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Isothermal Vapor Liquid Equilibrium for 2-Methylpropene + Methanol, + 1-Propanol, + 2-Propanol, + 2-Butanol, and + 2-Methyl-2-propanol Binary Systems at 364.5 K

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Vapor−liquid equilibrium data were measured using an automatic static total pressure apparatus for binary mixtures of 2-methylpropene + methanol, + 1-propanol, + 2-propanol, + 2-butanol, and + 2-methyl-2-propanol at 364.5 K. The measured p, T, z data were fitted against Legendre polynomials and reduced using Barker's method to obtain phase equilibrium data. In addition to Legendre polynomials, binary interaction parameters were also optimized for Wilson, UNIQUAC, and NRTL activity coefficient models. All binary data showed a positive deviation from the Raoult's law. In addition, azeotropic behavior was observed for the 2-methylpropene + methanol binary mixture.

Introduction

High-pressure vapor−liquid equilibrium (VLE) data are essential in design and operation of many chemical processes and separation operations that are conducted under high pressure[1]. In the United States, California, followed by some other states such as New York and Connecticut, has enacted legislation banning methyl *tert*-butyl ether (MTBE) in gasoline beginning in 2004. Thus, other alternatives have to be found. Isooctane is one of these alternatives that can be used to replace MTBE in gasoline. The interest of developing isooctene production processes from former MTBE processes has been a motive behind many VLE studies. 2-Methylpropene (isobutene), which is the key substance in the present study, can be used both in MTBE production and to produce isooctene, which can be further hydrated to isooctane, through dimerization.[2,3]

Experimental Section

Isothermal VLE data at 364.5 K were measured for binary mixtures of 2-methylpropene + methanol, + 1-propanol, + 2-propanol, + 2-butanol, and + 2-methyl-2-propanol (TBA). The measurements were conducted in an automatic static total pressure apparatus. To express the pressure as a function of the liquid concentration, a sufficient amount of compositions has to be measured. In the current work, in addition to pure component vapor pressures, 24 compositions were measured for the isobutene (1) + 2-butanol (2) binary pair and 25 for each of the remaining four binary pairs.

Materials. Suppliers and purities of the materials used are presented in Table 1. Before the degassing procedure, alcohols were dried over molecule sieves (Merck 3A) for at least 24 h. The degassing of the alcohols was performed with the procedure reported by Van Ness and Abbott[4] with modifications suggested by Fisher and Gmehling.[5] The degassing of isobutene was done in a syringe pump by opening the vacuum line valve 10 times in the period of 10 s. The successful degassing was verified for each experiment by double-checking the pure component vapor pressure (see Procedure section for details) and also by comparing the measured values with literature data. The measured vapor pressures along with some literature values are presented in Table 2. Apart from drying and degassing, no further purification was performed on the materials.

Table 1. Material Purities and Their Suppliers

compound	company	mass fraction purity
2-methylpropene	Messer Finland Oy	> 99.8 %
Methanol	Merck	99.8 %
1-propanol	Riedel-de Haën	99.8 %
2-propanol	Riedel-de Haën	99.8 %
2-butanol	Fluka	> 99.8 %
2-methyl-2-propanol	Fluka	> 99.7 %

Table 2. Measured Vapor Pressures Compared to the Values Calculated from the literature correlations

			P/kPa			
compound	T/K	P/kPa	ref 7	ref 8	ref 9	ref 10 and ref 11
isobutene	364.49	1546.0	1540.9	1556.4	1542.6	
	364.51	1546.6	1541.5	1557.0	1543.2	
	364.52	1546.3	1541.8	1557.3	1543.5	
methanol	364.49	267.0	267.5	266.7	267.3	269.6[a]
1-propanol	364.51	81.3	81.4	79.6	80.8	81.0[a]
2-propanol	364.51	144.5	144.8	142.2	142.7	144.1[a]
2-butanol	364.51	74.0	73.7	75.0	74.9	74.1[a]
2-methyl-2-propanol	364.52	142.8	142.4	141.7	143.1	142.5[b]

[a] Ref 10. [b] Ref 11.

Apparatus. The measurements were performed with an automatic static total pressure apparatus (Figure 1), which was suited for measurements below and above atmospheric pressure. The high-pressure VLE measurements reported here are the first to be published with this apparatus. The apparatus consists of an equilibrium cell, which was equipped with a magnetic stirrer and submerged into a water bath. Stability of the water bath was ± 0.02 K. The detailed description of the apparatus can be found in Ouni et al.,[6] apart from the pressure transducer, which was used to measure the cell pressure. The former pressure transducer was exchanged with a Digiquartz 31K-165-HT-CE for a higher pressure range of (0 to 6.9) MPa (compensated operating temperature range of the pressure transducer was from

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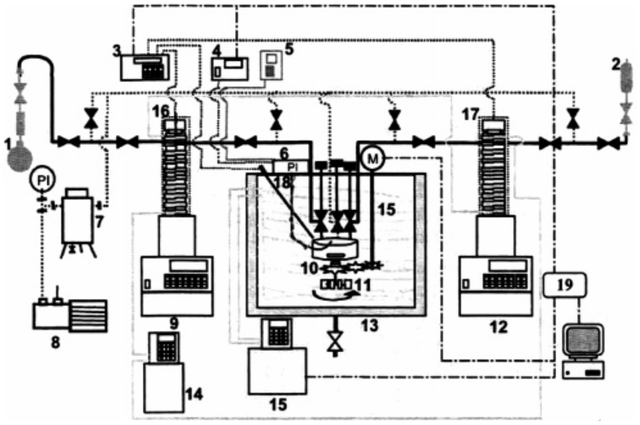

Figure 1. Static total pressure apparatus: 1 and 2, feed flask and cylinder; 3, temperature meter; 4, pressure display; 5, temperature controller for the electric tracing of the pressure transducer and the tube from the equilibrium cell to the pressure transducer; 6, pressure transducer; 7, liquid nitrogen trap; 8, vacuum pump; 9, 260 cm^3 syringe pump; 10, equilibrium cell; 11, bath liquid mixer; 12, 100 cm^3 syringe pump; 13, thermostated water bath; 14, circulator bath for syringe pump temperature control; 15, circulator bath for water bath temperature control; 16, 17, and 18, temperature probes (Pt-100); 19, PCI bus; —, feed line to cell and to syringe pump; gray line, water line for the temperature control of the syringe pump and the water bath; · · ·, vacuum line.

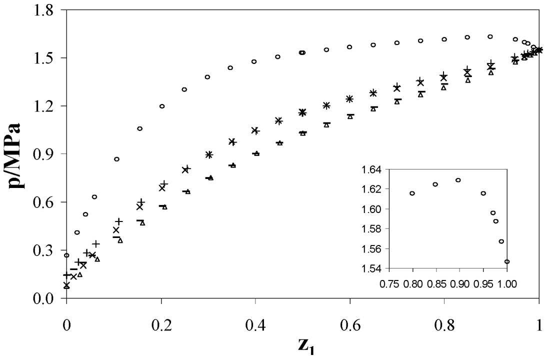

Figure 2. Total pressure presented as a function of total isobutene composition (z_1) at 364.5 K for binary pairs: ○, isobutene + methanol; ×, isobutene + 1-propanol; +, isobutene + 2-propanol; △, isobutene + 2-butanol; and —, isobutene + 2-methyl-2-propanol. The azeotropic point in shown enlarged.

0 °C to 150 °C). The information recorded at each data point was the temperature (T) of the cell and syringe pumps, pressure (p), and overall concentration (z). The number of moles was computed from the piston volumes. The equilibrium composition of the vapor phase (y) and the liquid phase (x) was obtained from the total pressure measurements through data reduction.

Procedure. The details concerning the process control are presented in Ouni et al.,[6] and only the general idea of the procedure is given here. The measurements of each binary pair were made in two parts. In the first part, component 1 was introduced into the cell, and its vapor pressure was measured. A second addition of the component 1 was then performed. An unchanged vapor pressure after the second addition indicated a successful degassing as the dissolved gases in the equilibrium cell would cause a rise in the equilibrium pressure. After the vapor pressure of component 1 had been measured, a predetermined volume of component 2 was added to the cell. The liquid was then mixed with a magnetic mixer and left to stabilize for about 35 min before measurement of the pressure. Injections of the component 2 were continued until a composition of about 0.5 mol fraction was reached after which the cell was emptied and evacuated. To improve the measurement accuracy of the overall composition, the injection-volumes of components 1 and 2 were optimized so that after the last addition the cell was approximately full, after which the cell was emptied and evacuated and the run was continued by starting over with component 2. First the pure vapor pressure of component 2 was measured, followed by the injections of component 1 until the target mole fraction of approximately 0.5 was reached. In this work, all data were considered to be good in quality as the measured cell pressures coincided at approximately 0.5 mol fraction when approached from different sides of the equilibrium (Figure 2). Data were considered valid if the difference in pressures at 0.5 mol fraction was less than the uncertainty for the measured cell pressure. Deviation of the measured cell pressures in 0.5 mol fraction would suggest errors in the measured data. Possible reasons might be a leakage in the equilibrium cell, erroneous density or feed volumes, or air contamination of the components.

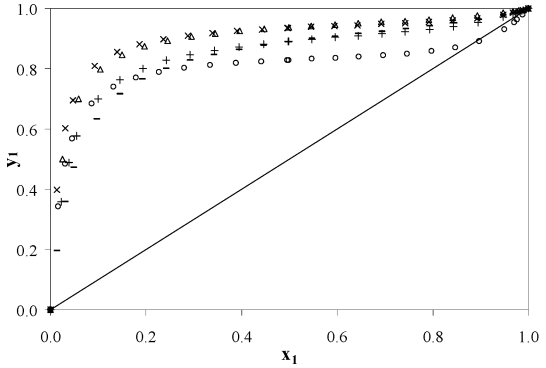

Figure 3. Composition diagram of ○, isobutene + methanol; ×, isobutene + 1-propanol; +, isobutene + 2-propanol; △, isobutene + 2-butanol; and —, isobutene + 2-methyl-2-propanol at 364.5 K. The method of Barker is used for data reduction to obtain equilibrium data from total pressure data.

Data Reduction

The compositions of the vapor and liquid phases were calculated from the total pressure data by the method of Barker[12] using VLEFIT software.[13] The Barker method is based on the general idea that activity coefficients derived from the total pressure measurements have higher accuracy than those obtained

Table 3. Properties of the Components Critical Temperature T_c, Critical Pressure p_c, Acentric Factor ω, Liquid Molar Volume V, UNIQUAC Volume and Area Parameters, R_{UNIQ} and Q_{UNIQ}, Respectively

	isobutene	methanol	1-propanol	2-propanol	2-butanol	2-methyl-2-propanol
T_c/K[a]	417.90	512.64	536.78	508.30	536.05	506.21
p_c/MPa[a]	4.000	8.097	5.175	4.762	4.179	3.973
ω[a]	0.199	0.565	0.629	0.665	0.574	0.613
V/cm^3·mol^{-1} [b]	94.46	40.73	75.14	76.92	92.35	94.88
R_{UNIQ}[b]	2.920	1.431	2.780	2.779	3.924	3.453
Q_{UNIQ}[b]	2.684	1.432	2.512	2.508	3.664	3.128

[a] Ref 7. [b] Ref 17.

Table 4. Parameters for the Activity Coefficient Models (Legendre, NRTL, Wilson, UNIQUAC) and Absolute Average Pressure Residuals $|\Delta P|$

1-component	isobutene				
2-component	methanol	1-propanol	2-propanol	2-butanol	2-methyl- 2-propanol
Legendre, $a_{1,0}$	1.982600	1.475450	1.312900	1.128526	0.947460
Legendre, $a_{2,0}$	0.090066	0.274410	0.200668	0.230757	0.185820
Legendre, $a_{3,0}$	0.136476	0.085962	0.067218	0.067839	0.047703
Legendre, $a_{4,0}$	0.017009	0.019390	0.010897	0.016455	0.007638
Legendre, $a_{5,0}$	0.011192	−0.005130	−0.007899	0.000630	−0.003303
Legendre, $a_{6,0}$	0.010126	−0.004517	−0.003943		
Legendre, $a_{7,0}$	0.005482	−0.004067	−0.003330		
Legendre, $a_{8,0}$	0.003762				
$|\Delta P|$/kPa	0.41	0.39	0.28	0.29	0.37
NRTL, λ_{12}/K	505.99	512.70	438.02	447.69	404.16
NRTL, λ_{21}/K	437.88	166.18	141.57	60.39	19.90
NRTL ($\alpha_{12} = \alpha_{21}$)	0.4	0.4	0.4	0.4	0.4
$|\Delta P|$/kPa	5.57	3.19	3.38	2.69	2.02
Wilson, λ_{12}/J·mol^{-1}	1344.37	1686.83	1507.16	1287.09	664.72
Wilson, λ_{21}/J·mol^{-1}	7200.42	10500.58	8661.53	7527.16	6597.16
$|\Delta P|$/kPa	9.90	0.92	1.36	1.07	1.33
UNIQUAC, λ_{12}/K	557.42	293.06	259.53	106.56	170.65
UNIQUAC, λ_{21}/K	21.08	−35.64	−35.69	36.36	−31.77
$|\Delta P|$/kPa	8.88	4.76	4.36	3.08	2.06

Table 5. VLE Data for Binary Pair Isobutene (1) + Methanol (2) at 364.5 K[a]

				P/kPa					
T/K	n_1/mol	n_2/mol	z_1	measd	Legendre	x_1	y_1	γ_1	γ_2
364.49	0.6625 ± 0.0068	0.0000 ± 0.0000	1.0000 ± 0.0000	1546.0	1546.0	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	9.55 ± 0.46
364.49	0.6625 ± 0.0068	0.0077 ± 0.0006	0.9885 ± 0.0009	1567.1	1568.4	0.9889 ± 0.0010	0.9794 ± 0.0019	1.00 ± 0.00	8.70 ± 0.30
364.50	0.6625 ± 0.0068	0.0160 ± 0.0011	0.9765 ± 0.0011	1587.5	1587.5	0.9771 ± 0.0018	0.9616 ± 0.0028	1.00 ± 0.00	7.95 ± 0.19
364.49	0.6625 ± 0.0068	0.0207 ± 0.0024	0.9697 ± 0.0012	1595.8	1595.8	0.9704 ± 0.0037	0.9528 ± 0.0049	1.00 ± 0.00	7.58 ± 0.21
364.49	0.6625 ± 0.0068	0.0354 ± 0.0016	0.9493 ± 0.0016	1615.1	1614.5	0.9501 ± 0.0026	0.9307 ± 0.0031	1.01 ± 0.00	6.64 ± 0.10
364.50	0.6625 ± 0.0068	0.0763 ± 0.0017	0.8968 ± 0.0024	1628.9	1630.6	0.8969 ± 0.0030	0.8925 ± 0.0032	1.03 ± 0.00	5.02 ± 0.06
364.50	0.6625 ± 0.0068	0.1189 ± 0.0026	0.8478 ± 0.0031	1624.3	1626.5	0.8471 ± 0.0042	0.8711 ± 0.0027	1.07 ± 0.00	4.05 ± 0.03
364.51	0.6625 ± 0.0068	0.1670 ± 0.0034	0.7987 ± 0.0037	1615.1	1616.0	0.7970 ± 0.0051	0.8577 ± 0.0024	1.11 ± 0.00	3.36 ± 0.04
364.50	0.6625 ± 0.0068	0.2223 ± 0.0042	0.7487 ± 0.0042	1603.5	1603.5	0.7463 ± 0.0057	0.8491 ± 0.0019	1.17 ± 0.01	2.83 ± 0.03
364.50	0.6625 ± 0.0068	0.2851 ± 0.0051	0.6991 ± 0.0047	1591.4	1591.1	0.6962 ± 0.0061	0.8435 ± 0.0016	1.24 ± 0.01	2.44 ± 0.03
364.51	0.6625 ± 0.0068	0.3587 ± 0.0060	0.6488 ± 0.0050	1578.4	1578.4	0.6457 ± 0.0063	0.8393 ± 0.0015	1.32 ± 0.01	2.14 ± 0.02
364.51	0.6625 ± 0.0068	0.4437 ± 0.0070	0.5989 ± 0.0052	1564.7	1564.7	0.5961 ± 0.0064	0.8355 ± 0.0014	1.41 ± 0.01	1.91 ± 0.02
364.50	0.6625 ± 0.0068	0.5429 ± 0.0082	0.5496 ± 0.0053	1549.2	1549.2	0.5474 ± 0.0064	0.8319 ± 0.0012	1.52 ± 0.02	1.73 ± 0.01
364.51	0.6625 ± 0.0068	0.6643 ± 0.0094	0.4993 ± 0.0053	1531.9	1530.9	0.4980 ± 0.0062	0.8280 ± 0.0014	1.65 ± 0.02	1.58 ± 0.01
364.51	0.6606 ± 0.0078	0.6695 ± 0.0072	0.4966 ± 0.0053	1528.5	1529.1	0.4953 ± 0.0058	0.8278 ± 0.0014	1.66 ± 0.02	1.57 ± 0.01
364.50	0.5403 ± 0.0066	0.6695 ± 0.0072	0.4466 ± 0.0053	1505.1	1505.1	0.4419 ± 0.0058	0.8233 ± 0.0015	1.83 ± 0.02	1.44 ± 0.01
364.52	0.4406 ± 0.0055	0.6695 ± 0.0072	0.3969 ± 0.0051	1475.6	1475.0	0.3882 ± 0.0057	0.8181 ± 0.0013	2.04 ± 0.03	1.34 ± 0.00
364.52	0.3557 ± 0.0046	0.6695 ± 0.0072	0.3470 ± 0.0049	1435.0	1434.7	0.3340 ± 0.0056	0.8115 ± 0.0011	2.30 ± 0.04	1.25 ± 0.00
364.51	0.2840 ± 0.0038	0.6695 ± 0.0072	0.2978 ± 0.0045	1378.8	1379.2	0.2806 ± 0.0052	0.8026 ± 0.0011	2.64 ± 0.05	1.17 ± 0.00
364.51	0.2217 ± 0.0031	0.6695 ± 0.0072	0.2488 ± 0.0041	1301.2	1301.2	0.2280 ± 0.0047	0.7895 ± 0.0010	3.06 ± 0.06	1.12 ± 0.00
364.51	0.1690 ± 0.0025	0.6695 ± 0.0072	0.2015 ± 0.0035	1196.7	1196.6	0.1786 ± 0.0041	0.7704 ± 0.0012	3.57 ± 0.08	1.07 ± 0.00
364.51	0.1224 ± 0.0018	0.6695 ± 0.0072	0.1546 ± 0.0029	1056.2	1056.2	0.1316 ± 0.0033	0.7398 ± 0.0009	4.22 ± 0.10	1.04 ± 0.00
364.51	0.0794 ± 0.0012	0.6695 ± 0.0072	0.1060 ± 0.0022	865.1	865.1	0.0860 ± 0.0024	0.6836 ± 0.0007	5.06 ± 0.15	1.02 ± 0.00
364.50	0.0418 ± 0.0010	0.6695 ± 0.0072	0.0588 ± 0.0014	628.6	629.2	0.0454 ± 0.0019	0.5687 ± 0.0011	6.05 ± 0.25	1.00 ± 0.00
364.49	0.0281 ± 0.0007	0.6695 ± 0.0072	0.0403 ± 0.0010	522.5	522.5	0.0304 ± 0.0013	0.4829 ± 0.0002	6.49 ± 0.30	1.00 ± 0.00
364.47	0.0147 ± 0.0004	0.6695 ± 0.0072	0.0215 ± 0.0007	408.0	407.6	0.0160 ± 0.0007	0.3406 ± 0.0012	6.95 ± 0.38	1.00 ± 0.00
364.47	0.0000 ± 0.0000	0.6695 ± 0.0072	0.0000 ± 0.0000	267.0	267.0	0.0000 ± 0.0000	0.0000 ± 0.0000	7.50 ± 0.52	1.00 ± 0.00

[a] T, experimental temperature; n_i, amount of component in the equilibrium cell; z_1, total mole fraction; x_1 and y_1, liquid and vapor phase equilibrium mole fractions; γ_i, experimental pressure and pressure calculated from the Legendre polynomial fit, activity coefficients.

from more laborious and difficult partial pressure measurements in which it might even be quite difficult to obtain a representative sample in true equilibrium.[12] Data were reduced using Legendre polynomials[14] as the activity coefficient model and the Soave−Redlich−Kwong[15] cubic equation as the equation of state. The scheme of data reduction is reported in more detail in Uusi-Kyyny et al.[16] VLE data resulting from the data reduction are presented in Figure 3.

Error Analysis

Regarding the error sources in the experiments, the overall uncertainty in the temperature measurements was ± 0.02 K for the water bath and ± 0.1 K for the syringe pump. The uncertainty for the pressure transducer used to measure the cell pressure was ± 0.7 kPa. The uncertainty for the pressure measurements in the pumps was ± 20 kPa. The uncertainty in the injection volumes was ± 0.02 cm^3, and it was obtained from calibration experiments with distilled water. Densities of the pure components were estimated from a density correlation.[17] The uncertainties in the correlated densities were less than 1.0 % for 2-methylpropane, methanol, 1-propanol, 2-propanal, and 2-methyl-2-propanol and less than 3.0 % for 2-butanol. The derivation of the maximum error for the injected mole amount is presented in detail in refs 6 and 18, and only the resulting equation is presented here. The theoretical maximum error for an injection is presented in eq 1:

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

Table 6. VLE Data for Binary Pair Isobutene (1) + 1-Propanol (2) at 364.5 K[a]

				P/kPa					
T/K	n_1/mol	n_2/mol	z_1	measd	Legendre	x_1	y_1	γ_1	γ_2
364.51	0.5171 ± 0.0054	0.0000 ± 0.0000	1.0000 ± 0.0000	1546.6	1546.6	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	6.31 ± 0.40
364.51	0.5171 ± 0.0054	0.0057 ± 0.0003	0.9892 ± 0.0007	1533.7	1534.3	0.9888 ± 0.0008	0.9945 ± 0.0006	1.00 ± 0.00	5.93 ± 0.27
364.51	0.5171 ± 0.0054	0.0104 ± 0.0007	0.9804 ± 0.0009	1523.5	1524.4	0.9796 ± 0.0016	0.9904 ± 0.0011	1.00 ± 0.00	5.64 ± 0.18
364.51	0.5171 ± 0.0054	0.0166 ± 0.0009	0.9690 ± 0.0011	1510.3	1511.7	0.9677 ± 0.0020	0.9857 ± 0.0012	1.00 ± 0.00	5.29 ± 0.10
364.50	0.5171 ± 0.0054	0.0277 ± 0.0009	0.9491 ± 0.0014	1489.3	1490.8	0.9470 ± 0.0023	0.9789 ± 0.0012	1.01 ± 0.00	4.74 ± 0.05
364.50	0.5171 ± 0.0054	0.0591 ± 0.0011	0.8975 ± 0.0023	1443.4	1443.4	0.8933 ± 0.0029	0.9667 ± 0.0014	1.03 ± 0.00	3.64 ± 0.05
364.51	0.5171 ± 0.0054	0.0926 ± 0.0017	0.8481 ± 0.0030	1407.6	1406.4	0.8424 ± 0.0039	0.9598 ± 0.0012	1.07 ± 0.00	2.94 ± 0.03
364.51	0.5171 ± 0.0054	0.1310 ± 0.0022	0.7979 ± 0.0037	1374.0	1373.2	0.7911 ± 0.0047	0.9550 ± 0.0010	1.11 ± 0.01	2.45 ± 0.02
364.51	0.5171 ± 0.0054	0.1732 ± 0.0028	0.7491 ± 0.0042	1342.6	1342.6	0.7418 ± 0.0053	0.9514 ± 0.0010	1.16 ± 0.01	2.12 ± 0.02
364.51	0.5171 ± 0.0054	0.2225 ± 0.0034	0.6992 ± 0.0046	1310.3	1310.9	0.6920 ± 0.0057	0.9480 ± 0.0010	1.22 ± 0.01	1.88 ± 0.01
364.51	0.5171 ± 0.0054	0.2797 ± 0.0041	0.6490 ± 0.0050	1277.1	1277.7	0.6423 ± 0.0059	0.9448 ± 0.0009	1.28 ± 0.01	1.69 ± 0.01
364.51	0.5171 ± 0.0054	0.3458 ± 0.0049	0.5993 ± 0.0052	1242.3	1242.6	0.5937 ± 0.0060	0.9417 ± 0.0009	1.35 ± 0.01	1.55 ± 0.01
364.52	0.5171 ± 0.0054	0.4237 ± 0.0057	0.5496 ± 0.0053	1204.7	1204.7	0.5455 ± 0.0060	0.9384 ± 0.0009	1.43 ± 0.02	1.44 ± 0.01
364.51	0.5171 ± 0.0054	0.5175 ± 0.0067	0.4998 ± 0.0053	1163.0	1163.0	0.4974 ± 0.0059	0.9349 ± 0.0009	1.52 ± 0.02	1.34 ± 0.01
364.51	0.5183 ± 0.0064	0.5226 ± 0.0055	0.4979 ± 0.0053	1161.9	1161.5	0.4956 ± 0.0058	0.9348 ± 0.0008	1.53 ± 0.02	1.34 ± 0.01
364.51	0.4244 ± 0.0054	0.5226 ± 0.0055	0.4482 ± 0.0053	1109.6	1109.5	0.4429 ± 0.0059	0.9305 ± 0.0008	1.64 ± 0.02	1.26 ± 0.00
364.51	0.3468 ± 0.0046	0.5226 ± 0.0055	0.3989 ± 0.0052	1049.5	1049.6	0.3907 ± 0.0058	0.9253 ± 0.0008	1.77 ± 0.03	1.19 ± 0.00
364.51	0.2809 ± 0.0039	0.5226 ± 0.0055	0.3496 ± 0.0050	978.8	979.1	0.3386 ± 0.0056	0.9188 ± 0.0008	1.92 ± 0.03	1.14 ± 0.00
364.51	0.2243 ± 0.0032	0.5226 ± 0.0055	0.3003 ± 0.0046	896.1	896.1	0.2869 ± 0.0053	0.9103 ± 0.0008	2.08 ± 0.04	1.10 ± 0.00
364.51	0.1746 ± 0.0026	0.5226 ± 0.0055	0.2504 ± 0.0042	798.7	798.4	0.2354 ± 0.0048	0.8984 ± 0.0008	2.27 ± 0.05	1.06 ± 0.00
364.51	0.1319 ± 0.0021	0.5226 ± 0.0055	0.2015 ± 0.0037	688.7	688.3	0.1861 ± 0.0042	0.8814 ± 0.0009	2.48 ± 0.06	1.04 ± 0.00
364.51	0.0955 ± 0.0016	0.5226 ± 0.0055	0.1545 ± 0.0031	568.5	568.5	0.1399 ± 0.0035	0.8560 ± 0.0009	2.70 ± 0.07	1.02 ± 0.00
364.51	0.0613 ± 0.0010	0.5226 ± 0.0055	0.1049 ± 0.0024	427.5	427.6	0.0930 ± 0.0025	0.8084 ± 0.0009	2.96 ± 0.10	1.01 ± 0.00
364.51	0.0302 ± 0.0009	0.5226 ± 0.0055	0.0546 ± 0.0016	268.8	268.8	0.0473 ± 0.0020	0.6959 ± 0.0026	3.24 ± 0.15	1.00 ± 0.00
364.51	0.0192 ± 0.0006	0.5226 ± 0.0055	0.0355 ± 0.0013	205.1	204.7	0.0304 ± 0.0013	0.6011 ± 0.0028	3.35 ± 0.19	1.00 ± 0.00
364.51	0.0081 ± 0.0003	0.5226 ± 0.0055	0.0152 ± 0.0009	135.2	134.7	0.0129 ± 0.0007	0.3949 ± 0.0048	3.46 ± 0.24	1.00 ± 0.00
364.51	0.0000 ± 0.0000	0.5226 ± 0.0055	0.0000 ± 0.0000	81.3	81.3	0.0000 ± 0.0000	0.0000 ± 0.0000	3.54 ± 0.29	1.00 ± 0.00

[a] T, experimental temperature; n_i, amount of component in the equilibrium cell; z_1, total mole fraction; x_1 and y_1, liquid and vapor phase equilibrium mole fractions; γ_i, experimental pressure and pressure calculated from the Legendre polynomial fit, activity coefficients.

The temperature derivative of density is calculated from the density correlation[17] and the compressibility of the liquid from the Hankinson−Brobst−Thomson model.[19] The calculation of the theoretical maximum error in the overall molar composition differs from that presented in refs 6 and 18. Its derivation is thus presented here. The differentiation of the overall molar composition for component 1:

$$\mathrm{d}z_1 = \mathrm{d}\left(\frac{n_1}{n_1 + n_2}\right) = \mathrm{d}\left(\frac{\dfrac{\rho_1(T, p)V_1}{M_1}}{\dfrac{\rho_1(T, p)V_1}{M_1} + \dfrac{\rho_2(T, p)V_2}{M_2}}\right) \tag{2}$$

$$\begin{aligned}\Delta z_1 = {}& \Delta V_1\left|\frac{\dfrac{\rho_1}{M_1}(n_1 + n_2) - \dfrac{\rho_1}{M_1}n_1}{(n_1 + n_2)^2}\right| + \Delta V_2\left|\frac{-\dfrac{\rho_2}{M_2}n_1}{(n_1 + n_2)^2}\right| + \\ & \Delta\rho_1\left|\frac{\dfrac{V_1}{M_1}(n_1 + n_2) - \dfrac{V_1}{M_1}n_1}{(n_1 + n_2)^2}\right| + \Delta\rho_2\left|\frac{-\dfrac{V_2}{M_2}n_1}{(n_1 + n_2)^2}\right| + \\ & \Delta T\left|\frac{\dfrac{V_1}{M_1}\left(\dfrac{\mathrm{d}\rho_1}{\mathrm{d}T}\right)(n_1 + n_2) - \left[\dfrac{V_1}{M_1}\left(\dfrac{\mathrm{d}\rho_1}{\mathrm{d}T}\right) + \dfrac{V_2}{M_2}\left(\dfrac{\mathrm{d}\rho_2}{\mathrm{d}T}\right)\right]n_1}{(n_1 + n_2)^2}\right| + \\ & \Delta p\left|\frac{\dfrac{V_1}{M_1}\left(\dfrac{\mathrm{d}\rho_1}{\mathrm{d}p}\right)(n_1 + n_2) - \left[\dfrac{V_1}{M_1}\left(\dfrac{\mathrm{d}\rho_1}{\mathrm{d}p}\right) + \dfrac{V_2}{M_2}\left(\dfrac{\mathrm{d}\rho_2}{\mathrm{d}T}\right)\right]n_1}{(n_1 + n_2)^2}\right|\end{aligned} \tag{3}$$

The pressure derivative of the density can be written as

$$\left(\frac{\mathrm{d}\rho}{\mathrm{d}p}\right) = -\frac{nM}{V^2}\left(\frac{\mathrm{d}V}{\mathrm{d}p}\right)\Big|_{\mathrm{T}} = \frac{nM}{V}\kappa \tag{4}$$

where it is noted that

$$-\frac{1}{V}\left(\frac{\mathrm{d}V}{\mathrm{d}p}\right)\Big|_{\mathrm{T}} = \kappa \tag{5}$$

The above presented modification of the pressure derivative is substituted to eq 3, and the maximum theoretical error of the overall molar composition of component 1 is

$$\begin{aligned}\Delta z_1 = \frac{n_1 n_2}{(n_1 + n_2)^2}\Bigg[&\left(\frac{\rho_1}{n_1 M_1} + \frac{\rho_2}{n_2 M_2}\right)\Delta V + \frac{\Delta\rho_1}{\rho_1} + \\ & \frac{\Delta\rho_2}{\rho_2} + \left|\frac{1}{\rho_1}\left(\frac{\mathrm{d}\rho_1}{\mathrm{d}T}\right) - \frac{1}{\rho_2}\left(\frac{\mathrm{d}\rho_2}{\mathrm{d}T}\right)\right|\Delta T + |\kappa_1 - \kappa_2|\Delta p\Bigg]\end{aligned} \tag{6}$$

The corresponding equation for component 2 can be obtained through an identical procedure.

Uncertainties for the gas and liquid composition and for the activity coefficients were approximated by performing the data reduction procedure using upper and lower boundary values for the parameters p, T, and n_i. Then the absolute maximum error was rounded up and set as the uncertainty for the calculated quantity in question. This was considered to give a representative scale of the error even though it has to be noted that the maximum error does not necessarily occur at the upper or lower boundaries of the measured quantities. The general description of the procedure in case of liquid composition can be presented by eq 7:

$$\Delta x = \mathrm{roundup}(\max(|x - x_-|, |x - x_+|)) \tag{7}$$

The measured VLE data are presented in greater accuracy than the theoretical maximum uncertainty. This is to allow the reader the possibility to refit the model parameters.

Results and Discussion

In all five experiments, the pressure coincided well when different sides of the binaries met. Thus, the measured data were

Table 7. VLE Data for Binary Pair Isobutene (1) + 2-Propanol (2) at 364.5 K[a]

				P/kPa					
T/K	n_1/mol	n_2/mol	z_1	measd	Legendre	x_1	y_1	γ_1	γ_2
364.51	0.5283 ± 0.0055	0.0000 ± 0.0000	1.0000 ± 0.0000	1546.5	1546.5	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	4.84 ± 0.18
364.50	0.5283 ± 0.0055	0.0061 ± 0.0003	0.9887 ± 0.0007	1537.1	1537.7	0.9884 ± 0.0007	0.9924 ± 0.0007	1.00 ± 0.00	4.61 ± 0.13
364.50	0.5283 ± 0.0055	0.0125 ± 0.0006	0.9769 ± 0.0009	1527.4	1528.4	0.9763 ± 0.0014	0.9853 ± 0.0012	1.00 ± 0.00	4.38 ± 0.08
364.49	0.5283 ± 0.0055	0.0171 ± 0.0011	0.9686 ± 0.0010	1520.1	1521.5	0.9678 ± 0.0024	0.9807 ± 0.0017	1.00 ± 0.00	4.22 ± 0.05
364.51	0.5283 ± 0.0055	0.0284 ± 0.0009	0.9490 ± 0.0014	1504.5	1505.6	0.9475 ± 0.0022	0.9709 ± 0.0016	1.01 ± 0.00	3.87 ± 0.06
364.51	0.5283 ± 0.0055	0.0598 ± 0.0011	0.8982 ± 0.0022	1464.9	1464.9	0.8951 ± 0.0028	0.9522 ± 0.0018	1.02 ± 0.00	3.14 ± 0.04
364.51	0.5283 ± 0.0055	0.0951 ± 0.0017	0.8475 ± 0.0030	1426.5	1426.4	0.8429 ± 0.0038	0.9397 ± 0.0017	1.05 ± 0.00	2.61 ± 0.01
364.51	0.5283 ± 0.0055	0.1334 ± 0.0023	0.7984 ± 0.0036	1391.5	1391.5	0.7929 ± 0.0046	0.9307 ± 0.0016	1.09 ± 0.01	2.24 ± 0.00
364.51	0.5283 ± 0.0055	0.1776 ± 0.0028	0.7484 ± 0.0041	1356.5	1356.5	0.7425 ± 0.0052	0.9233 ± 0.0015	1.13 ± 0.01	1.97 ± 0.01
364.50	0.5283 ± 0.0055	0.2274 ± 0.0035	0.6991 ± 0.0046	1320.6	1321.0	0.6932 ± 0.0056	0.9166 ± 0.0015	1.18 ± 0.01	1.77 ± 0.01
364.51	0.5283 ± 0.0055	0.2861 ± 0.0041	0.6487 ± 0.0049	1283.4	1283.4	0.6434 ± 0.0058	0.9101 ± 0.0014	1.24 ± 0.01	1.61 ± 0.00
364.49	0.5283 ± 0.0055	0.3533 ± 0.0049	0.5993 ± 0.0051	1243.6	1243.9	0.5949 ± 0.0060	0.9038 ± 0.0015	1.30 ± 0.01	1.49 ± 0.00
364.49	0.5283 ± 0.0055	0.4331 ± 0.0058	0.5495 ± 0.0052	1201.8	1201.8	0.5464 ± 0.0059	0.8972 ± 0.0015	1.36 ± 0.01	1.39 ± 0.00
364.52	0.5283 ± 0.0055	0.5293 ± 0.0067	0.4995 ± 0.0053	1157.4	1156.5	0.4981 ± 0.0058	0.8902 ± 0.0015	1.44 ± 0.02	1.31 ± 0.00
364.51	0.5276 ± 0.0065	0.5315 ± 0.0056	0.4982 ± 0.0053	1154.5	1154.8	0.4968 ± 0.0058	0.8900 ± 0.0015	1.44 ± 0.02	1.31 ± 0.00
364.54	0.4347 ± 0.0055	0.5315 ± 0.0056	0.4499 ± 0.0052	1102.7	1102.2	0.4460 ± 0.0058	0.8819 ± 0.0014	1.54 ± 0.02	1.24 ± 0.00
364.52	0.3553 ± 0.0047	0.5315 ± 0.0056	0.4007 ± 0.0051	1041.7	1041.7	0.3942 ± 0.0058	0.8723 ± 0.0014	1.64 ± 0.02	1.18 ± 0.00
364.51	0.2886 ± 0.0040	0.5315 ± 0.0056	0.3519 ± 0.0049	973.9	973.9	0.3430 ± 0.0056	0.8607 ± 0.0013	1.76 ± 0.03	1.13 ± 0.00
364.48	0.2308 ± 0.0033	0.5315 ± 0.0056	0.3028 ± 0.0045	895.9	896.1	0.2918 ± 0.0053	0.8461 ± 0.0012	1.90 ± 0.03	1.09 ± 0.00
364.51	0.1814 ± 0.0027	0.5315 ± 0.0056	0.2545 ± 0.0041	809.7	809.4	0.2421 ± 0.0048	0.8272 ± 0.0012	2.06 ± 0.04	1.06 ± 0.00
364.51	0.1381 ± 0.0022	0.5315 ± 0.0056	0.2063 ± 0.0036	711.2	711.2	0.1932 ± 0.0042	0.8011 ± 0.0012	2.23 ± 0.05	1.04 ± 0.00
364.51	0.0996 ± 0.0016	0.5315 ± 0.0056	0.1578 ± 0.0030	600.2	600.2	0.1453 ± 0.0035	0.7621 ± 0.0012	2.43 ± 0.06	1.02 ± 0.00
364.54	0.0663 ± 0.0011	0.5315 ± 0.0056	0.1108 ± 0.0023	479.4	479.6	0.1001 ± 0.0026	0.7004 ± 0.0009	2.65 ± 0.08	1.01 ± 0.00
364.52	0.0352 ± 0.0009	0.5315 ± 0.0056	0.0621 ± 0.0015	340.6	340.4	0.0549 ± 0.0021	0.5760 ± 0.0008	2.89 ± 0.11	1.00 ± 0.00
364.49	0.0239 ± 0.0007	0.5315 ± 0.0056	0.0430 ± 0.0011	282.1	282.2	0.0377 ± 0.0016	0.4881 ± 0.0006	2.98 ± 0.14	1.00 ± 0.00
364.49	0.0136 ± 0.0004	0.5315 ± 0.0056	0.0249 ± 0.0008	225.1	225.1	0.0216 ± 0.0010	0.3580 ± 0.0016	3.07 ± 0.17	1.00 ± 0.00
364.50	0.0000 ± 0.0000	0.5315 ± 0.0056	0.0000 ± 0.0000	144.5	144.5	0.0000 ± 0.0000	0.0000 ± 0.0000	3.19 ± 0.24	1.00 ± 0.00

[a] T, experimental temperature; n_i, amount of component in the equilibrium cell; z_1, total mole fraction; x_1 and y_1, liquid and vapor phase equilibrium mole fractions; γ_i, experimental pressure and pressure calculated from the Legendre polynomial fit, activity coefficients.

Table 8. VLE Data for Binary Pair Isobutene (1) + 2-Butanol (2) at 364.5 K[a]

				P/kPa					
T/K	n_1/mol	n_2/mol	z_1	measd	Legendre	x_1	y_1	γ_1	γ_2
364.51	0.4851± 0.0051	0.0000 ± 0.0000	1.0000 ± 0.0000	1546.5	1546.5	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	4.24 ± 0.21
364.51	0.4851 ± 0.0051	0.0049 ± 0.0003	0.9899 ± 0.0008	1530.8	1530.9	0.9893 ± 0.0007	0.9965 ± 0.0004	1.00 ± 0.00	4.02 ± 0.17
364.51	0.4851 ± 0.0051	0.0095 ± 0.0006	0.9809 ± 0.0012	1516.6	1517.3	0.9797 ± 0.0014	0.9936 ± 0.0007	1.00 ± 0.00	3.84 ± 0.13
364.52	0.4851 ± 0.0051	0.0152 ± 0.0007	0.9697 ± 0.0016	1500.2	1501.1	0.9679 ± 0.0019	0.9904 ± 0.0008	1.00 ± 0.00	3.64 ± 0.10
364.51	0.4851 ± 0.0051	0.0257 ± 0.0008	0.9496 ± 0.0023	1472.0	1473.6	0.9468 ± 0.0021	0.9854 ± 0.0009	1.01 ± 0.00	3.32 ± 0.07
364.51	0.4851 ± 0.0051	0.0552 ± 0.0010	0.8978 ± 0.0041	1410.4	1411.5	0.8926 ± 0.0028	0.9757 ± 0.0009	1.02 ± 0.00	2.69 ± 0.03
364.51	0.4851 ± 0.0051	0.0863 ± 0.0015	0.8489 ± 0.0055	1361.1	1361.1	0.8422 ± 0.0038	0.9691 ± 0.0009	1.05 ± 0.00	2.29 ± 0.01
364.52	0.4851 ± 0.0051	0.1223 ± 0.0020	0.7986 ± 0.0068	1314.7	1314.1	0.7911 ± 0.0046	0.9637 ± 0.0009	1.08 ± 0.01	2.00 ± 0.00
364.52	0.4851 ± 0.0051	0.1624 ± 0.0025	0.7492 ± 0.0079	1270.7	1270.0	0.7415 ± 0.0051	0.9593 ± 0.0008	1.12 ± 0.01	1.78 ± 0.00
364.52	0.4851 ± 0.0051	0.2088 ± 0.0031	0.6991 ± 0.0087	1226.1	1225.8	0.6917 ± 0.0055	0.9551 ± 0.0008	1.17 ± 0.01	1.62 ± 0.00
364.51	0.4851 ± 0.0051	0.2618 ± 0.0037	0.6495± 0.0094	1180.9	1181.0	0.6430± 0.0058	0.9511 ± 0.0008	1.21 ± 0.01	1.49 ± 0.00
364.52	0.4851 ± 0.0051	0.3236 ± 0.0044	0.5998 ± 0.0099	1134.5	1134.5	0.5946 ± 0.0059	0.9470 ± 0.0008	1.27 ± 0.01	1.39 ± 0.00
364.52	0.4851 ± 0.0051	0.3975 ± 0.0052	0.5496 ± 0.0102	1084.6	1084.6	0.5461 ± 0.0059	0.9426 ± 0.0008	1.32 ± 0.01	1.31 ± 0.00
364.51	0.4851 ± 0.0051	0.4852 ± 0.0061	0.4999 ± 0.0103	1032.3	1032.0	0.4983 ± 0.0058	0.9379 ± 0.0008	1.39 ± 0.02	1.25 ± 0.00
364.54	0.4886 ± 0.0061	0.4888 ± 0.0051	0.4999 ± 0.0103	1032.0	1032.0	0.4984 ± 0.0058	0.9379 ± 0.0008	1.39 ± 0.02	1.25 ± 0.00
364.51	0.4015 ± 0.0052	0.4888 ± 0.0051	0.4510 ± 0.0102	970.2	970.6	0.4472 ± 0.0059	0.9321 ± 0.0008	1.46 ± 0.02	1.19 ± 0.00
364.51	0.3286 ± 0.0044	0.4888 ± 0.0051	0.4020 ± 0.0099	903.8	903.7	0.3959 ± 0.0058	0.9253 ± 0.0008	1.54 ± 0.02	1.14 ± 0.00
364.51	0.2664 ± 0.0038	0.4888 ± 0.0051	0.3527 ± 0.0094	830.0	829.9	0.3445 ± 0.0057	0.9170 ± 0.0008	1.64 ± 0.03	1.10 ± 0.00
364.52	0.2141 ± 0.0031	0.4888 ± 0.0051	0.3046 ± 0.0088	751.0	751.0	0.2947 ± 0.0054	0.9066 ± 0.0008	1.74 ± 0.03	1.07 ± 0.00
364.53	0.1684 ± 0.0026	0.4888 ± 0.0051	0.2562 ± 0.0079	664.6	664.5	0.2452 ± 0.0049	0.8929 ± 0.0008	1.85 ± 0.04	1.05 ± 0.00
364.52	0.1285 ± 0.0021	0.4888 ± 0.0051	0.2082 ± 0.0069	570.6	570.7	0.1968 ± 0.0044	0.8737 ± 0.0007	1.97 ± 0.04	1.03 ± 0.00
364.51	0.0938 ± 0.0016	0.4888 ± 0.0051	0.1610 ± 0.0057	470.7	470.7	0.1501 ± 0.0036	0.8454 ± 0.0006	2.09 ± 0.05	1.02 ± 0.00
364.52	0.0623 ± 0.0011	0.4888 ± 0.0051	0.1130 ± 0.0043	361.0	361.2	0.1038 ± 0.0028	0.7969 ± 0.0003	2.23 ± 0.07	1.01 ± 0.00
364.51	0.0343 ± 0.0007	0.4888 ± 0.0051	0.0656 ± 0.0028	245.4	245.3	0.0593 ± 0.0019	0.6993 ± 0.0002	2.38 ± 0.08	1.00 ± 0.00
364.51	0.0140 ± 0.0004	0.4888 ± 0.0051	0.0278 ± 0.0014	148.1	148.1	0.0248 ± 0.0009	0.5005 ± 0.0004	2.50 ± 0.10	1.00 ± 0.00
364.51	0.0000 ± 0.0000	0.4888 ± 0.0051	0.0000 ± 0.0000	74.0	74.0	0.0000 ± 0.0000	0.0000 ± 0.0000	2.59 ± 0.12	1.00 ± 0.00

[a] T, experimental temperature; n_i, amount of component in the equilibrium cell; z_1, total mole fraction; x_1 and y_1, liquid and vapor phase equilibrium mole fractions; γ_i, experimental pressure and pressure calculated from the Legendre polynomial fit, activity coefficients.

considered to be of good quality. The number of parameters used in the Legendre polynomial fit was based on the average error obtained. This should be less than the uncertainty in the measured pressure. If the average error was well below 0.7 kPa with five parameters, this was considered sufficient. If the average absolute error was close to that (from 0.5 kPa to 0.7 kPa), which was the case for binary pairs of isobutene (1) + methanol (2), + 1-propanol (2), and + 2-propanol (2), more parameters were used in attempt to gain a better fit. Parameters were added until the absolute average was less than 0.5 kPa. This was sufficient when considering the uncertainty for the pressure transducer.

In addition to the Legendre polynomial fit, the total pressure data were also fitted using Wilson,[20] UNIQUAC,[21] and NRTL[22] activity coefficient models. The physical properties required are presented in Table 3, and the results are presented in Table 4.

Table 9. VLE Data for Binary Pair Isobutene (1) + 2-Methyl-2-propanol (2) at 364.5 K[a]

				P/kPa					
T/K	n_1/mol	n_2/mol	z_1	measd	Legendre	x_1	y_1	γ_1	γ_2
364.52	0.4757 ± 0.0050	0.0000 ± 0.0000	1.0000 ± 0.0000	1546.3	1546.3	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	3.27 ± 0.16
364.51	0.4757 ± 0.0050	0.0044 ± 0.0003	0.9908 ± 0.0006	1534.2	1534.8	0.9903 ± 0.0007	0.9955 ± 0.0005	1.00 ± 0.00	3.16 ± 0.13
364.52	0.4757 ± 0.0050	0.0103 ± 0.0005	0.9789 ± 0.0008	1519.5	1520.4	0.9779 ± 0.0012	0.9901 ± 0.0009	1.00 ± 0.00	3.02 ± 0.11
364.51	0.4757 ± 0.0050	0.0145 ± 0.0009	0.9704 ± 0.0010	1509.0	1510.3	0.9690 ± 0.0021	0.9865 ± 0.0013	1.00 ± 0.00	2.93 ± 0.08
364.52	0.4757 ± 0.0050	0.0252 ± 0.0007	0.9498 ± 0.0013	1484.2	1485.9	0.9473 ± 0.0020	0.9785 ± 0.0013	1.00 ± 0.00	2.72 ± 0.06
364.52	0.4757 ± 0.0050	0.0530 ± 0.0009	0.8998 ± 0.0022	1430.2	1431.1	0.8953 ± 0.0027	0.9629 ± 0.0014	1.02 ± 0.00	2.32 ± 0.03
364.52	0.4757 ± 0.0050	0.0840 ± 0.0014	0.8500 ± 0.0029	1380.5	1380.6	0.8440 ± 0.0037	0.9508 ± 0.0015	1.04 ± 0.00	2.03 ± 0.02
364.53	0.4757 ± 0.0050	0.1189 ± 0.0019	0.8001 ± 0.0035	1333.4	1332.8	0.7932 ± 0.0045	0.9409 ± 0.0016	1.07 ± 0.01	1.81 ± 0.01
364.52	0.4757 ± 0.0050	0.1585 ± 0.0024	0.7501 ± 0.0041	1286.7	1286.2	0.7429 ± 0.0051	0.9321 ± 0.0016	1.10 ± 0.01	1.64 ± 0.01
364.52	0.4757 ± 0.0050	0.2037 ± 0.0030	0.7002 ± 0.0045	1239.9	1239.7	0.6933 ± 0.0055	0.9239 ± 0.0016	1.13 ± 0.01	1.51 ± 0.01
364.52	0.4757 ± 0.0050	0.2558 ± 0.0036	0.6503 ± 0.0048	1192.1	1192.1	0.6442 ± 0.0057	0.9159 ± 0.0017	1.17 ± 0.01	1.40 ± 0.01
364.52	0.4757 ± 0.0050	0.3171 ± 0.0043	0.6000 ± 0.0051	1141.8	1142.1	0.5952 ± 0.0058	0.9076 ± 0.0017	1.22 ± 0.01	1.32 ± 0.01
364.52	0.4757 ± 0.0050	0.3885 ± 0.0050	0.5505 ± 0.0052	1090.3	1090.3	0.5472 ± 0.0058	0.8989 ± 0.0016	1.27 ± 0.01	1.26 ± 0.00
364.52	0.4757 ± 0.0050	0.4746 ± 0.0059	0.5006 ± 0.0052	1035.6	1035.1	0.4991 ± 0.0057	0.8893 ± 0.0016	1.32 ± 0.01	1.20 ± 0.00
364.52	0.4747 ± 0.0059	0.4765 ± 0.0050	0.4990 ± 0.0052	1031.9	1032.9	0.4976 ± 0.0058	0.8890 ± 0.0016	1.32 ± 0.01	1.20 ± 0.00
364.52	0.3895 ± 0.0050	0.4765 ± 0.0050	0.4498 ± 0.0052	969.3	969.6	0.4462 ± 0.0058	0.8774 ± 0.0016	1.38 ± 0.02	1.16 ± 0.00
364.50	0.3171 ± 0.0043	0.4765 ± 0.0050	0.3996 ± 0.0051	900.1	900.2	0.3939 ± 0.0058	0.8636 ± 0.0016	1.44 ± 0.02	1.12 ± 0.00
364.51	0.2564 ± 0.0036	0.4765 ± 0.0050	0.3498 ± 0.0048	826.7	826.4	0.3423 ± 0.0056	0.8471 ± 0.0016	1.52 ± 0.02	1.09 ± 0.00
364.52	0.2048 ± 0.0030	0.4765 ± 0.0050	0.3006 ± 0.0045	748.6	748.2	0.2916 ± 0.0053	0.8268 ± 0.0017	1.60 ± 0.03	1.06 ± 0.00
364.51	0.1601 ± 0.0025	0.4765 ± 0.0050	0.2515 ± 0.0040	664.6	664.6	0.2415 ± 0.0049	0.8007 ± 0.0018	1.68 ± 0.03	1.04 ± 0.00
364.50	0.1210 ± 0.0020	0.4765 ± 0.0050	0.2025 ± 0.0035	575.2	575.4	0.1923 ± 0.0043	0.7653 ± 0.0018	1.78 ± 0.04	1.03 ± 0.00
364.52	0.0874 ± 0.0015	0.4765 ± 0.0050	0.1550 ± 0.0029	483.1	483.2	0.1455 ± 0.0035	0.7158 ± 0.0013	1.88 ± 0.05	1.01 ± 0.00
364.50	0.0558 ± 0.0010	0.4765 ± 0.0050	0.1048 ± 0.0022	379.1	379.1	0.0970 ± 0.0026	0.6323 ± 0.0004	1.99 ± 0.06	1.01 ± 0.00
364.50	0.0271 ± 0.0008	0.4765 ± 0.0050	0.0538 ± 0.0013	267.1	267.1	0.0491 ± 0.0020	0.4711 ± 0.0003	2.10 ± 0.09	1.00 ± 0.00
364.51	0.0166 ± 0.0005	0.4765 ± 0.0050	0.0336 ± 0.0009	220.9	220.9	0.0304 ± 0.0014	0.3579 ± 0.0008	2.15 ± 0.11	1.00 ± 0.00
364.52	0.0071 ± 0.0003	0.4765 ± 0.0050	0.0146 ± 0.0006	177.2	177.0	0.0132 ± 0.0007	0.1955 ± 0.0003	2.19 ± 0.13	1.00 ± 0.00
364.52	0.0000 ± 0.0000	0.4765 ± 0.0050	0.0000 ± 0.0000	142.7	142.7	0.0000 ± 0.0000	0.0000 ± 0.0000	2.22 ± 0.14	1.00 ± 0.00

[a] T, experimental temperature; n_i, amount of component in the equilibrium cell; z_1, total mole fraction; x_1 and y_1, liquid and vapor phase equilibrium mole fractions; γ_i, experimental pressure and pressure calculated from the Legendre polynomial fit, activity coefficients.

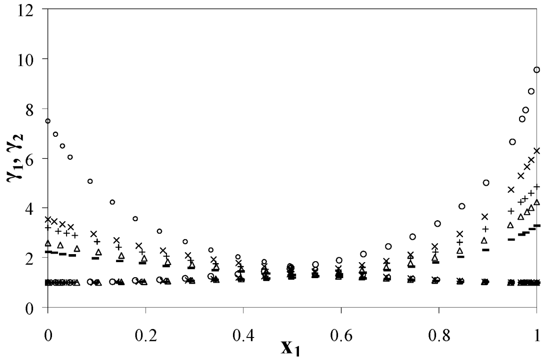

Figure 4. Activity coefficients composition diagram of ○, isobutene + methanol; ×, isobutene + 1-propanol; +, isobutene + 2-propanol; △, isobutene + 2-butanol; and −, isobutene + 2-methyl-2-propanol at 364.5 K.

VLE data obtained through data reduction are presented in Tables 5−9. An azeotropic point was found for isobutene (1) + methanol (2). On the basis on the Legendre polynomial fit, it is located at $x_1 = 0.8857$, $T = 364.5$ K, and $p = 1631.7$ kPa. The azeotropic behavior of isobutene + methanol was also found by Ouni et al.[6] No other mixtures showed azeotropic behavior at the experimental conditions.

The parameter fitting for the Wilson, UNIQUAC, and NRTL activity coefficient models was done using the total pressure data along with Barker's data reduction method. This yielded smaller values for the pressure residuals than when using the p, T, x, y data obtained from the Legendre polynomial fit. However, in case of isobutene (1) + methanol (2), the attempt to obtain a good fit using the total pressure data failed. Hence the parameters for the Wilson activity coefficient had to be obtained using the VLE data. This results in about a decade larger values of the absolute average pressure residuals in comparison with the other four binary pairs. In case of isobutene (1) + methanol (2), larger values of pressure residuals can also been seen for UNIQUAC and NRTL activity coefficient models. This is somewhat expected as, in addition to the azeotropic behavior, the overall behavior of isobutene (1) + methanol (2) was substantially more unideal as compared to the other four binaries measured.

Motivated by the work of Xu et al.,[23] who did some research on the field of phase stability analysis for asymmetric models, a stability analysis was conducted for the NRTL and UNIQUAC parameters obtained in the current work in the experimental conditions. As a result, the computations were found stable for all five binary systems.

The activity coefficient determined in this work are presented in Figure 4. Miyano determined activity coefficients for 2-methylpropene in 2-methyl-propanol[24] and for 2-methylpropene in 2-butanol[24] at infinite dilution. A gas stripping method was used in both cases, and the temperature ranges were (300 to 330) K and (249.99 to 330) K, respectively. By extrapolating Miyano's data to the temperature of the current study (365.5 K) and comparing the results with the current data, the activity coefficients determined in this work are consistent with Miyano[24,25] data with approximately 4 % and 5 % deviation in infinite dilution activity coefficient of 2-methylpropene in 1-methyl-propanol and in 2-butanol, respectively.

Supporting Information Available:

Excel spreadsheet detailing pump related errors and injected volumes for isobutene (1) + TBA (2), + 2-butanol (2), + 2-propanol (2), + 1-propanol (2), or + methanol (2). This material is available free of charge via the Internet at http://pubs.acs.org.

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