Vapor−Liquid Equilibrium for 1-Butanol + 1-Butene at (318.4 and 364.5) K and Vapor−Liquid Equilibrium of 1-Butanol + 2-Methylpropane, + *n*-Butane and 1-Butene + 2-Methylpropane at 318.4 K

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Isothermal vapor−liquid equilibrium (VLE) data for 1-butanol + 1-butene were measured at (318.4 and 364.5) K with a static total pressure apparatus. In addition, isothermal VLE data for 1-butanol + 2-methylpropane, + *n*-butane and 1-butene + 2-methylpropane were measured at 318.4 K with the same apparatus. Measured $p-T-z$ data were reduced to liquid and vapor phase compositions using the Barker method. For the reduced data, the Wilson parameters were regressed. Using the measurements reported in the literature (when available) for the infinite dilution activity coefficients and the excess enthalpy together with the reduced $p-T-x-y$ data in the parameter regression, another set of Wilson parameters was obtained with better predictive capabilities. UNIFAC-Dortmund was tested against the VLE data reported here and also the literature measurements. The approximate 95 % confidence limits are given to all regressed parameters presented in this article.

Introduction

Vapor−liquid equilibrium (VLE) data are needed when modeling chemical processes. If experimental data are not available, often predictive methods, e.g., UNIFAC,[1] UNIFAC-Dortmund,[2] or COSMO-RS,[3] are used to determine the equilibrium compositions. These methods are very useful at the preliminary stages in designing chemical equipment, but for detailed design, experimental data are preferred especially when dealing with nonideal mixtures and systems having an azeotropic point.

In this work, four binary systems were measured: 1-butene + 1-butanol (system 1), 2-methylpropane + 1-butanol (system 2), *n*-butane + 1-butanol (system 3), and 2-methylpropane + 1-butene (system 4). System 1 was measured at 318.4 K and at 364.5 K. The rest of the systems were measured only at 318.4 K.

Miyano[4] published the infinite dilution activity coefficient of 1-butene, 2-methylpropane, and *n*-butane in 1-butanol at (250 to 330) K. Excess enthalpy of the mixture of 1-butanol + *n*-butane has been determined by McFall et al.[5] at 298.15 K. Sipowska et al.[6] published excess enthalpies for the same system at temperatures of (298.15, 323.15, and 348.15) K and pressures of (5, 10, and 15) MPa. Dell'Era et al.[7] have measured VLE for 1-butanol + *n*-butane at 364.15 K. Déak et al.[8] have measured high pressure VLE for 1-butanol + *n*-butane.

Wilson parameters were regressed to our VLE data. The effect of using the above-mentioned measurements found from the literature in the regression of Wilson parameters together with our own VLE data was investigated. In addition, the predictive capabilities of UNIFAC-Dortmund were tested against the VLE data reported here and also against the literature measurements.

Experimental

Isothermal data for binary mixtures of 1-butene + 1-butanol (system 1), 2-methylpropane + 1-butanol (system 2), *n*-butane + 1-butanol (system 3), and in addition 2-methylpropane + 1-butene (system 4) were measured. System 1 was measured at two temperatures (318.4 and 364.5) K, and the rest of the systems were measured only at 318.4 K. Twenty-six or 27 experimental points for each system were measured, including vapor pressures for both pure components of the binary mixture measured.

Materials. The suppliers and purities of the used material are presented in Table 1. 1-Butanol was dried over molecular sieves (Merck 3A) for at least 24 h. After drying, 1-butanol was degassed using the procedure presented by Uusi-Kyyny et al.[9] 1-Butene, *n*-butane, and 2-methylpropane were degassed in the syringe pump by opening and keeping the valve to the vacuum line open for 10 s. This procedure was repeated 10 times. The purity of the materials was checked by measuring the pure component vapor pressures and comparing them to the values computed with the vapor pressure correlations presented in the literature[10−13] (Table 2).

Apparatus. The experiments were conducted in an automated static total pressure apparatus. Detailed information of the apparatus can be found from Uusi-Kyyny et al.,[9] and the automation of the apparatus is described by Ouni et al.[14] For system 1 at 318.4 K and system 4, the pressure was measured with a Diqiquartz 2100A-101-CE pressure transducer. For system 1 at 364.5 K, the pressure was measured with a Diqiquartz 31K-165-HT-CE pressure transducer. For systems 2 and 3, the pressure was measured with a Diqiquartz 2300A-101. For systems 2 and 3, the volume of the cell used was 103.3 cm^3. For the other systems, the volume of the cell used was 112.68 cm^3. The cell was placed into a water bath.

Procedure. The detailed description of the experimental procedure can be found in Uusi-Kyyny et al.[9] Only the general idea is given here.

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Table 1. Material Suppliers, Their Purities, Critical Properties[10] and Acentric Factors[10]

compound	company	mass fraction purity	T_c/K[10]	p_c/MPa[10]	ω[10]
1-butene	Messer Suomi Oy	99.4 %	419.50 ± 0.84	4.020 ± 0.040	0.1922
1-butanol	Riedel-de Haën	99.50 %	563.00 ± 1.13	4.414 ± 0.044	0.5895
2-methylpropane	AGA Oy	99.95 %	407.80 ± 0.82	3.640 ± 0.036	0.1835
n-butane	AGA Oy	99.95 %	425.12 ± 0.85	3.796 ± 0.038	0.2002

Table 2. Measured Vapor Pressures Compared to the Values Calculated from the Literature Correlations

component	T/K	this work p/kPa	ref 10[a] p/kPa	ref 11 p/kPa	ref 12 p/kPa	ref 13 p/kPa
1-butene	318.3	525.2	524.6 ± 15.7	527.1	524.4	533.2
	318.4	525.8	525.7 ± 15.8	528.2	525.5	534.3
	364.5	1509.4	1513.0 ± 45.4	1517.7	1512.5	1526.9
1-butanol	318.4	3.6	3.4 ± 0.1	3.4	3.5	3.5
	318.4	3.9	3.4 ± 0.1	3.4	3.5	3.5
	364.5	36.3	36.4 ± 1.1	36.4	36.1	36.0
2-methylpropane	318.3	608.1	607.3 ± 18.2	606.9	608.6	610.7
	318.4	607.8	608.1 ± 18.3	609.4	608.1	611.4
n-butane	318.4	436.2	437.1 ± 13.1	437.9	437.1	437.3

[a] The value after ± is computed using an error of 3 % reported in BYU-DIPPR.[10]

An experimental plan was made with a spreadsheet program giving the target injection volumes of component 1 and component 2. The objective of the planning was that after all injections have been done the cell would be almost full with the liquid mixture of components 1 and 2.

First, component 1 was introduced into the cell, and the pure component vapor pressure was measured. Then, a predetermined amount of component 2 was introduced to the system and the cell was stirred for 30 min. At this point, the mixture was assumed to be in equilibrium. The temperature and pressure of the cell were recorded. The procedure was repeated until approximately an equimolar mixture was reached.

This procedure was also done vice versa so that first component 2 was introduced into the cell and then predetermined amounts of component 1 were injected to the system.

Data Analysis. The Barker method[15] was used to convert the total amounts of moles fed into the cell to mole fractions in both vapor and liquid phases. The reduction was considered sufficient when the average absolute deviation of the pressure was smaller than the uncertainty of the pressure measurement. The fugacity coefficients were calculated using the Soave−Redlich−Kwong[16] equation of state. The Rackett[17] equation was used to calculate the liquid molar volume in the Poynting correction. In the course of the data reduction, the parameters for the Legendre polynomial,[18] which was used for the computation of the liquid phase activity coefficients, were regressed. The critical properties that were needed in the calculations are presented in Table 1. The calculations were made with the VLEFIT[19] software that is developed at the Helsinki University of Technology. The details of the calculation scheme are presented in Uusi-Kyyny et al.[9] The following objective function in the regression of Legendre polynomial parameters was used

$$\mathrm{O.F.} = \sum_i \frac{|p_{\mathrm{cal},i} - p_{\mathrm{meas},i}|}{p_{\mathrm{meas},i}} \tag{1}$$

The $x-y$ data obtained with the Barker method and measured temperatures and pressures were used for the regression of parameters for the Wilson[20] activity coefficient model. The objective function (1) above was used. For Wilson's parameters, the following equation for the temperature dependence of the parameters was used:

$$\Delta\lambda_{ij} = a_{0,ij} + a_{1,ij}(T/\mathrm{K}) \tag{2}$$

Regression of Wilson's parameters was done using either VLE data from our laboratory or using both VLE data from our laboratory and the data found from the literature. In case infinite dilution activity coefficients were available for the system, eq 3 was added up to eq 1

$$\mathrm{O.F.} = \sum_j \frac{|\gamma^{\mathrm{inf}}_{\mathrm{cal},j} - \gamma^{\mathrm{inf}}_{\mathrm{meas},j}|}{\gamma^{\mathrm{inf}}_{\mathrm{meas},j}} \tag{3}$$

If excess enthalpy measurements were available, then eq 4 was added up to eq 1

$$\mathrm{O.F.} = \sum_j \frac{|H^{\mathrm{ex}}_{\mathrm{cal},j} - H^{\mathrm{ex}}_{\mathrm{meas},j}|}{H^{\mathrm{ex}}_{\mathrm{meas},j}} \tag{4}$$

Also, a predictive activity coefficient model, UNIFAC-Dortmund,[2] was tested against the measured VLE data and the available literature data.

Error Analysis. The uncertainty of vapor and liquid mole fractions depends on the uncertainties of the measurement of cell temperature, pressure, and overall composition of the mixture in the cell.

The uncertainty of the overall composition of the mixture in the cell depends on the uncertainty of injections with syringe

Table 3. Parameters for the Legendre Activity Coefficient Model with the Approximate 95 % Confidence Limits and Absolute Average Pressure Residuals |Δ*p*| for the Different Binary Systems[a]

	System 1 (T = 318.4 K)		System 1 (T = 364.5 K)		System 2 (T = 318.4 K)		System 3 (T = 318.4 K)		System 4 (T = 318.4 K)	
	value	95 % confidence limit	value	95 % confidence limit	value	95 % confidence limit	value	95 % confidence limit	value	95 % confidence limit
$a_{1,0}$	1.59936	0.05187	1.37365	0.00547	1.83090	0.04845	1.80099	0.07688	0.05005	0.00023
$a_{2,0}$	0.56936	0.08031	0.34987	0.00683	0.62642	0.07521	0.62881	0.15042	0.00093	0.00074
$a_{3,0}$	0.25021	0.08113	0.11427	0.00874	0.32603	0.07347	0.33620	0.17365		
$a_{4,0}$	0.12230	0.06771	0.03555	0.00741	0.16985	0.06498	0.17318	0.17768		
$a_{5,0}$	0.05696	0.05081	0.00782	0.00533	0.09836	0.04674	0.09256	0.14954		
$a_{6,0}$	0.02041	0.02846			0.03289	0.03475	0.03861	0.11384		
$a_{7,0}$	0.00604	0.01719			0.01906	0.01870	0.01604	0.07509		
$a_{8,0}$					0.00009	0.01457				
$\|\Delta p\|$/kPa	0.23		0.39		0.49		0.33		0.05	

[a] 1-Butene + 1-butanol (system 1), 2-methylpropane + 1-butanol (system 2), *n*-butane + 1-butanol (system 3), 1-butene + 2-methylpropane (system 4).

Table 4. VLE Data for 1-Butene (1) + 1-Butanol (2) at 318.4 K^a (System 1)

n_1	n_2		T	p_{exp}	p_{calc}				
mol	mol	z_1	K	kPa	kPa	x_1	y_1	γ_1	γ_2
0.4935 ± 0.0053	0.0000 ± 0.0000	1.0000 ± 0.0000	318.40	525.8	526.9 ± 0.3	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	13.80 ± 0.84
0.4935 ± 0.0053	0.0061 ± 0.0003	0.9877 ± 0.0007	318.40	519.4	520.7 ± 0.6	0.9874 ± 0.0007	0.9987 ± 0.0002	1.00 ± 0.00	11.20 ± 0.44
0.4935 ± 0.0053	0.0119 ± 0.0003	0.9765 ± 0.0009	318.40	515.4	516.2 ± 0.6	0.9759 ± 0.0009	0.9979 ± 0.0003	1.00 ± 0.00	9.45 ± 0.26
0.4935 ± 0.0053	0.0164 ± 0.0004	0.9679 ± 0.0011	318.40	512.9	513.2 ± 0.7	0.9671 ± 0.0011	0.9975 ± 0.0003	1.01 ± 0.00	8.39 ± 0.18
0.4935 ± 0.0053	0.0269 ± 0.0005	0.9483 ± 0.0014	318.40	508.2	507.7 ± 0.8	0.9470 ± 0.0015	0.9968 ± 0.0004	1.02 ± 0.00	6.60 ± 0.06
0.4935 ± 0.0053	0.0570 ± 0.0008	0.8965 ± 0.0023	318.40	498.6	497.9 ± 1.0	0.8942 ± 0.0024	0.9959 ± 0.0004	1.06 ± 0.00	4.13 ± 0.03
0.4935 ± 0.0053	0.0887 ± 0.0011	0.8476 ± 0.0030	318.40	490.5	490.5 ± 0.9	0.8446 ± 0.0031	0.9955 ± 0.0004	1.11 ± 0.01	3.08 ± 0.02
0.4935 ± 0.0053	0.1252 ± 0.0015	0.7977 ± 0.0037	318.40	482.2	482.6 ± 0.7	0.7942 ± 0.0038	0.9951 ± 0.0005	1.16 ± 0.01	2.49 ± 0.01
0.4935 ± 0.0053	0.1664 ± 0.0019	0.7478 ± 0.0042	318.40	473.6	473.9 ± 0.6	0.7441 ± 0.0043	0.9948 ± 0.0005	1.22 ± 0.01	2.11 ± 0.01
0.4935 ± 0.0053	0.2133 ± 0.0024	0.6982 ± 0.0046	318.40	464.6	464.6 ± 0.5	0.6946 ± 0.0047	0.9945 ± 0.0005	1.28 ± 0.01	1.85 ± 0.01
0.4935 ± 0.0053	0.2674 ± 0.0029	0.6485 ± 0.0049	318.40	454.7	454.5 ± 0.4	0.6451 ± 0.0050	0.9942 ± 0.0006	1.35 ± 0.01	1.66 ± 0.00
0.4935 ± 0.0053	0.3303 ± 0.0036	0.5990 ± 0.0052	318.40	443.7	443.6 ± 0.4	0.5961 ± 0.0052	0.9938 ± 0.0006	1.43 ± 0.01	1.51 ± 0.00
0.4935 ± 0.0053	0.4052 ± 0.0043	0.5491 ± 0.0053	318.40	431.0	431.0 ± 0.4	0.5468 ± 0.0053	0.9935 ± 0.0006	1.52 ± 0.02	1.39 ± 0.00
0.4935 ± 0.0053	0.4953 ± 0.0052	0.4991 ± 0.0053	318.40	416.2	416.2 ± 0.3	0.4976 ± 0.0053	0.9931 ± 0.0007	1.62 ± 0.02	1.30 ± 0.00
0.4957 ± 0.0053	0.4974 ± 0.0053	0.4991 ± 0.0053	318.40	416.3	416.2 ± 0.3	0.4977 ± 0.0053	0.9931 ± 0.0007	1.62 ± 0.02	1.30 ± 0.00
0.4065 ± 0.0044	0.4974 ± 0.0053	0.4497 ± 0.0053	318.41	398.0	398.1 ± 0.4	0.4472 ± 0.0053	0.9925 ± 0.0007	1.73 ± 0.02	1.23 ± 0.00
0.3320 ± 0.0036	0.4974 ± 0.0053	0.4003 ± 0.0052	318.41	376.1	376.2 ± 0.5	0.3966 ± 0.0052	0.9919 ± 0.0008	1.85 ± 0.02	1.17 ± 0.00
0.2683 ± 0.0030	0.4974 ± 0.0053	0.3504 ± 0.0049	318.41	349.8	349.7 ± 0.4	0.3456 ± 0.0049	0.9911 ± 0.0008	1.99 ± 0.03	1.12 ± 0.00
0.2146 ± 0.0024	0.4974 ± 0.0053	0.3014 ± 0.0046	318.41	319.2	319.1 ± 0.4	0.2958 ± 0.0046	0.9900 ± 0.0009	2.13 ± 0.03	1.08 ± 0.00
0.1679 ± 0.0019	0.4974 ± 0.0053	0.2524 ± 0.0042	318.41	283.2	283.2 ± 0.5	0.2461 ± 0.0042	0.9884 ± 0.0010	2.29 ± 0.04	1.06 ± 0.00
0.1266 ± 0.0015	0.4974 ± 0.0053	0.2029 ± 0.0037	318.40	241.1	241.1 ± 0.4	0.1964 ± 0.0036	0.9861 ± 0.0012	2.46 ± 0.05	1.03 ± 0.00
0.0899 ± 0.0011	0.4974 ± 0.0053	0.1531 ± 0.0030	318.40	192.5	192.5 ± 0.6	0.1469 ± 0.0030	0.9822 ± 0.0016	2.65 ± 0.05	1.02 ± 0.00
0.0578 ± 0.0008	0.4974 ± 0.0053	0.1042 ± 0.0023	318.40	138.6	138.5 ± 0.7	0.0990 ± 0.0022	0.9749 ± 0.0022	2.85 ± 0.06	1.01 ± 0.00
0.0290 ± 0.0005	0.4974 ± 0.0053	0.0550 ± 0.0015	318.40	78.3	78.3 ± 0.4	0.0518 ± 0.0014	0.9548 ± 0.0037	3.05 ± 0.09	1.00 ± 0.00
0.0188 ± 0.0004	0.4974 ± 0.0053	0.0364 ± 0.0011	318.40	53.8	53.8 ± 0.4	0.0341 ± 0.0011	0.9339 ± 0.0053	3.14 ± 0.11	1.00 ± 0.00
0.0085 ± 0.0003	0.4974 ± 0.0053	0.0168 ± 0.0008	318.40	27.2	27.2 ± 0.5	0.0156 ± 0.0007	0.8683 ± 0.0105	3.23 ± 0.14	1.00 ± 0.00
0.0000 ± 0.0000	0.4974 ± 0.0053	0.0000 ± 0.0000	318.40	3.6	3.6 ± 0.3	0.0000 ± 0.0000	0.0000 ± 0.0000	3.32 ± 0.19	1.00 ± 0.00

[a] n_i, amount of component *i* in the equilibrium cell; z_1 total mole fraction of component 1; T, experimental temperature; p_{exp}, experimental pressure; p_{calc}, computed pressure; x_1 and y_1, computed liquid and vapor phase equilibrium mole fractions; γ_i, computed activity coefficient of component i.

Table 5. VLE Data for 1-Butene (1) + 1-Butanol (2) at 364.5 K^a (System 1)

n_1	n_2		T	p_{exp}	p_{calc}				
mol	mol	z_1	K	kPa	kPa	x_1	y_1	γ_1	γ_2
0.4724 ± 0.0051	0.0000 ± 0.0000	1.0000 ± 0.0000	364.53	1509.4	1509.4 ± 0.7	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	6.56 ± 0.32
0.4724 ± 0.0051	0.0046 ± 0.0003	0.9903 ± 0.0007	364.53	1492.9	1493.5 ± 1.4	0.9897 ± 0.0007	0.9973 ± 0.0003	1.00 ± 0.00	6.07 ± 0.23
0.4724 ± 0.0051	0.0092 ± 0.0003	0.9808 ± 0.0008	364.52	1477.3	1478.4 ± 1.4	0.9796 ± 0.0009	0.9951 ± 0.0005	1.00 ± 0.00	5.64 ± 0.18
0.4724 ± 0.0051	0.0146 ± 0.0004	0.9700 ± 0.0011	364.52	1460.6	1462.5 ± 1.5	0.9680 ± 0.0012	0.9929 ± 0.0006	1.00 ± 0.00	5.22 ± 0.13
0.4724 ± 0.0051	0.0259 ± 0.0005	0.9480 ± 0.0015	364.52	1432.1	1434.0 ± 1.7	0.9447 ± 0.0016	0.9893 ± 0.0007	1.01 ± 0.00	4.50 ± 0.07
0.4724 ± 0.0051	0.0534 ± 0.0008	0.8984 ± 0.0023	364.52	1382.5	1382.5 ± 2.0	0.8926 ± 0.0026	0.9840 ± 0.0007	1.04 ± 0.00	3.40 ± 0.02
0.4724 ± 0.0051	0.0842 ± 0.0011	0.8488 ± 0.0030	364.51	1342.7	1341.4 ± 2.0	0.8412 ± 0.0033	0.9808 ± 0.0007	1.07 ± 0.00	2.72 ± 0.01
0.4724 ± 0.0051	0.1189 ± 0.0014	0.7989 ± 0.0037	364.49	1306.1	1304.9 ± 1.7	0.7903 ± 0.0040	0.9786 ± 0.0008	1.11 ± 0.01	2.28 ± 0.01
0.4724 ± 0.0051	0.1584 ± 0.0018	0.7489 ± 0.0042	364.51	1271.5	1271.0 ± 1.3	0.7399 ± 0.0045	0.9767 ± 0.0008	1.17 ± 0.01	1.97 ± 0.00
0.4724 ± 0.0051	0.2038 ± 0.0023	0.6986 ± 0.0046	364.52	1236.2	1236.2 ± 0.9	0.6900 ± 0.0049	0.9750 ± 0.0008	1.22 ± 0.01	1.75 ± 0.00
0.4724 ± 0.0051	0.2554 ± 0.0028	0.6491 ± 0.0050	364.52	1199.4	1199.8 ± 1.0	0.6413 ± 0.0052	0.9734 ± 0.0009	1.28 ± 0.01	1.59 ± 0.00
0.4724 ± 0.0051	0.3160 ± 0.0034	0.5992 ± 0.0052	364.51	1159.8	1160.0 ± 1.1	0.5928 ± 0.0053	0.9717 ± 0.0009	1.35 ± 0.01	1.47 ± 0.00
0.4724 ± 0.0051	0.3879 ± 0.0042	0.5491 ± 0.0053	364.50	1116.5	1116.5 ± 1.0	0.5445 ± 0.0054	0.9699 ± 0.0010	1.42 ± 0.01	1.37 ± 0.00
0.4724 ± 0.0051	0.4735 ± 0.0050	0.4994 ± 0.0053	364.52	1069.5	1069.5 ± 0.7	0.4969 ± 0.0054	0.9680 ± 0.0010	1.50 ± 0.02	1.29 ± 0.00
0.4727 ± 0.0051	0.4756 ± 0.0050	0.4985 ± 0.0053	364.53	1068.7	1068.7 ± 0.7	0.4960 ± 0.0054	0.9679 ± 0.0010	1.50 ± 0.02	1.29 ± 0.00
0.3877 ± 0.0042	0.4756 ± 0.0050	0.4491 ± 0.0053	364.50	1009.7	1009.7 ± 1.0	0.4439 ± 0.0053	0.9654 ± 0.0010	1.60 ± 0.02	1.22 ± 0.00
0.3165 ± 0.0035	0.4756 ± 0.0050	0.3996 ± 0.0052	364.49	943.2	943.0 ± 1.2	0.3917 ± 0.0052	0.9624 ± 0.0010	1.71 ± 0.02	1.16 ± 0.00
0.2559 ± 0.0028	0.4756 ± 0.0050	0.3499 ± 0.0049	364.52	867.4	867.3 ± 1.0	0.3394 ± 0.0049	0.9586 ± 0.0011	1.84 ± 0.03	1.11 ± 0.00
0.2046 ± 0.0023	0.4756 ± 0.0050	0.3008 ± 0.0046	364.52	782.2	782.2 ± 0.9	0.2884 ± 0.0046	0.9536 ± 0.0012	1.97 ± 0.03	1.08 ± 0.00
0.1595 ± 0.0019	0.4756 ± 0.0050	0.2511 ± 0.0042	364.52	684.9	685.0 ± 1.1	0.2374 ± 0.0041	0.9467 ± 0.0014	2.12 ± 0.04	1.05 ± 0.00
0.1205 ± 0.0015	0.4756 ± 0.0050	0.2022 ± 0.0037	364.53	578.3	578.5 ± 1.2	0.1883 ± 0.0036	0.9366 ± 0.0016	2.27 ± 0.04	1.03 ± 0.00
0.0854 ± 0.0011	0.4756 ± 0.0050	0.1523 ± 0.0030	364.52	458.9	458.9 ± 1.1	0.1394 ± 0.0029	0.9200 ± 0.0018	2.44 ± 0.05	1.02 ± 0.00
0.0549 ± 0.0008	0.4756 ± 0.0050	0.1036 ± 0.0023	364.52	333.0	332.6 ± 1.5	0.0931 ± 0.0022	0.8897 ± 0.0021	2.62 ± 0.07	1.01 ± 0.00
0.0269 ± 0.0005	0.4756 ± 0.0050	0.0536 ± 0.0015	364.53	194.0	194.0 ± 1.8	0.0473 ± 0.0014	0.8116 ± 0.0038	2.81 ± 0.10	1.00 ± 0.00
0.0168 ± 0.0004	0.4756 ± 0.0050	0.0342 ± 0.0011	364.53	138.6	138.0 ± 1.3	0.0299 ± 0.0010	0.7355 ± 0.0048	2.89 ± 0.12	1.00 ± 0.00
0.0069 ± 0.0003	0.4756 ± 0.0050	0.0142 ± 0.0007	364.53	79.0	79.0 ± 1.6	0.0124 ± 0.0007	0.5397 ± 0.0103	2.97 ± 0.15	1.00 ± 0.00
0.0000 ± 0.0000	0.4756 ± 0.0050	0.0000 ± 0.0000	364.52	36.3	36.3 ± 0.7	0.0000 ± 0.0000	0.0000 ± 0.0000	3.04 ± 0.16	1.00 ± 0.00

[a] n_i, amount of component *i* in the equilibrium cell; z_1 total mole fraction of component 1; T, experimental temperature; p_{exp}, experimental pressure; p_{calc}, computed pressure; x_1 and y_1, computed liquid and vapor phase equilibrium mole fractions; γ_i, computed activity coefficient of component *i*.

pumps (one pump for each component). The uncertainty of injection volumes ± 0.02 cm^3 was obtained from the calibration experiments with distilled water. The estimated inaccuracies of temperature and pressure measurement in the syringe pumps feeding components into the cell were ± 0.1 K and ± 20 kPa, respectively. The temperature in the syringe pumps was about 289.3 K, and the pressure was 1800 kPa (system 1) or 1000 kPa (system 2, system 3, system 4). For the computation of densities, the correlation and parameters presented in BYU-DIPPR[10] were used. The error in the values computed from the correlation is < 1 % for all components used in this study.[10] The temperature derivate of the density was calculated from the density correlation. The compressibility of the liquid was obtained from the Hankinson−Brobst−Thompson model.[11]

Table 6. VLE Data for 2-Methylpropane (1) + 1-Butanol (2) at 318.4 K[a] (System 2)

n_1	n_2		T	p_{exp}	p_{calc}				
mol	mol	z_1	K	kPa	kPa	x_1	y_1	γ_1	γ_2
0.4386 ± 0.0047	0.0000 ± 0.0000	1.0000 ± 0.0000	318.34	608.1	608.1 ± 0.4	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	22.28 ± 2.13
0.4386 ± 0.0047	0.0045 ± 0.0003	0.9899 ± 0.0007	318.34	602.5	602.6 ± 0.8	0.9896 ± 0.0007	0.9984 ± 0.0003	1.00 ± 0.00	17.55 ± 0.97
0.4386 ± 0.0047	0.0134 ± 0.0004	0.9704 ± 0.0011	318.34	596.8	595.2 ± 1.0	0.9696 ± 0.0011	0.9968 ± 0.0005	1.01 ± 0.00	11.89 ± 0.34
0.4386 ± 0.0047	0.0231 ± 0.0005	0.9499 ± 0.0015	318.34	592.5	590.2 ± 1.3	0.9485 ± 0.0015	0.9960 ± 0.0005	1.02 ± 0.00	8.57 ± 0.11
0.4386 ± 0.0047	0.0488 ± 0.0007	0.9000 ± 0.0023	318.34	583.8	583.0 ± 1.6	0.8973 ± 0.0024	0.9954 ± 0.0006	1.07 ± 0.01	4.93 ± 0.11
0.4386 ± 0.0047	0.0777 ± 0.0010	0.8496 ± 0.0030	318.34	575.8	576.5 ± 1.1	0.8460 ± 0.0032	0.9951 ± 0.0006	1.12 ± 0.01	3.51 ± 0.05
0.4386 ± 0.0047	0.1095 ± 0.0013	0.8002 ± 0.0037	318.34	568.1	568.8 ± 0.7	0.7961 ± 0.0038	0.9948 ± 0.0006	1.18 ± 0.01	2.79 ± 0.02
0.4386 ± 0.0047	0.1461 ± 0.0017	0.7501 ± 0.0042	318.35	560.2	560.2 ± 1.0	0.7458 ± 0.0044	0.9945 ± 0.0006	1.24 ± 0.01	2.35 ± 0.01
0.4386 ± 0.0047	0.1877 ± 0.0021	0.7004 ± 0.0046	318.35	552.1	551.5 ± 0.9	0.6960 ± 0.0048	0.9942 ± 0.0007	1.31 ± 0.01	2.03 ± 0.01
0.4386 ± 0.0047	0.2362 ± 0.0026	0.6500 ± 0.0050	318.35	543.1	542.6 ± 0.6	0.6460 ± 0.0051	0.9940 ± 0.0007	1.40 ± 0.01	1.80 ± 0.01
0.4386 ± 0.0047	0.2913 ± 0.0032	0.6009 ± 0.0052	318.34	533.1	533.1 ± 0.4	0.5974 ± 0.0053	0.9937 ± 0.0007	1.49 ± 0.01	1.62 ± 0.01
0.4386 ± 0.0047	0.3573 ± 0.0038	0.5511 ± 0.0053	318.34	521.5	521.8 ± 0.5	0.5483 ± 0.0054	0.9935 ± 0.0007	1.59 ± 0.02	1.48 ± 0.00
0.4386 ± 0.0047	0.4372 ± 0.0046	0.5008 ± 0.0053	318.34	507.8	507.9 ± 0.6	0.4991 ± 0.0054	0.9932 ± 0.0008	1.71 ± 0.02	1.37 ± 0.00
0.4380 ± 0.0047	0.4382 ± 0.0047	0.4999 ± 0.0053	318.34	507.6	507.6 ± 0.6	0.4982 ± 0.0054	0.9932 ± 0.0008	1.71 ± 0.02	1.37 ± 0.00
0.3593 ± 0.0039	0.4382 ± 0.0047	0.4505 ± 0.0053	318.34	489.8	489.5 ± 0.7	0.4473 ± 0.0053	0.9928 ± 0.0008	1.84 ± 0.02	1.28 ± 0.00
0.2929 ± 0.0032	0.4382 ± 0.0047	0.4006 ± 0.0052	318.34	467.2	466.8 ± 0.8	0.3958 ± 0.0052	0.9923 ± 0.0009	2.00 ± 0.03	1.21 ± 0.00
0.2370 ± 0.0026	0.4382 ± 0.0047	0.3510 ± 0.0050	318.34	439.6	439.1 ± 0.7	0.3445 ± 0.0050	0.9917 ± 0.0009	2.17 ± 0.03	1.15 ± 0.00
0.1896 ± 0.0021	0.4382 ± 0.0047	0.3020 ± 0.0046	318.35	405.8	405.8 ± 0.4	0.2942 ± 0.0046	0.9908 ± 0.0010	2.37 ± 0.04	1.10 ± 0.00
0.1474 ± 0.0017	0.4382 ± 0.0047	0.2518 ± 0.0042	318.35	363.0	363.5 ± 0.6	0.2429 ± 0.0042	0.9896 ± 0.0011	2.59 ± 0.05	1.07 ± 0.00
0.1114 ± 0.0013	0.4382 ± 0.0047	0.2027 ± 0.0037	318.35	312.7	312.7 ± 0.9	0.1935 ± 0.0036	0.9878 ± 0.0013	2.83 ± 0.06	1.04 ± 0.00
0.0805 ± 0.0010	0.4382 ± 0.0047	0.1551 ± 0.0031	318.34	254.8	253.6 ± 1.5	0.1463 ± 0.0030	0.9848 ± 0.0017	3.07 ± 0.07	1.02 ± 0.00
0.0520 ± 0.0007	0.4382 ± 0.0047	0.1061 ± 0.0024	318.34	185.6	183.7 ± 1.6	0.0986 ± 0.0023	0.9789 ± 0.0023	3.34 ± 0.09	1.01 ± 0.00
0.0263 ± 0.0005	0.4382 ± 0.0047	0.0565 ± 0.0015	318.34	105.3	105.3 ± 0.8	0.0518 ± 0.0015	0.9630 ± 0.0038	3.66 ± 0.12	1.00 ± 0.00
0.0169 ± 0.0004	0.4382 ± 0.0047	0.0372 ± 0.0012	318.35	72.4	72.4 ± 0.6	0.0338 ± 0.0011	0.9461 ± 0.0054	3.82 ± 0.14	1.00 ± 0.00
0.0080 ± 0.0003	0.4382 ± 0.0047	0.0178 ± 0.0008	318.35	38.0	37.9 ± 0.8	0.0161 ± 0.0008	0.8971 ± 0.0110	4.01 ± 0.21	1.00 ± 0.00
0.0000 ± 0.0000	0.4382 ± 0.0047	0.0000 ± 0.0000	318.35	3.9	3.9 ± 0.4	0.0000 ± 0.0000	0.0000 ± 0.0000	4.24 ± 0.29	1.00 ± 0.00

[a] n_i, amount of component i in the equilibrium cell; z_1, total mole fraction of component 1; T, experimental temperature; p_{exp}, experimental pressure; p_{calc}, computed pressure; x_1 and y_1, computed liquid and vapor phase equilibrium mole fractions; γ_i, computed activity coefficient of component i.

Table 7. VLE Data for *n*-Butane (1) + 1-Butanol (2) at 318.4 K[a] (System 3)

n_1	n_2		T	p_{exp}	p_{calc}				
mol	mol	z_1	K	kPa	kPa	x_1	y_1	γ_1	γ_2
0.4531 ± 0.0048	0.0000 ± 0.0000	1.0000 ± 0.0000	318.35	436.2	436.2 ± 0.4	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	21.97 ± 3.15
0.4531 ± 0.0048	0.0048 ± 0.0003	0.9895 ± 0.0007	318.35	433.2	432.6 ± 0.8	0.9893 ± 0.0007	0.9981 ± 0.0004	1.00 ± 0.00	17.13 ± 1.85
0.4531 ± 0.0048	0.0141 ± 0.0004	0.9698 ± 0.0011	318.35	429.6	427.6 ± 1.3	0.9692 ± 0.0011	0.9963 ± 0.0006	1.01 ± 0.00	11.57 ± 0.48
0.4531 ± 0.0048	0.0242 ± 0.0005	0.9493 ± 0.0015	318.35	426.7	424.3 ± 1.9	0.9483 ± 0.0015	0.9954 ± 0.0006	1.02 ± 0.00	8.36 ± 0.18
0.4531 ± 0.0048	0.0504 ± 0.0007	0.8999 ± 0.0023	318.35	420.8	419.5 ± 2.5	0.8982 ± 0.0024	0.9947 ± 0.0007	1.07 ± 0.00	4.86 ± 0.12
0.4531 ± 0.0048	0.0811 ± 0.0010	0.8481 ± 0.0031	318.34	415.0	415.0 ± 1.8	0.8458 ± 0.0031	0.9943 ± 0.0007	1.13 ± 0.01	3.42 ± 0.05
0.4531 ± 0.0048	0.1134 ± 0.0014	0.7998 ± 0.0037	318.34	409.6	409.9 ± 0.8	0.7971 ± 0.0038	0.9940 ± 0.0007	1.18 ± 0.01	2.74 ± 0.02
0.4531 ± 0.0048	0.1515 ± 0.0018	0.7494 ± 0.0042	318.35	403.9	403.9 ± 0.4	0.7465 ± 0.0043	0.9936 ± 0.0008	1.24 ± 0.01	2.30 ± 0.01
0.4531 ± 0.0048	0.1947 ± 0.0022	0.6994 ± 0.0046	318.35	397.8	397.6 ± 0.6	0.6966 ± 0.0047	0.9933 ± 0.0008	1.31 ± 0.01	1.99 ± 0.01
0.4531 ± 0.0048	0.2452 ± 0.0027	0.6489 ± 0.0050	318.35	391.0	390.8 ± 0.6	0.6462 ± 0.0050	0.9930 ± 0.0009	1.39 ± 0.01	1.76 ± 0.01
0.4531 ± 0.0048	0.3041 ± 0.0033	0.5984 ± 0.0052	318.35	383.2	383.2 ± 0.6	0.5961 ± 0.0052	0.9927 ± 0.0009	1.48 ± 0.01	1.59 ± 0.00
0.4531 ± 0.0048	0.3678 ± 0.0039	0.5519 ± 0.0053	318.34	375.0	375.0 ± 0.8	0.5502 ± 0.0053	0.9923 ± 0.0009	1.58 ± 0.02	1.47 ± 0.00
0.4531 ± 0.0048	0.4533 ± 0.0048	0.4999 ± 0.0053	318.35	364.2	363.9 ± 0.7	0.4988 ± 0.0053	0.9919 ± 0.0010	1.69 ± 0.02	1.36 ± 0.00
0.4529 ± 0.0048	0.4527 ± 0.0048	0.5001 ± 0.0053	318.35	363.6	363.9 ± 0.7	0.4991 ± 0.0053	0.9919 ± 0.0010	1.69 ± 0.02	1.36 ± 0.00
0.3708 ± 0.0040	0.4527 ± 0.0048	0.4503 ± 0.0053	318.35	350.3	350.4 ± 0.5	0.4482 ± 0.0053	0.9914 ± 0.0010	1.82 ± 0.02	1.27 ± 0.00
0.3016 ± 0.0033	0.4527 ± 0.0048	0.3999 ± 0.0052	318.35	333.8	333.8 ± 0.7	0.3967 ± 0.0052	0.9908 ± 0.0011	1.96 ± 0.03	1.20 ± 0.00
0.2454 ± 0.0027	0.4527 ± 0.0048	0.3516 ± 0.0050	318.36	314.5	314.4 ± 0.7	0.3474 ± 0.0050	0.9900 ± 0.0012	2.12 ± 0.03	1.15 ± 0.00
0.1947 ± 0.0022	0.4527 ± 0.0048	0.3008 ± 0.0046	318.35	289.6	289.6 ± 0.6	0.2957 ± 0.0046	0.9888 ± 0.0013	2.31 ± 0.04	1.10 ± 0.00
0.1506 ± 0.0017	0.4527 ± 0.0048	0.2496 ± 0.0042	318.35	258.9	259.1 ± 0.9	0.2438 ± 0.0042	0.9872 ± 0.0015	2.52 ± 0.05	1.07 ± 0.00
0.1133 ± 0.0014	0.4527 ± 0.0048	0.2002 ± 0.0036	318.35	223.3	223.4 ± 1.0	0.1941 ± 0.0036	0.9849 ± 0.0017	2.75 ± 0.06	1.04 ± 0.00
0.0811 ± 0.0010	0.4527 ± 0.0048	0.1519 ± 0.0030	318.36	182.0	181.9 ± 0.6	0.1460 ± 0.0030	0.9811 ± 0.0022	3.00 ± 0.06	1.02 ± 0.00
0.0518 ± 0.0007	0.4527 ± 0.0048	0.1027 ± 0.0023	318.35	132.5	132.5 ± 1.1	0.0977 ± 0.0022	0.9736 ± 0.0031	3.28 ± 0.07	1.01 ± 0.00
0.0255 ± 0.0005	0.4527 ± 0.0048	0.0533 ± 0.0015	318.35	75.2	75.4 ± 0.6	0.0501 ± 0.0014	0.9529 ± 0.0052	3.62 ± 0.11	1.00 ± 0.00
0.0156 ± 0.0004	0.4527 ± 0.0048	0.0332 ± 0.0011	318.35	49.7	49.7 ± 0.7	0.0311 ± 0.0011	0.9281 ± 0.0077	3.77 ± 0.15	1.00 ± 0.00
0.0061 ± 0.0003	0.4527 ± 0.0048	0.0133 ± 0.0007	318.35	22.7	22.7 ± 0.4	0.0124 ± 0.0007	0.8419 ± 0.0157	3.94 ± 0.23	1.00 ± 0.00
0.0000 ± 0.0000	0.4527 ± 0.0048	0.0000 ± 0.0000	318.35	3.6	3.6 ± 0.4	0.0000 ± 0.0000	0.0000 ± 0.0000	4.06 ± 0.32	1.00 ± 0.00

[a] n_i, amount of component i in the equilibrium cell; z_1, total mole fraction of component 1; T, experimental temperature; p_{exp}, experimental pressure; p_{calc}, computed pressure; x_1 and y_1, computed liquid and vapor phase equilibrium mole fractions; γ_i, computed activity coefficient of component *i*.

Using the information presented above, the maximum level of uncertainty in the molar amount of component injected into the cell can be computed from the equation presented by Laakkonen et al.[21] To compute the uncertainties for the gas and liquid phase composition and for the activity coefficients the procedure described by Hynynen et al.[22] was used in the VLEFIT[19] software.

The method used for the computation of the approximate 95 % confidence limits of the Wilson model parameters is described in Pokki.[23]

The uncertainties of the temperature measurements were ± 0.03 K for the water bath. The uncertainty of the pressure measurement with transducer used for system 1 at 318.4 K and system 4 was ± 0.3 kPa. The uncertainty of the pressure

Table 8. VLE Data for 1-Butene (1) + 2-Methylpropane (2) at 318.4 K^a (System 4)

n_1 / mol	n_2 / mol	z_1	T / K	p_{exp} / kPa	p_{calc} / kPa	x_1	y_1	γ_1	γ_2
0.4787 ± 0.0051	0.0000 ± 0.0000	1.0000 ± 0.0000	318.32	525.2	525.2 ± 0.3	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	1.05 ± 0.00
0.4787 ± 0.0051	0.0062 ± 0.0003	0.9872 ± 0.0007	318.32	526.6	526.7 ± 0.3	0.9872 ± 0.0007	0.9848 ± 0.0007	1.00 ± 0.00	1.05 ± 0.00
0.4787 ± 0.0051	0.0160 ± 0.0004	0.9677 ± 0.0010	318.32	528.9	528.9 ± 0.3	0.9678 ± 0.0010	0.9620 ± 0.0011	1.00 ± 0.00	1.05 ± 0.00
0.4787 ± 0.0051	0.0264 ± 0.0005	0.9477 ± 0.0014	318.32	531.1	531.2 ± 0.3	0.9479 ± 0.0014	0.9389 ± 0.0014	1.00 ± 0.00	1.05 ± 0.00
0.4787 ± 0.0051	0.0545 ± 0.0008	0.8978 ± 0.0023	318.32	536.6	536.6 ± 0.3	0.8982 ± 0.0023	0.8822 ± 0.0023	1.00 ± 0.00	1.04 ± 0.00
0.4787 ± 0.0051	0.0852 ± 0.0011	0.8489 ± 0.0030	318.32	541.8	541.8 ± 0.3	0.8494 ± 0.0030	0.8278 ± 0.0030	1.00 ± 0.00	1.04 ± 0.00
0.4787 ± 0.0051	0.1201 ± 0.0014	0.7994 ± 0.0036	318.32	546.9	546.9 ± 0.3	0.8000 ± 0.0036	0.7741 ± 0.0036	1.00 ± 0.00	1.03 ± 0.00
0.4787 ± 0.0051	0.1598 ± 0.0018	0.7497 ± 0.0042	318.33	551.9	552.0 ± 0.3	0.7502 ± 0.0042	0.7212 ± 0.0042	1.00 ± 0.00	1.03 ± 0.00
0.4787 ± 0.0051	0.2051 ± 0.0023	0.7000 ± 0.0046	318.33	556.7	556.8 ± 0.3	0.7005 ± 0.0046	0.6694 ± 0.0046	1.00 ± 0.00	1.02 ± 0.00
0.4787 ± 0.0051	0.2574 ± 0.0028	0.6503 ± 0.0050	318.33	561.3	561.4 ± 0.3	0.6507 ± 0.0050	0.6185 ± 0.0050	1.01 ± 0.00	1.02 ± 0.00
0.4787 ± 0.0051	0.3180 ± 0.0035	0.6008 ± 0.0052	318.34	565.8	565.9 ± 0.3	0.6011 ± 0.0052	0.5686 ± 0.0052	1.01 ± 0.00	1.02 ± 0.00
0.4787 ± 0.0051	0.3898 ± 0.0042	0.5512 ± 0.0053	318.34	570.2	570.2 ± 0.3	0.5514 ± 0.0053	0.5193 ± 0.0054	1.01 ± 0.00	1.02 ± 0.00
0.4787 ± 0.0051	0.4762 ± 0.0051	0.5013 ± 0.0054	318.34	574.4	574.4 ± 0.3	0.5014 ± 0.0054	0.4704 ± 0.0054	1.01 ± 0.00	1.01 ± 0.00
0.2911 ± 0.0032	0.2900 ± 0.0032	0.5009 ± 0.0055	318.35	574.7	574.6 ± 0.3	0.5016 ± 0.0055	0.4706 ± 0.0055	1.01 ± 0.00	1.01 ± 0.00
0.2382 ± 0.0027	0.2900 ± 0.0032	0.4509 ± 0.0055	318.35	578.6	578.5 ± 0.3	0.4517 ± 0.0055	0.4224 ± 0.0055	1.02 ± 0.00	1.01 ± 0.00
0.1945 ± 0.0022	0.2900 ± 0.0032	0.4015 ± 0.0054	318.35	582.3	582.3 ± 0.3	0.4023 ± 0.0054	0.3752 ± 0.0054	1.02 ± 0.00	1.01 ± 0.00
0.1570 ± 0.0018	0.2900 ± 0.0032	0.3512 ± 0.0052	318.34	586.0	585.9 ± 0.3	0.3522 ± 0.0052	0.3276 ± 0.0052	1.02 ± 0.00	1.01 ± 0.00
0.1249 ± 0.0015	0.2900 ± 0.0032	0.3010 ± 0.0048	318.34	589.6	589.5 ± 0.3	0.3019 ± 0.0049	0.2804 ± 0.0048	1.02 ± 0.00	1.00 ± 0.00
0.0973 ± 0.0012	0.2900 ± 0.0032	0.2512 ± 0.0044	318.34	592.8	592.9 ± 0.4	0.2521 ± 0.0044	0.2338 ± 0.0044	1.03 ± 0.00	1.00 ± 0.00
0.0730 ± 0.0010	0.2900 ± 0.0032	0.2011 ± 0.0039	318.34	596.0	596.2 ± 0.4	0.2019 ± 0.0039	0.1871 ± 0.0039	1.03 ± 0.00	1.00 ± 0.00
0.0517 ± 0.0007	0.2900 ± 0.0032	0.1512 ± 0.0033	318.33	599.2	599.2 ± 0.4	0.1519 ± 0.0033	0.1406 ± 0.0033	1.04 ± 0.00	1.00 ± 0.00
0.0327 ± 0.0005	0.2900 ± 0.0032	0.1012 ± 0.0025	318.33	602.1	602.2 ± 0.3	0.1017 ± 0.0025	0.0941 ± 0.0025	1.04 ± 0.00	1.00 ± 0.00
0.0152 ± 0.0004	0.2900 ± 0.0032	0.0499 ± 0.0017	318.34	605.1	605.3 ± 0.3	0.0501 ± 0.0017	0.0464 ± 0.0016	1.05 ± 0.00	1.00 ± 0.00
0.0086 ± 0.0003	0.2900 ± 0.0032	0.0287 ± 0.0013	318.33	606.2	606.3 ± 0.3	0.0288 ± 0.0013	0.0267 ± 0.0013	1.05 ± 0.00	1.00 ± 0.00
0.0027 ± 0.0002	0.2900 ± 0.0032	0.0094 ± 0.0009	318.33	607.3	607.3 ± 0.3	0.0094 ± 0.0009	0.0087 ± 0.0009	1.05 ± 0.00	1.00 ± 0.00
0.0000 ± 0.0000	0.2900 ± 0.0032	0.0000 ± 0.0000	318.33	607.8	607.8 ± 0.3	0.0000 ± 0.0000	0.0000 ± 0.0000	1.05 ± 0.00	1.00 ± 0.00

[a] n_i, amount of component i in the equilibrium cell; z_1 total mole fraction of component 1; T, experimental temperature; p_{exp}, experimental pressure; p_{calc}, computed pressure; x_1 and y_1, computed liquid and vapor phase equilibrium mole fractions; γ_i, computed activity coefficient of component i.

Table 9. Averages of Absolute Pressure Residuals |Δ*p*|, While Using Either the Legendre Polynomial or UNIFAC-Dortmund as the Activity Coefficient Model^a

	system 1^b (T = 318.4 K)	system 1^b (T = 364.5 K)	system 2^b (T = 318.4 K)	system 3^b (T = 318.4 K)	system 4^b (T = 318.4 K)
	Legendre				
Δp/kPa	0.23	0.39	0.49	0.33	0.05
γ^{inf}_1	3.32	3.04	4.24	4.06	1.05
γ^{inf}_2	13.80	6.56	22.28	21.97	1.05
	UNIFAC-Dortmund				
Δp/kPa	5.86	11.57	8.43	7.48	2.77
γ^{inf}_1	2.92	2.70	3.63	3.63	1.08
γ^{inf}_2	13.48	6.60	32.24	32.23	1.07

[a] Also, computed infinite dilution activity coefficients, γ^{inf}, are given for both components of the binary mixture. [b] 1-butene + 1-butanol (system 1), 2-methylpropane + 1-butanol (system 2), *n*-butane + 1-butanol (system 3), 1-butene + 2-methylpropane (system 4).

measurement with transducer used for system 1 at 364.5 K was ± 0.7 kPa. The uncertainty of the pressure measurement with transducer used for systems 2 and 3 was ± 0.4 kPa.

Results and Discussion

The vapor pressure of pure 1-butene at 364.5 K was measured to be 1509.4 kPa, which is 3.1 kPa lower than the lowest vapor pressure given by the different vapor pressure correlations. The difference is not explained by the uncertainty in the pressure measurement, which was 0.7 kPa in this case. The vapor pressure of pure *n*-butane was 0.9 kPa lower than the lowest vapor pressure given by the different correlations. The uncertainty in the pressure measurement was 0.4 kPa for this measurement. However, there is some inaccuracy in the vapor pressure correlations also. For instance, for the correlations presented in BYU-DIPPR,[10] the error is stated to be less than 3 %. Using this value (3 %) for the computation of the error limits for the vapor pressure predictions with BYU-DIPPR correlations, the error limits are so wide that the vapor pressures measured in this study are within those limits and thus can be considered acceptable. For all the other measured vapor pressures, the deviation between the measured value and prediction closest to the measurement was less than the uncertainty of the pressure measurement.

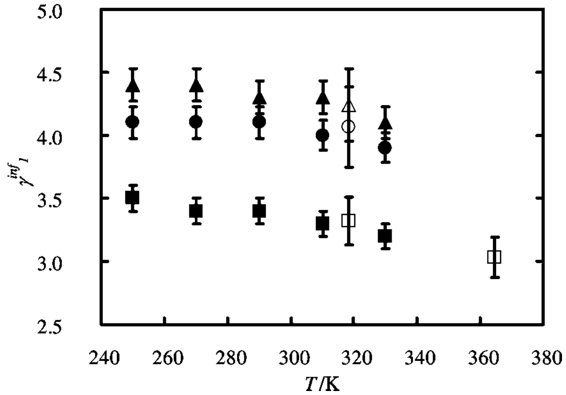

Figure 1. Infinite dilution activity coefficients of: Δ, 2-methylpropane; ○, *n*-butane; △, 1-butene in 1-butanol as a function of temperature. Filled symbols are for measurements from Miyano,[4] and open symbols are for values computed in our study. An error limit of 3 % for the measurements from Miyano[4] is used, and for our values, the computed error limits are reported in Tables 4 to 8.

The VLE measurements and the results of Barker data reduction are presented in Tables 4 to 8. Also, the error limits are shown.

In Table 3, the regressed parameters of the Legendre polynomial are presented. The objective in the regression was that the average absolute pressure error is less than the error in the measurement of the cell pressure. This target was obtained for all the other systems except for the system 2. This system is very nonideal especially when the mole fraction of 1-butanol is small as can be concluded from the high values of activity coefficients presented in Table 6.

Table 10. Parameters for the Wilson Activity Coefficient Model with the Approximate 95 % Confidence Limits and Absolute Average Pressure Residuals $|\Delta p|$ for the Different Binary Systems[a] Regressed Using VLE Data from our Research Group (the First Parameter Set) and Using Both VLE Data from our Research Group and the Data Found from the Literature (the Second Parameter Set)

	system 1		system 2		system 3		system 4	
	value	95 % confidence limit	value	95 % confidence limit	value	95 % confidence limit	value	95 % confidence limit
Wilson volume ratio[b]	0.87		0.95		0.94		1.09	
			Wilson 1st parameter set					
data sets used in the fitting	[c]		[c]		ref 7[c]		[c]	
$a_{0,12}$	−22.05	16.52	121.31	11.55	137.53	7.94	160.33	81.15
$a_{0,21}$	1859.61	78.80	969.16	106.82	692.71	29.07	11.04	78.40
$a_{1,12}$	0.35	0.05						
$a_{1,21}$	−3.46	0.22						
$|\Delta p|$/kPa[d]	1.82		2.86		5.56		0.82	
$|\Delta \gamma^{\mathrm{inf}}_1|$[e]	0.080		0.223		0.302			
$|\Delta H^{\mathrm{ex}}|/\mathrm{kJ \cdot mol^{-1}}$[f]					0.163			
			Wilson 2nd parameter set					
data sets used in the fitting	ref 4[c]		ref 4[c]		refs 4 5, 6, 7[c]			
$a_{0,12}$	−48.63	12.61	196.90	28.38	17.65	4.49		
$a_{0,21}$	1969.49	78.87	−1469.60	556.66	2617.13	65.61		
$a_{1,12}$	0.42	0.04	−0.25	0.09	0.27	0.06		
$a_{1,21}$	−3.77	0.23	7.71	1.81	−5.08	0.17		
$|\Delta p|$/kPa[d]	1.95		3.04		3.64			
$|\Delta \gamma^{\mathrm{inf}}_1|$[e]	0.050		0.038		0.038			
$|\Delta H^{\mathrm{ex}}|/\mathrm{kJ \cdot mol^{-1}}$[f]					0.036			
UNIFAC-Dortmund								
$|\Delta \gamma^{\mathrm{inf}}_1|$[e]	0.322		0.559		0.299			
$|\Delta H^{\mathrm{ex}}|/\mathrm{kJ \cdot mol^{-1}}$[f]					0.035			

[a] 1-Butene + 1-butanol (system 1), 2-methylpropane + 1-butanol (system 2), *n*-butane + 1-butanol (system 3), 1-butene + 2-methylpropane (system 4). [b] Defined as v_1/v_2, where v_i is the liquid molar volume of component i at the normal boiling point. Liquid molar volume computed here using the correlation and normal boiling point reported in BYU-DIPPR.[10] [c] VLE data presented in this article. [d] Average of absolute pressure residuals. [e] Average of absolute deviation between computed and measured infinite dilution activity coefficient of component 1. [f] Average of absolute deviation between computed and measured excess enthalpy of mixing.

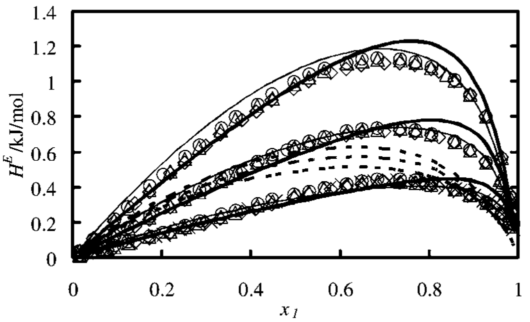

Figure 2. Excess enthalpy for *n*-butane (1) + 1-butanol (2) at temperatures 298.15 K (lowest H^E set), 323.15 K (intermediate H^E set), and 348.15 K (highest H^E set) at pressures: ×, 2.98 MPa; ◇, 5.00 MPa; Δ, 10.00 MPa; ○, 15.00 MPa taken from McFall et al.[5] UNIFAC-Dortmund prediction with the thin line. The Wilson prediction with a bold ticked line with the first parameter set obtained using only VLE data. Wilson prediction with the bold line with the second parameter set obtained using also H^E measurement.

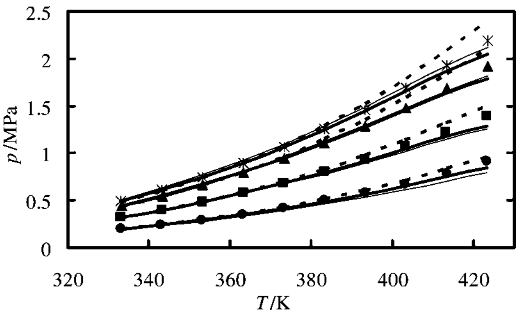

Figure 3. Bubble point pressure as a function of temperature for *n*-butane (1) + 1-butanol (2). ●, x_1 = 0.1019; ■, x_1 = 0.2007; ▲, x_1 = 0.3354; *, x_1 = 0.4174 are measurements taken from Déak et al.[8] Wilson's prediction using the first parameter set with bold ticked line. Wilson's prediction using the second parameter set with bold solid line, and UNIFAC-Dortmund prediction with thin solid line.

The comparison between the predictive UNIFAC-Dortmund and the experimental results are presented in Table 9. For the infinite dilution activity coefficient of 1-butanol in systems 2 and 3, UNIFAC-Dortmund predicts a much higher value than is obtained from the measurements. The possibility that in these highly nonideal compositions the regression of Legendre polynomial parameters has failed was thus investigated. Indeed, for system 3 the deviation between the measured and predicted pressure is highest when the mole fraction of 1-butanol becomes smaller (see Table 7). However, for system 2, this is not the case; instead, the pressure residuals are higher in both ends of the mole fraction scale (see Table 6). For other infinite dilution activity coefficients, the differences are much smaller.

In Figure 1, the activity coefficients computed along Barker's data reduction with the Legendre polynomial are shown with their error limits together with the measurements from Miyano.[4] From Figure 1 it can be concluded that the infinite dilution activity coefficients computed from the measured data presented here are well in line with Miyano's measurements.

The parameters for the Wilson model are presented in Table 10. With the first set of Wilson parameters, the average of absolute pressure residual is smaller than with the second set. With the inclusion of the infinite dilution data to the fitting of systems 1 and 2, the error for pressure slightly increases, but naturally, the error for the infinite dilution data becomes smaller. For system 3, a lot of information is available in the literature resulting in narrow confidence limits for the parameters.

The capabilities of the UNIFAC-Dortmund model to predict the literature data are also shown in Table 10. The average absolute deviation between the computed and the measured infinite dilution activity coefficient is higher with

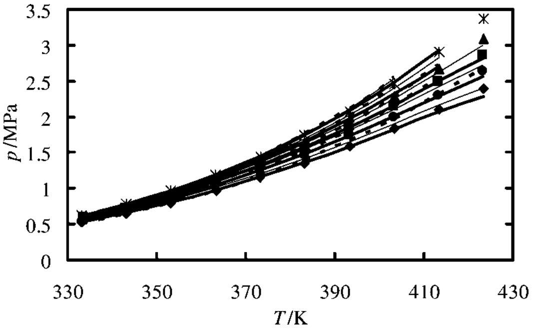

Figure 4. Bubble point pressure as a function of temperature for *n*-butane (1) + 1-butanol (2). ◆, $x_1 = 0.5018$; ●, $x_1 = 0.6072$; ■, $x_1 = 0.7065$; ▲, $x_1 = 0.8114$; *, $x_1 = 0.9031$ are measurements taken from Déak et al.[8] Wilson's prediction using the first parameter set with bold ticked line. Wilson's prediction using the second parameter set with bold solid line and UNIFAC-Dortmund prediction with thin solid line.

the UNIFAC-Dortmund for systems 1 and 2 than with the Wilson model using the first parameter set, which was obtained using only VLE data. However, the UNIFAC-Dortmund model predicts the excess enthalpy of mixing well for system 3. This is also demonstrated in Figure 2. The Wilson model with the first parameter set does not predict the influence of temperature on the excess enthalpy. Using also the excess enthalpy and infinite dilution activity coefficient data in the regression improves the Wilson predictions in small mole fractions of *n*-butane, but UNIFAC-Dortmund performs better when the mole fraction of *n*-butane is high. Also, the shape of the curve is better predicted with UNIFAC-Dortmund. Further, the average of the absolute deviation between computed and measured excess enthalpies of mixing is smaller with UNIFAC-Dortmund than with Wilson with the second parameter set, which was obtained using the literature data in addition to VLE data.

Finally, in Figures 3 and 4, the predictions of the Wilson model with the first and second parameter set and UNIFAC-Dortmund for the bubble point pressure of *n*-butane + 1-butanol (system 3) are shown together with data from Déak et al.[8] It should be emphasized that these data were not used in the regression of Wilson model parameters. The computations are limited below the critical point of *n*-butane because the pure component vapor pressure correlation needed in the VLE computation is not valid above the component's critical point. With small mole fractions of *n*-butane, the UNIFAC-Dortmund prediction for the bubble point pressure is smaller than the Wilson model prediction with second parameter set. When the mole fraction of *n*-butane is increased, the UNIFAC-Dortmund prediction for the bubble point pressure becomes higher than the Wilson model prediction with the second parameter set. The average of the absolute pressure residuals was (43.3, 16.4, and 39.8) kPa for the Wilson model with the first and second parameter set and UNIFAC-Dortmund, respectively. Thus, the Wilson model with the second parameter set describes better this bubble point data than UNIFAC-Dortmund. Also, usage of other literature data in addition to VLE data improves the prediction.

The 1-butene + 2-methylpropane system showed very ideal behavior, so it was tested for whether it is justifiable to assume ideal liquid phase behavior for this system. With the ideal assumption for the liquid phase, the average absolute pressure deviation was 4.7 kPa compared to 0.05 kPa using the Legendre polynomial as the activity coefficient model. This indicates that although the system is nearly ideal, it is beneficial to use an activity coefficient model for the description of the system. For this system, additional data from the literature were not found. Thus, the Wilson parameter set was obtained using only the VLE data measured at one temperature. Using the Wilson model with these parameters at other conditions is then questionable. However, for this system, UNIFAC-Dortmund gave the best prediction (Table 9).

Conclusions

In this work, VLE data for four binary systems were presented along with an error analysis. Wilson model parameters were regressed against the experimental data. It was also demonstrated that if different types of vapor−liquid equilibrium data from the literature are used, the Wilson model predictions become more accurate. In all cases, the correlative Wilson model performs better than the predictive UNIFAC-Dortmund model except for the excess enthalpy estimation for system 3. The shape of the excess enthalpy of mixing curve is also better predicted with UNIFAC-Dortmund. Further, it was observed that although the 1-butene + 2-methylpropane system is very ideal the usage of an activity coefficient model enables a more accurate description of the system.

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