-\frac{1}{V_1}\left(\frac{\mathrm{d}V_1}{\mathrm{d}p}\right)_T\right)\Delta p + \frac{\Delta V_1}{V_1}\right) \tag{4}$$

Table 5. VLE Data for the 2-Methylpropene (1) + Ethanol (2) System at 323.15 K[a]

				P/kPa					
T/K	n_1	n_2	z_1	exp	calc	x_1	y_1	γ_1	γ_2
323.17 ± 0.03	0.0000 ± 0.0	0.7807 ± 0.0082	0.0000 ± 0.0	29.27 ± 0.17	29.27	0.0000	0.0000	5.41	1.00
323.20 ± 0.03	0.0308 ± 0.0005	0.7807 ± 0.0082	0.0379 ± 0.0010	120.27 ± 0.17	120.63	0.0353	0.7592	4.76	1.00
323.20 ± 0.03	0.0475 ± 0.0007	0.7807 ± 0.0082	0.0573 ± 0.0014	161.37 ± 0.17	161.54	0.0538	0.8210	4.49	1.01
323.21 ± 0.03	0.0919 ± 0.0011	0.7807 ± 0.0082	0.1053 ± 0.0022	249.96 ± 0.17	248.97	0.1002	0.8854	3.92	1.02
323.21 ± 0.03	0.1417 ± 0.0016	0.7807 ± 0.0082	0.1536 ± 0.0029	321.96 ± 0.17	321.08	0.1480	0.9125	3.47	1.03
323.21 ± 0.03	0.1986 ± 0.0022	0.7807 ± 0.0082	0.2028 ± 0.0035	380.45 ± 0.17	380.45	0.1974	0.9274	3.09	1.06
323.21 ± 0.03	0.2630 ± 0.0029	0.7807 ± 0.0082	0.2520 ± 0.0040	426.55 ± 0.17	427.41	0.2474	0.9366	2.77	1.09
323.21 ± 0.03	0.3376 ± 0.0036	0.7807 ± 0.0082	0.3019 ± 0.0045	462.95 ± 0.17	464.06	0.2983	0.9427	2.49	1.14
323.21 ± 0.03	0.4227 ± 0.0045	0.7807 ± 0.0082	0.3513 ± 0.0048	491.35 ± 0.17	491.44	0.3488	0.9468	2.25	1.19
323.20 ± 0.03	0.5228 ± 0.0055	0.7807 ± 0.0082	0.4011 ± 0.0050	514.15 ± 0.17	512.22	0.3998	0.9498	2.04	1.27
323.14 ± 0.03	0.5150 ± 0.0054	0.7733 ± 0.0081	0.3998 ± 0.0050	511.45 ± 0.17	511.45	0.3984	0.9497	2.04	1.26
323.14 ± 0.03	0.5150 ± 0.0054	0.6302 ± 0.0067	0.4497 ± 0.0052	526.95 ± 0.17	526.63	0.4474	0.9519	1.87	1.35
323.14 ± 0.03	0.5150 ± 0.0054	0.5147 ± 0.0055	0.5002 ± 0.0053	539.65 ± 0.17	538.93	0.4971	0.9537	1.72	1.45
323.13 ± 0.03	0.5150 ± 0.0054	0.4205 ± 0.0046	0.5505 ± 0.0053	550.94 ± 0.17	549.38	0.5468	0.9553	1.59	1.58
323.14 ± 0.03	0.5150 ± 0.0054	0.3415 ± 0.0038	0.6013 ± 0.0051	558.34 ± 0.17	558.36	0.5972	0.9569	1.48	1.74
323.14 ± 0.03	0.5150 ± 0.0054	0.2751 ± 0.0031	0.6519 ± 0.0049	565.84 ± 0.17	566.49	0.6475	0.9584	1.39	1.94
323.13 ± 0.03	0.5150 ± 0.0054	0.2184 ± 0.0025	0.7022 ± 0.0046	572.54 ± 0.17	573.65	0.6979	0.9598	1.30	2.21
323.14 ± 0.03	0.5150 ± 0.0054	0.1695 ± 0.0020	0.7524 ± 0.0042	578.84 ± 0.17	579.77	0.7484	0.9613	1.23	2.58
323.13 ± 0.03	0.5150 ± 0.0054	0.1255 ± 0.0016	0.8041 ± 0.0036	585.14 ± 0.17	585.10	0.8006	0.9627	1.16	3.16
323.14 ± 0.03	0.5150 ± 0.0054	0.0878 ± 0.0012	0.8543 ± 0.0030	591.44 ± 0.17	589.94	0.8516	0.9644	1.10	4.07
323.14 ± 0.03	0.5150 ± 0.0054	0.0539 ± 0.0009	0.9052 ± 0.0023	598.14 ± 0.17	595.81	0.9035	0.9676	1.05	5.75
323.13 ± 0.03	0.5150 ± 0.0054	0.0250 ± 0.0006	0.9537 ± 0.0015	605.04 ± 0.17	603.65	0.9531	0.9758	1.01	8.94
323.13 ± 0.03	0.5150 ± 0.0054	0.0137 ± 0.0005	0.9741 ± 0.0011	608.04 ± 0.17	607.40	0.9738	0.9831	1.00	11.22
323.15 ± 0.03	0.5150 ± 0.0054	0.0000 ± 0.0	1.0000 ± 0.0000	611.04 ± 0.17	611.04	1.0000	1.0000	1.00	15.61

[a] Key: Experimental temperature, T; moles of components in the equilibrium cell, n_1 and n_2; total composition, z_1; experimental pressure, P_{exp}; pressure calculated from the Legendre polynomial fit P_{calc}; calculated liquid- and vapor-phase mole fractions x_1 and y_1; activity coefficients, γ_i.

Table 6. VLE Data for the 2-Methylpropene (1) + 2-Propanol (2) System at 323.15 K[a]

				P/kPa					
T/K	n_1	n_2	z_1	exp	calc	x_1	y_1	γ_1	γ_2
323.16 ± 0.03	0.0000 ± 0.0	0.5308 ± 0.0057	0.0000 ± 0.0	23.47 ± 0.17	23.47	0.0000	0.0000	3.89	1.00
323.15 ± 0.03	0.0249 ± 0.0005	0.5308 ± 0.0057	0.0447 ± 0.0013	101.27 ± 0.17	101.58	0.0414	0.7717	3.51	1.00
323.16 ± 0.03	0.0400 ± 0.0006	0.5308 ± 0.0057	0.0700 ± 0.0017	141.17 ± 0.17	141.17	0.0653	0.8370	3.32	1.01
323.16 ± 0.03	0.0675 ± 0.0009	0.5308 ± 0.0057	0.1129 ± 0.0024	202.26 ± 0.17	201.79	0.1065	0.8876	3.04	1.01
323.15 ± 0.03	0.1014 ± 0.0013	0.5308 ± 0.0057	0.1604 ± 0.0031	260.96 ± 0.17	260.58	0.1531	0.9145	2.78	1.03
323.16 ± 0.03	0.1401 ± 0.0017	0.5308 ± 0.0057	0.2088 ± 0.0037	311.96 ± 0.17	311.96	0.2015	0.9300	2.54	1.05
323.16 ± 0.03	0.1834 ± 0.0021	0.5308 ± 0.0057	0.2568 ± 0.0042	354.46 ± 0.17	354.94	0.2500	0.9398	2.33	1.07
323.16 ± 0.03	0.2331 ± 0.0026	0.5308 ± 0.0057	0.3051 ± 0.0046	390.45 ± 0.17	391.09	0.2993	0.9466	2.14	1.11
323.16 ± 0.03	0.2904 ± 0.0032	0.5308 ± 0.0057	0.3537 ± 0.0050	420.65 ± 0.17	421.11	0.3490	0.9515	1.97	1.15
323.16 ± 0.03	0.3563 ± 0.0039	0.5308 ± 0.0057	0.4017 ± 0.0052	445.85 ± 0.17	445.85	0.3983	0.9552	1.83	1.21
323.16 ± 0.03	0.4362 ± 0.0047	0.5308 ± 0.0057	0.4511 ± 0.0053	467.65 ± 0.17	467.34	0.4491	0.9583	1.69	1.28
323.16 ± 0.03	0.5519 ± 0.0059	0.5308 ± 0.0057	0.5097 ± 0.0053	489.45 ± 0.17	489.11	0.5092	0.9614	1.56	1.38
323.16 ± 0.03	0.6484 ± 0.0069	0.5308 ± 0.0057	0.5499 ± 0.0053	501.15 ± 0.17	502.14	0.5502	0.9633	1.48	1.46
323.13 ± 0.03	0.5265 ± 0.0056	0.6433 ± 0.0068	0.4501 ± 0.0053	469.95 ± 0.17	467.66	0.4493	0.9583	1.69	1.28
323.13 ± 0.03	0.5265 ± 0.0056	0.5266 ± 0.0056	0.4999 ± 0.0053	487.15 ± 0.17	485.54	0.4983	0.9609	1.58	1.36
323.13 ± 0.03	0.5265 ± 0.0056	0.3519 ± 0.0038	0.5994 ± 0.0052	515.95 ± 0.17	515.94	0.5964	0.9653	1.40	1.57
323.13 ± 0.03	0.5265 ± 0.0056	0.2845 ± 0.0032	0.6492 ± 0.0049	528.35 ± 0.17	529.17	0.6458	0.9673	1.33	1.72
323.13 ± 0.03	0.5265 ± 0.0056	0.2267 ± 0.0026	0.6990 ± 0.0046	539.95 ± 0.17	541.16	0.6954	0.9693	1.26	1.91
323.13 ± 0.03	0.5265 ± 0.0056	0.1758 ± 0.0020	0.7497 ± 0.0042	551.04 ± 0.17	552.04	0.7461	0.9712	1.20	2.19
323.14 ± 0.03	0.5265 ± 0.0056	0.1336 ± 0.0016	0.7976 ± 0.0037	561.24 ± 0.17	561.24	0.7943	0.9731	1.14	2.56
323.14 ± 0.03	0.5265 ± 0.0056	0.0952 ± 0.0012	0.8468 ± 0.0030	571.64 ± 0.17	570.12	0.8441	0.9752	1.09	3.14
323.14 ± 0.03	0.5265 ± 0.0056	0.0608 ± 0.0009	0.8965 ± 0.0023	582.04 ± 0.17	579.57	0.8945	0.9781	1.05	4.14
323.14 ± 0.03	0.5265 ± 0.0056	0.0302 ± 0.0006	0.9457 ± 0.0015	593.04 ± 0.17	591.35	0.9447	0.9838	1.01	5.96
323.15 ± 0.03	0.5265 ± 0.0056	0.0073 ± 0.0003	0.9864 ± 0.0008	604.44 ± 0.17	604.23	0.9862	0.9941	1.00	8.83
323.14 ± 0.03	0.5265 ± 0.0056	0.0000 ± 0.0	1.0000 ± 0.0000	609.14 ± 0.17	609.14	1.0000	1.0000	1.00	10.29

[a] Key: Experimental temperature, T; moles of components in the equilibrium cell, n_1 and n_2; total composition, z_1; experimental pressure, P_{exp}; pressure calculated from the Legendre polynomial fit P_{calc}; calculated liquid- and vapor-phase mole fractions x_1 and y_1; activity coefficients, γ_i.

and setting

$$\kappa_1 = -\frac{1}{V_1}\left(\frac{\mathrm{d}V_1}{\mathrm{d}p}\right)_T \tag{5}$$

which is the isothermal compressibility. We obtain finally

$$\Delta n_1 = n_1\left(\frac{\Delta\rho_1}{\rho_1} + \frac{1}{\rho_1}\left|\frac{\mathrm{d}\rho_1}{\mathrm{d}T}\right|\Delta T + \kappa_1\Delta p + \frac{\Delta V_1}{V_1}\right) \tag{6}$$

The corresponding equation is valid also for the component 2. In eq 6, the temperature derivative of density was calculated from the density correlation[15] and the isothermal compressibility of liquid from the Hankinson−Brobst−Thompson model.[8]

Errors in overall mole fractions were determined from

$$\Delta z_1 = \left|\frac{n_1}{n_1 + n_2} - \frac{(n_1 + \Delta n_1)}{(n_1 + \Delta n_1) + (n_2 - \Delta n_2)}\right| \tag{7}$$

Table 7. VLE Data for the 2-Methylpropene (1) + 2-Butanol (2) System at 323.15 K[a]

				P/kPa					
T/K	n_1	n_2	z_1	exp	calc	x_1	y_1	γ_1	γ_2
323.11 ± 0.03	0.0000 ± 0.0	0.4934 ± 0.0052	0.0000 ± 0.0	10.57 ± 0.17	10.57	0.0000	0.0000	3.15	1.00
323.11 ± 0.03	0.0222 ± 0.0004	0.4934 ± 0.0052	0.0430 ± 0.0013	72.87 ± 0.17	73.26	0.0402	0.8575	2.91	1.00
323.10 ± 0.03	0.0324 ± 0.0005	0.4934 ± 0.0052	0.0616 ± 0.0016	98.07 ± 0.17	98.31	0.0578	0.8944	2.82	1.00
323.11 ± 0.03	0.0613 ± 0.0008	0.4934 ± 0.0052	0.1105 ± 0.0024	159.57 ± 0.17	159.57	0.1049	0.9361	2.60	1.01
323.10 ± 0.03	0.0936 ± 0.0012	0.4934 ± 0.0052	0.1594 ± 0.0031	214.36 ± 0.17	214.18	0.1529	0.9533	2.41	1.02
323.10 ± 0.03	0.1297 ± 0.0015	0.4934 ± 0.0052	0.2082 ± 0.0037	262.46 ± 0.17	262.46	0.2013	0.9627	2.24	1.04
323.09 ± 0.03	0.1709 ± 0.0020	0.4934 ± 0.0052	0.2572 ± 0.0042	305.06 ± 0.17	305.15	0.2507	0.9687	2.08	1.06
323.09 ± 0.03	0.2174 ± 0.0024	0.4934 ± 0.0052	0.3058 ± 0.0047	341.86 ± 0.17	341.99	0.3000	0.9727	1.94	1.09
323.09 ± 0.03	0.2723 ± 0.0030	0.4934 ± 0.0052	0.3556 ± 0.0050	374.55 ± 0.17	374.70	0.3507	0.9758	1.81	1.13
323.10 ± 0.03	0.3364 ± 0.0037	0.4934 ± 0.0052	0.4054 ± 0.0052	403.15 ± 0.17	403.15	0.4016	0.9781	1.69	1.17
323.09 ± 0.03	0.4099 ± 0.0044	0.4934 ± 0.0052	0.4538 ± 0.0053	427.55 ± 0.17	427.48	0.4512	0.9799	1.59	1.23
323.10 ± 0.03	0.4731 ± 0.0051	0.4934 ± 0.0052	0.4895 ± 0.0053	443.75 ± 0.17	443.73	0.4877	0.9811	1.53	1.28
323.10 ± 0.03	0.4988 ± 0.0053	0.4934 ± 0.0052	0.5028 ± 0.0053	449.45 ± 0.17	449.44	0.5013	0.9815	1.50	1.29
323.12 ± 0.03	0.5254 ± 0.0056	0.4710 ± 0.0050	0.5273 ± 0.0053	459.75 ± 0.17	459.47	0.5259	0.9822	1.46	1.33
323.12 ± 0.03	0.5254 ± 0.0056	0.4311 ± 0.0046	0.5493 ± 0.0053	467.85 ± 0.17	467.85	0.5475	0.9828	1.43	1.37
323.12 ± 0.03	0.5254 ± 0.0056	0.3510 ± 0.0038	0.5995 ± 0.0051	485.25 ± 0.17	485.81	0.5970	0.9841	1.35	1.47
323.12 ± 0.03	0.5254 ± 0.0056	0.2835 ± 0.0031	0.6495 ± 0.0049	501.15 ± 0.17	502.19	0.6465	0.9852	1.29	1.59
323.12 ± 0.03	0.5254 ± 0.0056	0.2258 ± 0.0025	0.6994 ± 0.0046	515.95 ± 0.17	517.10	0.6961	0.9863	1.23	1.75
323.11 ± 0.03	0.5254 ± 0.0056	0.1761 ± 0.0020	0.7489 ± 0.0041	529.75 ± 0.17	530.53	0.7455	0.9874	1.18	1.97
323.11 ± 0.03	0.5254 ± 0.0056	0.1315 ± 0.0016	0.7998 ± 0.0036	543.35 ± 0.17	543.17	0.7966	0.9884	1.12	2.29
323.11 ± 0.03	0.5254 ± 0.0056	0.0931 ± 0.0012	0.8494 ± 0.0029	556.24 ± 0.17	555.02	0.8466	0.9896	1.08	2.78
323.11 ± 0.03	0.5254 ± 0.0056	0.0584 ± 0.0008	0.9000 ± 0.0022	569.84 ± 0.17	568.07	0.8978	0.9912	1.04	3.59
323.12 ± 0.03	0.5254 ± 0.0056	0.0256 ± 0.0005	0.9535 ± 0.0013	586.44 ± 0.17	585.91	0.9524	0.9942	1.01	5.17
323.11 ± 0.03	0.5254 ± 0.0056	0.0038 ± 0.0003	0.9927 ± 0.0006	604.24 ± 0.17	604.63	0.9925	0.9988	1.00	7.33
323.11 ± 0.03	0.5254 ± 0.0056	0.0000 ± 0.0	1.0000 ± 0.0000	608.94 ± 0.17	608.94	1.0000	1.0000	1.00	7.89

[a] Key: Experimental temperature, T; moles of components in the equilibrium cell, n_1 and n_2; total composition, z_1; experimental pressure, P_{exp}; pressure calculated from the Legendre polynomial fit P_{calc}; calculated liquid- and vapor-phase mole fractions x_1 and y_1; activity coefficients, γ_i.

Table 8. VLE Data for the 2-Methylpropene (1) + 2-Methyl-2-Propanol (2) System at 313.15 K[a]

				P/kPa					
T/K	n_1	n_2	z_1	exp	calc	x_1	y_1	γ_1	γ_2
313.13 ± 0.03	0.0000 ± 0.0	0.4840 ± 0.0051	0.0000 ± 0.0	13.77 ± 0.17	13.77	0.0000	0.0000	2.88	1.00
313.13 ± 0.03	0.0069 ± 0.0003	0.4840 ± 0.0051	0.0140 ± 0.0007	28.87 ± 0.17	29.21	0.0132	0.5315	2.79	1.00
313.13 ± 0.03	0.0197 ± 0.0004	0.4840 ± 0.0051	0.0390 ± 0.0012	55.07 ± 0.17	55.26	0.0371	0.7552	2.66	1.00
313.13 ± 0.03	0.0481 ± 0.0007	0.4840 ± 0.0051	0.0904 ± 0.0021	103.47 ± 0.17	103.47	0.0866	0.8726	2.43	1.01
313.13 ± 0.03	0.0798 ± 0.0010	0.4840 ± 0.0051	0.1416 ± 0.0029	146.57 ± 0.17	146.13	0.1368	0.9122	2.25	1.02
313.13 ± 0.03	0.1172 ± 0.0014	0.4840 ± 0.0051	0.1949 ± 0.0036	186.16 ± 0.17	185.82	0.1898	0.9331	2.09	1.03
313.13 ± 0.03	0.1590 ± 0.0018	0.4840 ± 0.0051	0.2473 ± 0.0042	220.56 ± 0.17	220.56	0.2423	0.9454	1.95	1.05
313.12 ± 0.03	0.2067 ± 0.0023	0.4840 ± 0.0051	0.2992 ± 0.0046	250.96 ± 0.17	251.25	0.2947	0.9537	1.83	1.08
313.12 ± 0.03	0.2625 ± 0.0029	0.4840 ± 0.0051	0.3517 ± 0.0050	278.36 ± 0.17	278.81	0.3478	0.9598	1.72	1.11
313.12 ± 0.03	0.3265 ± 0.0036	0.4840 ± 0.0051	0.4028 ± 0.0052	302.46 ± 0.17	302.80	0.3998	0.9643	1.62	1.15
313.12 ± 0.03	0.4026 ± 0.0044	0.4840 ± 0.0051	0.4541 ± 0.0053	324.36 ± 0.17	324.36	0.4519	0.9680	1.54	1.20
313.12 ± 0.03	0.4373 ± 0.0047	0.4840 ± 0.0051	0.4747 ± 0.0053	332.56 ± 0.17	332.41	0.4729	0.9693	1.50	1.22
313.12 ± 0.03	0.4681 ± 0.0050	0.4840 ± 0.0051	0.4917 ± 0.0053	339.16 ± 0.17	338.82	0.4902	0.9703	1.48	1.24
313.12 ± 0.03	0.4938 ± 0.0053	0.4840 ± 0.0051	0.5050 ± 0.0053	344.26 ± 0.17	343.72	0.5038	0.9710	1.46	1.26
313.13 ± 0.03	0.5052 ± 0.0054	0.5067 ± 0.0054	0.4992 ± 0.0053	342.66 ± 0.17	341.79	0.4983	0.9707	1.46	1.25
313.12 ± 0.03	0.5052 ± 0.0054	0.4152 ± 0.0044	0.5489 ± 0.0053	358.46 ± 0.17	358.45	0.5472	0.9732	1.40	1.32
313.13 ± 0.03	0.5052 ± 0.0054	0.3384 ± 0.0037	0.5989 ± 0.0052	373.25 ± 0.17	373.80	0.5966	0.9755	1.33	1.40
313.13 ± 0.03	0.5052 ± 0.0054	0.2732 ± 0.0030	0.6490 ± 0.0049	386.95 ± 0.17	387.78	0.6464	0.9776	1.28	1.51
313.13 ± 0.03	0.5052 ± 0.0054	0.2172 ± 0.0024	0.6993 ± 0.0046	399.75 ± 0.17	400.39	0.6964	0.9795	1.22	1.65
313.13 ± 0.03	0.5052 ± 0.0054	0.1682 ± 0.0019	0.7502 ± 0.0041	411.75 ± 0.17	411.75	0.7473	0.9813	1.17	1.85
313.13 ± 0.03	0.5052 ± 0.0054	0.1260 ± 0.0015	0.8004 ± 0.0036	422.85 ± 0.17	421.78	0.7976	0.9830	1.12	2.13
313.13 ± 0.03	0.5052 ± 0.0054	0.0886 ± 0.0011	0.8508 ± 0.0029	433.45 ± 0.17	431.23	0.8484	0.9849	1.08	2.58
313.13 ± 0.03	0.5052 ± 0.0054	0.0559 ± 0.0008	0.9004 ± 0.0022	443.65 ± 0.17	440.99	0.8987	0.9873	1.04	3.30
313.13 ± 0.03	0.5052 ± 0.0054	0.0270 ± 0.0005	0.9493 ± 0.0014	454.15 ± 0.17	452.69	0.9483	0.9913	1.01	4.55
313.12 ± 0.03	0.5052 ± 0.0054	0.0058 ± 0.0003	0.9887 ± 0.0006	465.15 ± 0.17	465.32	0.9885	0.9973	1.00	6.36
313.12 ± 0.03	0.5052 ± 0.0054	0.0000±0.0	1.0000 ± 0.0000	469.75 ± 0.17	469.75	1.0000	1.0000	1.00	7.10

[a] Key: Experimental temperature, T; moles of components in the equilibrium cell, n_1 and n_2; total composition, z_1; experimental pressure, P_{exp}; pressure calculated from the Legendre polynomial fit P_{calc}; calculated liquid- and vapor-phase mole fractions x_1 and y_1; activity coefficients, γ_i.

Results and Discussion

The results from each six runs are presented in Tables 4−9. Injected amounts of moles are presented in Tables 4−9 using more significant digits than their maximum theoretical errors would indicate. This is required if someone wants to recalculate the measured data. In Figure 2, the experimental pressures are plotted against liquid and vapor compositions. In all measured sets, the two sides of the isotherms coincide well, which indicates that degassing of the components has been successful. Figure 3 shows activity coefficients calculated from the Legendre polynomial as a function of liquid-phase composition. Optimized

Table 9. VLE Data for the 2-Methylpropene (1) + 2-Methyl-2-Propanol (2) System at 322.77 K[a]

				P/kPa					
T/K	n_1	n_2	z_1	exp	calc	x_1	y_1	γ_1	γ_2
322.78 ± 0.03	0.0000 ± 0.0	0.3082 ± 0.0033	0.0000 ± 0.0	23.07 ± 0.17	23.07	0.0000	0.0000	2.79	1.00
322.77 ± 0.03	0.0103 ± 0.0003	0.3082 ± 0.0033	0.0324 ± 0.0013	62.57 ± 0.17	62.73	0.0286	0.6365	2.62	1.00
322.78 ± 0.03	0.0142 ± 0.0004	0.3082 ± 0.0033	0.0439 ± 0.0015	76.17 ± 0.17	76.17	0.0390	0.7020	2.56	1.00
322.79 ± 0.03	0.0334 ± 0.0006	0.3082 ± 0.0033	0.0978 ± 0.0024	134.87 ± 0.17	134.87	0.0887	0.8355	2.35	1.01
322.79 ± 0.03	0.0546 ± 0.0008	0.3082 ± 0.0033	0.1506 ± 0.0032	187.56 ± 0.17	187.12	0.1389	0.8844	2.17	1.02
322.79 ± 0.03	0.0771 ± 0.0010	0.3082 ± 0.0033	0.2001 ± 0.0038	232.56 ± 0.17	232.14	0.1871	0.9092	2.04	1.03
322.78 ± 0.03	0.1059 ± 0.0013	0.3082 ± 0.0033	0.2556 ± 0.0044	278.06 ± 0.17	278.06	0.2423	0.9266	1.90	1.05
322.78 ± 0.03	0.1349 ± 0.0016	0.3082 ± 0.0033	0.3044 ± 0.0048	314.16 ± 0.17	314.52	0.2915	0.9371	1.79	1.07
322.77 ± 0.03	0.1671 ± 0.0019	0.3082 ± 0.0033	0.3515 ± 0.0051	345.96 ± 0.17	346.36	0.3396	0.9446	1.69	1.10
322.77 ± 0.03	0.2072 ± 0.0023	0.3082 ± 0.0033	0.4020 ± 0.0053	376.85 ± 0.17	377.16	0.3916	0.9509	1.60	1.14
322.77 ± 0.03	0.2529 ± 0.0028	0.3082 ± 0.0033	0.4507 ± 0.0054	403.95 ± 0.17	403.94	0.4419	0.9558	1.52	1.18
322.77 ± 0.03	0.3086 ± 0.0034	0.3082 ± 0.0033	0.5003 ± 0.0055	429.05 ± 0.17	428.75	0.4933	0.9599	1.44	1.24
322.77 ± 0.03	0.3626 ± 0.0039	0.3082 ± 0.0033	0.5406 ± 0.0054	447.85 ± 0.17	447.35	0.5350	0.9629	1.38	1.29
322.77 ± 0.03	0.4554 ± 0.0049	0.4465 ± 0.0048	0.5049 ± 0.0053	433.25 ± 0.17	433.08	0.5028	0.9607	1.43	1.25
322.75 ± 0.03	0.4554 ± 0.0049	0.3657 ± 0.0039	0.5546 ± 0.0053	454.35 ± 0.17	454.35	0.5516	0.9641	1.36	1.32
322.75 ± 0.03	0.4554 ± 0.0049	0.2989 ± 0.0033	0.6037 ± 0.0052	473.55 ± 0.17	473.91	0.6000	0.9671	1.30	1.40
322.75 ± 0.03	0.4554 ± 0.0049	0.2423 ± 0.0027	0.6527 ± 0.0049	491.45 ± 0.17	492.10	0.6485	0.9699	1.25	1.50
322.77 ± 0.03	0.4554 ± 0.0049	0.1934 ± 0.0022	0.7019 ± 0.0046	508.15 ± 0.17	509.03	0.6974	0.9726	1.20	1.62
322.76 ± 0.03	0.4554 ± 0.0049	0.1476 ± 0.0017	0.7552 ± 0.0041	525.35 ± 0.17	525.89	0.7508	0.9754	1.15	1.82
322.76 ± 0.03	0.4554 ± 0.0049	0.1110 ± 0.0013	0.8040 ± 0.0036	540.05 ± 0.17	540.04	0.7999	0.9779	1.11	2.07
322.76 ± 0.03	0.4554 ± 0.0049	0.0777 ± 0.0010	0.8543 ± 0.0029	554.54 ± 0.17	553.89	0.8508	0.9807	1.07	2.47
322.76 ± 0.03	0.4554 ± 0.0049	0.0487 ± 0.0007	0.9034 ± 0.0022	568.84 ± 0.17	567.87	0.9008	0.9842	1.03	3.10
322.77 ± 0.03	0.4554 ± 0.0049	0.0225 ± 0.0004	0.9530 ± 0.0013	584.64 ± 0.17	584.44	0.9517	0.9897	1.01	4.24
322.78 ± 0.03	0.4554 ± 0.0049	0.0037 ± 0.0002	0.9920 ± 0.0006	600.74 ± 0.17	601.10	0.9917	0.9976	1.00	5.84
322.79 ± 0.03	0.4554 ± 0.0049	0.0000 ± 0.0	1.0000 ± 0.0000	605.14 ± 0.17	605.14	1.0000	1.0000	1.00	6.30

[a] Key: Experimental temperature, T; moles of components in the equilibrium cell, n_1 and n_2; total composition, z_1; experimental pressure, P_{exp}; pressure calculated from the Legendre polynomial fit P_{calc}; calculated liquid- and vapor-phase mole fractions x_1 and y_1; activity coefficients, γ_i.

Table 10. Activity Coefficient Model Parameters: Legendre,[11] Wilson,[17] NRTL,[18] UNIQUAC[20] [a]

	system					
	1	2	3	4	5	6
Legendre, $a_{1.0}$	2.2575	1.9415	1.6188	1.4108	1.3002	1.2343
Legendre, $a_{2.0}$	0.3350	0.4457	0.4116	0.3964	0.4019	0.3536
Legendre, $a_{3.0}$	0.2894	0.2410	0.2005	0.1762	0.2025	0.1763
Legendre, $a_{4.0}$	0.0761	0.0835	0.0741	0.0625	0.0603	0.0530
Legendre, $a_{5.0}$	0.0286	0.0359	0.0260	0.0199	0.0233	0.0228
Δp/kPa	0.132	0.292	0.216	−0.026	0.252	−0.014
$\|\Delta p\|$/kPa	0.656	0.734	0.689	0.369	0.555	0.309

	system				
	1	2	3	4	5 + 6
Wilson, λ_{12}/J·mol^{-1}	1123.624	778.0515	735.289	749.6408	1700.039
Wilson, λ_{21}/J·mol^{-1}	9234.105	7977.172	5780.05	4757.432	1857.574
Wilson, λ_{12}/J·K^{-1}·mol^{-1}					−3.9549
Wilson, λ_{21}/J·K^{-1}·mol^{-1}					8.089727
Δp/kPa	0.026	0.719	0.651	1.484	1.675
$\|\Delta p\|$/kPa	1.805	1.892	2.571	2.565	4.001
NRTL, λ_{12}/K	623.31	624.86	536.5	509.33	338.57
NRTL, λ_{21}/K	395.69	244.57	149.31	87.568	−198.63
NRTL, λ_{12}					0.4408
NRTL, λ_{21}					0.7763
NRTL, $\alpha_{12} = \alpha_{21}$	0.4	0.4	0.4	0.4	0.4
Δp/kPa	2.464	2.972	2.660	2.820	2.543
$\|\Delta p\|$/kPa	7.823	6.370	5.603	5.235	6.167
UNIQUAC, λ_{12}/K	614.81	437.58	295.04	191.45	151.54
UNIQUAC, λ_{21}/K	9.091	−39.681	−37.263	−15.511	6.713
UNIQUAC, λ_{12}					0.167
UNIQUAC, λ_{21}					−0.130
Δp/kPa	3.876	5.271	3.260	−0.771	2.627
$\|\Delta p\|$/kPa	11.198	9.152	6.824	6.837	5.743

[a] Data regressed with the Legendre polynomials, average pressure residual Δp, absolute average pressure residual $|\Delta p|$, 2-methylpropene + methanol at 323.15 K (system 1), 2-methylpropene + ethanol at 323.15 K (system 2), 2-methylpropene + 2-propanol at 323.15 K (system 3), 2-methylpropene + 2-butanol at 323.15 K (system 4), 2-methylpropene + 2-methyl-2-propanol at 313.15 K (system 5), and 2-methylpropene + 2-methyl-2-propanol at 322.77 K (system 6).

sets of parameters for Legendre polynomial, Wilson,[17] UNIQUAC,[18] and (nonrandom two-liquid) NRTL[19] methods are presented in Table 10. These optimizations are based on phase compositions given by Barker's method that uses the Legendre polymial to calculate liquid-phase activity coefficients. For the 2-methylpropene + 2-methyl-2-pro-

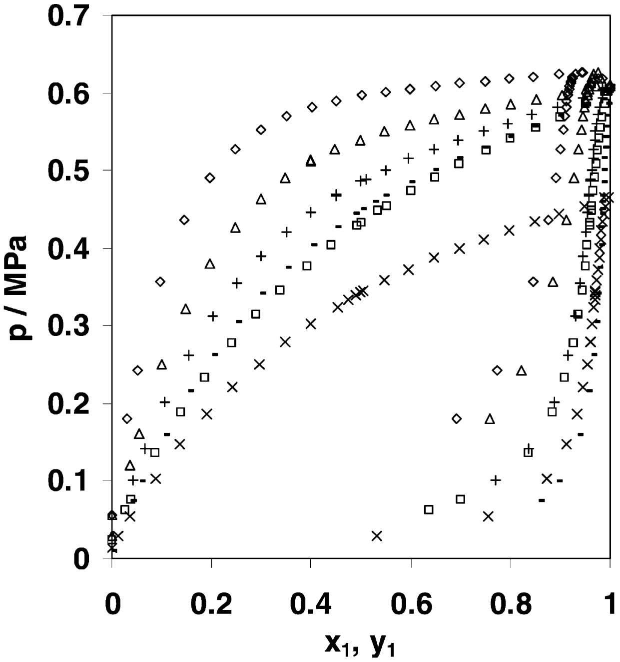

Figure 2. Pressure composition diagram of 2-methylpropene (1) + alcohol (2) at 323.15 K (313.15 K): ◇, 2-methylpropene + methanol; △, 2-methylpropene + ethanol; +, 2-methylpropene + 2-propanol; -, 2-methylpropene + 2-butanol; □, 2-methylpropene + 2-methyl-2-propanol (322.77 K); ×, 2-methylpropene + 2-methyl-2-propanol (313.15 K).

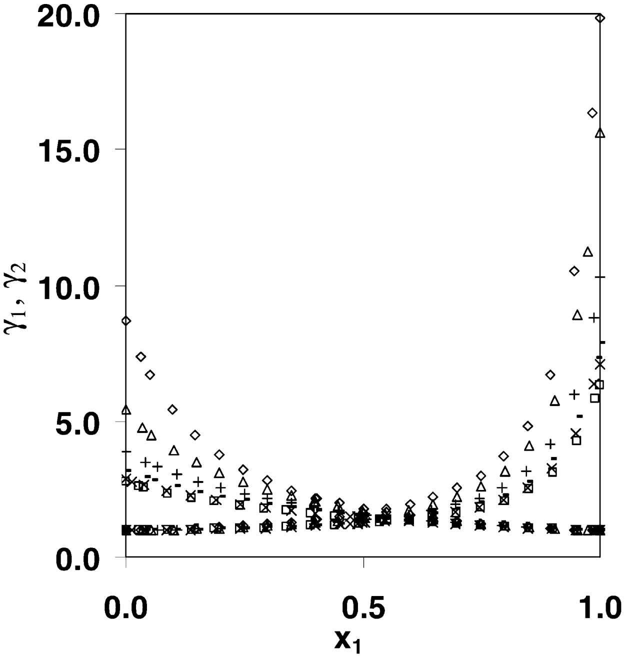

Figure 3. Activity coefficient composition diagram of 2-methylpropene (1) + alcohol (2) at 323.15 K (313.15 K): ◇, 2-methylpropene + methanol; △, 2-methylpropene + ethanol; +, 2-methylpropene + 2-propanol; -, 2-methylpropene + 2-butanol; ×, 2-methylpropene + 2-methyl-2-propanol (322.77 K); □, 2-methylpropene + 2-methyl-2-propanol (313.15 K).

panol binary system, also temperature-dependent parameters for Wilson, UNIQUAC, and NRTL methods were fitted.

All five binary pairs measured showed positive deviation from Raoult's law. The azeotropic point was found for 2-methylpropene (1) + methanol (2) pair experimentally and from Legendre polynomial at point $x_1 = 0.941$, $T = 323.14$ K, and $p = 623.1$ kPa. Other 2-methylpropene + alcohol binaries did not show azeotropic behavior at these temperatures. Fischer et al.[5] studied the vapor−liquid equilibrium between 2-methylpropene and ethanol at 363 K and found azeotropic behavior at this temperature. Also Verracci and Kikic[4] report an azeotrope for 2-methylpropene and ethanol at 374.56 K but not at 323.78 K. In neither of these studies could the azeotropes be measured but were found based on model predictions. The azeotropic compositions occur at low alcohol mole fractions where both experimental methods and models have large uncertainties.

Miyano et al.[6] used the gas-stripping method for determining Henry's constant and infinite dilution activity coefficients for 2-methylpropene in methanol at 320.02 K. They reported a value of 9.1 for γ_{inf} of 2-methylpropene. Our prediction with the Legendre polynomial for γ_{inf} of 2-methylpropene at 323.14 K is 8.71, which is in agreement with results of Miyano et al., even though the results were obtained with different methods.

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