Vapor−Liquid Equilibrium for 1-Butene + Methanol, + 1-Propanol, + 2-Propanol, + 2-Butanol, and 2-Methyl-2-propanol (TBA) at 364.5 K

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Vapor−liquid equilibrium (VLE) data for 1-butene + methanol, + 1-propanol, + 2-propanol, + 2-butanol, and + 2-methyl-2-propanol were measured at 364.5 K with a static total pressure apparatus. Measured p, T, z data were reduced to liquid and vapor phase compositions using the Barker method. Azeotropic points were found for the 1-butene + methanol system ($x_1 = 0.877$, $T = 364.5$ K, $p = 1606.2$ kPa). From measured data, the Wilson, NRTL, and UNIQUAC parameters were calculated. The fitted Legendre polynomial was compared with the predictive UNIFAC and UNIFAC-Dortmund methods, and an error analysis was made.

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; however, for detailed design, experimental data are needed, especially when dealing with nonideal mixtures and where the system has an azeotrope.

In this work, five binary systems were measured. Miyano et al.[4] provided the Henry's law constants and activity coefficients at infinite dilutions for 1-butene + methanol from (374 to 490) K. For other systems at high temperature, no data were found. Previously, Laakkonen et al.[5] provided VLE data for 1-butene + methanol, 1-butene + 2-propanol, 1-butene + 2-butanol, and 1-butene + 2-methyl-2-propanol at 323 K with the same equipment as in this work

Experimental

Isothermal data for binary mixtures of 1-butene and methanol, 1-propanol, 2-propanol, 2-butanol, or 2-methyl-2-propanol (TBA) were measured. To express the pressure as a function of composition, a sufficient amount of experimental data is needed. In our work, 27 experimental points for each system were measured, including vapor pressures for both components. In this article, 1-butene is always addressed as component (1) and alcohol as component (2).

Materials. The suppliers and purities of the used material are presented in Table 1. Alcohols were dried over molecular sieves (Merck 3A) for at least 24 h. 1-Butene was used as such.

After drying, the alcohols were degassed using vacuum rectification. A detailed description of the degassing procedure is explained by Uusi-Kyyny et al.[6] 1-Butene was degassed in a syringe pump by opening the vacuum line 10 times in 10 s. The quality of degassing was checked by measuring the pure vapor pressures and comparing them to literature values[7–9] (Table 2).

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Apparatus. The detailed information of the apparatus can be found in Uusi-Kyyny et al.,[6] and the automation of the apparatus is described by Ouni et al.[10] In these experiments, the pressure was measured with a pressure transducer (Diqiquartz 2300A-101-CE). The used Pt100 thermometer probes were connected to a thermometer (Systemtek S2541 Thermoanalyzer). The cell was placed into a waterbath, where the temperature variation was of ± 0.03 K. The cell volume was 112.68 cm^3.

Procedure. Temperatures of the syringe pumps were measured at each equilibrium point to get the accurate amount of injected component.

The detailed version of the procedure can be found from our previous articles, such as Uusi-Kyyny et al.[6] and Laakkonen et al.[5] Only the general idea is given here.

First, component 1 was introduced to the system, and the vapor pressure was measured. Then, a predetermined volume 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. The injections were also predetermined so that in the end the cell was nearly full of the mixture.

This procedure was also vice versa so that first component 2 was introduced to the system and predetermined amounts of component 1 were injected into the system. Data were considered valid if the measured pressure difference between equimolar points of these two experiments was less than the uncertainty of the pressure transducer.

Data Analysis. The Barker method[11] was used to convert the total amount of moles fed into the cell to mole fractions in both the vapor and liquid phases. This method assumes that there is an activity coefficient model that predicts the bubble point pressure with better accuracy than experimental pressure. The reduction was considered sufficient when the averaged absolute deviation of the pressure was smaller than the uncertainty of the pressure transducer. The fugacity coefficients were calculated using the Soave−Redlich−Kwong[12] equation of state. The Rackett[13] equation was used to calculate the liquid molar volume in the Poynting correction. Liquid phase activity coefficients were calculated using the Legendre polynomial.[14] This method is very flexible and therefore suitable for most binary systems.

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Table 1. Material Purities, Their Suppliers, and Critical Properties

compound	manufacturer	purity/wt %	T_c/K	p_c/MPa	ω
1-butene	Messer Finland Oy	99.4	512.58 ± 1.03	8.084 ± 0.081	0.5658
methanol	Merck	99.8	536.78 ± 1.07	5.169 ± 0.052	0.6204
1-propanol	Riedel-de Haën	99.8	508.31 ± 1.02	4.764 ± 0.048	0.6669
2-propanol	Riedel-de Haën	99.8	536.01 ± 1.07	4.202 ± 0.042	0.5768
2-butanol	Fluka	>99.8	506.21 ± 1.01	3.972 ± 0.040	0.6152
2-methyl-2-propanol (TBA)	Fluka	>99.8	512.58 ± 1.03	8.084 ± 0.081	0.5658

Table 2. Vapor Pressures Measured and Calculated from Literature Values[a]

		this work	Reid et al.[7]	Yaws[9]	Perry and Green [8]
component	T/K	p/kPa	p/kPa	p/kPa	p/kPa
1-butene	364.51	1509.9	1512.6	1524.5	1510.1
	364.51	1510.7	1512.6	1524.5	1510.1
	364.51	1511.0	1512.6	1524.5	1510.1
	364.51	1510.5	1512.6	1524.5	1510.1
	364.50	1509.8	1512.3	1524.2	1509.8
methanol	364.52	267.4	267.3	266.5	267.1
1-propanol	364.52	81.3	81.3	81.3	80.7
2-propanol	364.51	144.5	144.6	141.9	142.4
2-butanol	364.51	74.5	73.6	74.9	74.7
2-methyl-2-propanol (TBA)	364.51	142.7	142.3	141.6	143.1

[a] The vapor pressure values for 1-butene were obtained from five different experiments.

Table 3. VLE Data for 1-Butene (1) + Methanol (2) at 364.5 K

				p_{exptl}	p_{calcd}				
n_1	n_2	z_1	T/K	kPa	kPa	x_1	y_1	γ_1	γ_2
0.6431 ± 0.0068	0.0000 ± 0.0000	1.0000 ± 0.0000	364.51	1509.9	1509.9 ± 0.4	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	7.69 ± 0.04
0.6431 ± 0.0068	0.0052 ± 0.0006	0.9919 ± 0.0009	364.52	1527.6	1522.9 ± 1.2	0.9921 ± 0.0009	0.9873 ± 0.0014	1.00 ± 0.00	7.42 ± 0.06
0.6431 ± 0.0068	0.0115 ± 0.0006	0.9825 ± 0.0011	364.53	1545.9	1536.4 ± 1.2	0.9829 ± 0.0011	0.9736 ± 0.0015	1.00 ± 0.00	7.11 ± 0.06
0.6431 ± 0.0068	0.0187 ± 0.0007	0.9717 ± 0.0013	364.51	1561.9	1548.9 ± 1.1	0.9723 ± 0.0013	0.9594 ± 0.0016	1.00 ± 0.00	6.79 ± 0.06
0.6431 ± 0.0068	0.0352 ± 0.0009	0.9482 ± 0.0017	364.51	1586.8	1569.1 ± 0.9	0.9488 ± 0.0017	0.9328 ± 0.0017	1.01 ± 0.00	6.13 ± 0.06
0.6431 ± 0.0068	0.0716 ± 0.0012	0.8999 ± 0.0025	364.51	1601.8	1584.7 ± 0.6	0.9001 ± 0.0025	0.8933 ± 0.0018	1.02 ± 0.00	5.02 ± 0.05
0.6431 ± 0.0068	0.1152 ± 0.0017	0.8481 ± 0.0033	364.51	1598.4	1582.2 ± 1.0	0.8475 ± 0.0033	0.8663 ± 0.0018	1.05 ± 0.00	4.12 ± 0.04
0.6431 ± 0.0068	0.1625 ± 0.0021	0.7982 ± 0.0039	364.51	1589.9	1572.3 ± 1.3	0.7966 ± 0.0040	0.8500 ± 0.0018	1.09 ± 0.00	3.45 ± 0.03
0.6431 ± 0.0068	0.2156 ± 0.0027	0.7489 ± 0.0044	364.51	1579.8	1560.4 ± 1.4	0.7465 ± 0.0045	0.8399 ± 0.0017	1.15 ± 0.00	2.94 ± 0.03
0.6431 ± 0.0068	0.2775 ± 0.0033	0.6986 ± 0.0048	364.51	1568.5	1548.8 ± 1.4	0.6956 ± 0.0049	0.8336 ± 0.0016	1.21 ± 0.01	2.53 ± 0.02
0.6431 ± 0.0068	0.3470 ± 0.0040	0.6495 ± 0.0051	364.51	1556.8	1538.8 ± 1.3	0.6463 ± 0.0052	0.8300 ± 0.0015	1.30 ± 0.01	2.21 ± 0.02
0.6431 ± 0.0068	0.4310 ± 0.0049	0.5987 ± 0.0053	364.51	1543.6	1529.9 ± 1.1	0.5956 ± 0.0054	0.8278 ± 0.0014	1.40 ± 0.01	1.96 ± 0.01
0.6431 ± 0.0068	0.5282 ± 0.0059	0.5490 ± 0.0054	364.51	1529.2	1521.9 ± 0.8	0.5464 ± 0.0055	0.8265 ± 0.0013	1.52 ± 0.01	1.75 ± 0.01
0.6431 ± 0.0068	0.6454 ± 0.0070	0.4991 ± 0.0054	364.51	1512.8	1513.3 ± 0.5	0.4973 ± 0.0055	0.8253 ± 0.0012	1.66 ± 0.02	1.59 ± 0.01
0.6443 ± 0.0068	0.6566 ± 0.0072	0.4953 ± 0.0054	364.52	1513.1	1513.1 ± 0.4	0.4936 ± 0.0055	0.8252 ± 0.0012	1.67 ± 0.02	1.58 ± 0.01
0.5269 ± 0.0056	0.6566 ± 0.0072	0.4452 ± 0.0053	364.51	1490.5	1500.1 ± 0.8	0.4401 ± 0.0055	0.8235 ± 0.0011	1.87 ± 0.02	1.43 ± 0.01
0.4291 ± 0.0046	0.6566 ± 0.0072	0.3952 ± 0.0052	364.51	1461.7	1479.6 ± 1.0	0.3860 ± 0.0053	0.8207 ± 0.0011	2.10 ± 0.03	1.32 ± 0.01
0.3465 ± 0.0038	0.6566 ± 0.0072	0.3454 ± 0.0049	364.53	1423.4	1446.1 ± 1.2	0.3318 ± 0.0051	0.8157 ± 0.0010	2.40 ± 0.04	1.23 ± 0.00
0.2755 ± 0.0030	0.6566 ± 0.0072	0.2955 ± 0.0046	364.52	1368.2	1391.0 ± 1.1	0.2775 ± 0.0047	0.8072 ± 0.0010	2.76 ± 0.05	1.15 ± 0.00
0.2143 ± 0.0024	0.6566 ± 0.0072	0.2461 ± 0.0041	364.52	1291.0	1306.2 ± 0.9	0.2244 ± 0.0041	0.7931 ± 0.0010	3.19 ± 0.06	1.10 ± 0.00
0.1614 ± 0.0019	0.6566 ± 0.0072	0.1973 ± 0.0036	364.52	1184.1	1184.1 ± 0.4	0.1735 ± 0.0035	0.7702 ± 0.0010	3.71 ± 0.07	1.06 ± 0.00
0.1146 ± 0.0014	0.6566 ± 0.0072	0.1486 ± 0.0029	364.51	1035.9	1017.8 ± 1.2	0.1253 ± 0.0028	0.7316 ± 0.0012	4.31 ± 0.09	1.03 ± 0.00
0.0734 ± 0.0010	0.6566 ± 0.0072	0.1006 ± 0.0022	364.51	842.0	810.5 ± 1.9	0.0810 ± 0.0020	0.6632 ± 0.0016	4.99 ± 0.11	1.01 ± 0.00
0.0365 ± 0.0006	0.6566 ± 0.0072	0.0526 ± 0.0014	364.51	596.8	567.4 ± 2.4	0.0406 ± 0.0012	0.5220 ± 0.0025	5.74 ± 0.13	1.00 ± 0.00
0.0225 ± 0.0004	0.6566 ± 0.0072	0.0332 ± 0.0010	364.52	482.4	460.3 ± 2.4	0.0252 ± 0.0008	0.4134 ± 0.0034	6.06 ± 0.13	1.00 ± 0.00
0.0093 ± 0.0003	0.6566 ± 0.0072	0.0140 ± 0.0006	364.52	361.1	350.7 ± 2.4	0.0105 ± 0.0005	0.2340 ± 0.0050	6.39 ± 0.14	1.00 ± 0.00
0.0000 ± 0.0000	0.6566 ± 0.0072	0.0000 ± 0.0000	364.52	267.4	267.4 ± 0.4	0.0000 ± 0.0000	0.0000 ± 0.0000	6.64 ± 0.14	1.00 ± 0.00

The parameters for the Legendre polynomial are presented in Table 8, and the critical properties[15] that were needed for the calculation are presented in Table 1. The calculations were made with the in-house simulator VLEFIT that was developed at the Helsinki University of Technology.

With the regression of the Legendre polynomial the data were also converted into regular VLE data, and for the fitting of thermodynamic models Wilson,[16] NRTL,[17] and UNIQUAC[18] and predictive models UNIFAC and UNIFAC-Dortmund, both data were tested.

Error Analysis. The uncertainties of the temperature measurements were ± 0.03 K for the water bath and ± 0.1 K for the syringe pumps. The pressure uncertainty for the transducer was ± 0.7 kPa and ± 20 kPa for syringe pumps. The uncertainty of the injected volumes was ± 0.02 cm^3, which was calibrated with distilled water. The total uncertainty can be the calculated theoretical standard error. In our case, the same uncertainty was used as Zaytseva et al.[19]

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

The densities for the uncertainty equation were calculated from density correlations presented by Daubert and Danner,[20] and the uncertainties of the densities were less than 3.7 % for 1-butene + methanol, 2.3 % for 1-butene + 2-methyl-2-propanol, and 2.2 % for other systems. The compressibility of the liquid was calculated using the Hankinson−Brobst−Thomson model, which, e.g., is described by Hynynen et al.[21]

In principle, this factorial method approximates the maximum error by first calculating the upper and lower limits for ranges

Table 4. VLE Data for 1-Butene (1) + 1-Propanol (2) at 364.5 K

				p_{exptl}	p_{calcd}				
n_1	n_2	z_1	T/K	kPa	kPa	x_1	y_1	γ_1	γ_1
0.5147 ± 0.0055	0.0000 ± 0.0000	1.0000 ± 0.0000	364.51	1510.7	1510.7 ± 0.4	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	6.86 ± 0.17
0.5147 ± 0.0055	0.0052 ± 0.0003	0.9900 ± 0.0007	364.51	1499.4	1500.5 ± 0.8	0.9897 ± 0.0008	0.9945 ± 0.0005	1.00 ± 0.00	6.38 ± 0.12
0.5147 ± 0.0055	0.0120 ± 0.0004	0.9772 ± 0.0010	364.51	1485.7	1487.7 ± 0.8	0.9764 ± 0.0010	0.9884 ± 0.0007	1.00 ± 0.00	5.83 ± 0.09
0.5147 ± 0.0055	0.0159 ± 0.0004	0.9700 ± 0.0011	364.51	1478.4	1480.6 ± 0.8	0.9689 ± 0.0012	0.9854 ± 0.0008	1.00 ± 0.00	5.56 ± 0.07
0.5147 ± 0.0055	0.0288 ± 0.0006	0.9470 ± 0.0015	364.51	1455.9	1458.6 ± 0.7	0.9449 ± 0.0016	0.9775 ± 0.0009	1.01 ± 0.00	4.81 ± 0.04
0.5147 ± 0.0055	0.0587 ± 0.0009	0.8976 ± 0.0024	364.51	1415.1	1416.8 ± 0.6	0.8936 ± 0.0025	0.9662 ± 0.0010	1.03 ± 0.00	3.68 ± 0.01
0.5147 ± 0.0055	0.0926 ± 0.0012	0.8475 ± 0.0031	364.51	1380.9	1380.9 ± 0.4	0.8419 ± 0.0033	0.9591 ± 0.0010	1.07 ± 0.00	2.96 ± 0.01
0.5147 ± 0.0055	0.1304 ± 0.0016	0.7979 ± 0.0037	364.51	1349.4	1348.9 ± 0.5	0.7913 ± 0.0040	0.9542 ± 0.0010	1.11 ± 0.01	2.48 ± 0.01
0.5147 ± 0.0055	0.1733 ± 0.0020	0.7481 ± 0.0042	364.51	1319.0	1318.6 ± 0.5	0.7410 ± 0.0045	0.9503 ± 0.0009	1.16 ± 0.01	2.14 ± 0.01
0.5147 ± 0.0055	0.2220 ± 0.0025	0.6987 ± 0.0047	364.52	1288.8	1288.6 ± 0.5	0.6916 ± 0.0049	0.9470 ± 0.0010	1.22 ± 0.01	1.89 ± 0.01
0.5147 ± 0.0055	0.2787 ± 0.0031	0.6487 ± 0.0050	364.53	1257.3	1257.3 ± 0.4	0.6423 ± 0.0052	0.9438 ± 0.0010	1.29 ± 0.01	1.70 ± 0.00
0.5147 ± 0.0055	0.3453 ± 0.0038	0.5985 ± 0.0052	364.52	1223.3	1223.6 ± 0.5	0.5931 ± 0.0054	0.9407 ± 0.0010	1.36 ± 0.01	1.56 ± 0.00
0.5147 ± 0.0055	0.4228 ± 0.0046	0.5490 ± 0.0053	364.52	1187.1	1187.6 ± 0.6	0.5450 ± 0.0054	0.9375 ± 0.0010	1.44 ± 0.01	1.44 ± 0.00
0.5255 ± 0.0056	0.5270 ± 0.0056	0.4993 ± 0.0053	364.52	1148.8	1148.2 ± 0.7	0.4974 ± 0.0054	0.9341 ± 0.0009	1.53 ± 0.02	1.35 ± 0.00
0.5147 ± 0.0055	0.5170 ± 0.0055	0.4989 ± 0.0053	364.52	1146.4	1147.1 ± 0.7	0.4966 ± 0.0054	0.9340 ± 0.0009	1.53 ± 0.02	1.35 ± 0.00
0.4301 ± 0.0046	0.5270 ± 0.0056	0.4494 ± 0.0053	364.52	1098.6	1098.0 ± 0.7	0.4447 ± 0.0054	0.9298 ± 0.0010	1.65 ± 0.02	1.26 ± 0.00
0.3508 ± 0.0038	0.5270 ± 0.0056	0.3996 ± 0.0052	364.52	1039.9	1039.7 ± 0.6	0.3920 ± 0.0052	0.9246 ± 0.0010	1.78 ± 0.02	1.20 ± 0.00
0.2845 ± 0.0031	0.5270 ± 0.0056	0.3506 ± 0.0049	364.52	972.1	972.1 ± 0.4	0.3402 ± 0.0050	0.9183 ± 0.0010	1.93 ± 0.03	1.14 ± 0.00
0.2274 ± 0.0025	0.5270 ± 0.0056	0.3014 ± 0.0046	364.52	892.2	892.4 ± 0.5	0.2887 ± 0.0046	0.9100 ± 0.0010	2.10 ± 0.03	1.10 ± 0.00
0.1773 ± 0.0020	0.5270 ± 0.0056	0.2517 ± 0.0042	364.53	797.7	797.8 ± 0.6	0.2373 ± 0.0041	0.8984 ± 0.0011	2.29 ± 0.04	1.07 ± 0.00
0.1341 ± 0.0016	0.5270 ± 0.0056	0.2028 ± 0.0037	364.52	689.8	689.8 ± 0.4	0.1879 ± 0.0036	0.8817 ± 0.0011	2.50 ± 0.05	1.04 ± 0.00
0.0955 ± 0.0012	0.5270 ± 0.0056	0.1534 ± 0.0030	364.52	565.1	564.8 ± 0.7	0.1393 ± 0.0029	0.8550 ± 0.0011	2.74 ± 0.06	1.02 ± 0.00
0.0608 ± 0.0008	0.5270 ± 0.0056	0.1034 ± 0.0023	364.51	422.9	422.5 ± 0.9	0.0918 ± 0.0022	0.8061 ± 0.0012	3.01 ± 0.07	1.01 ± 0.00
0.0308 ± 0.0005	0.5270 ± 0.0056	0.0552 ± 0.0015	364.51	270.9	270.9 ± 0.6	0.0479 ± 0.0014	0.6981 ± 0.0015	3.29 ± 0.10	1.00 ± 0.00
0.0187 ± 0.0004	0.5270 ± 0.0056	0.0343 ± 0.0011	364.52	200.8	200.9 ± 0.8	0.0294 ± 0.0010	0.5936 ± 0.0024	3.42 ± 0.11	1.00 ± 0.00
0.0083 ± 0.0003	0.5270 ± 0.0056	0.0155 ± 0.0007	364.52	135.6	136.2 ± 1.3	0.0132 ± 0.0007	0.4018 ± 0.0055	3.54 ± 0.13	1.00 ± 0.00
0.0000 ± 0.0000	0.5270 ± 0.0056	0.0000 ± 0.0000	364.52	81.3	81.3 ± 0.4	0.0000 ± 0.0000	0.0000 ± 0.0000	3.64 ± 0.14	1.00 ± 0.00

Table 5. VLE Data for 1-Butene (1) + 2-Propanol (2) at 364.5 K

				p_{exptl}	p_{calcd}				
n_1	n_2	z_1	T/K	kPa	kPa	x_1	y_1	γ_1	γ_2
0.5150 ± 0.0055	0.0000 ± 0.0000	1.0000 ± 0.0000	364.51	1511.0	1511.0 ± 0.4	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	4.66 ± 0.06
0.5150 ± 0.0055	0.0057 ± 0.0003	0.9891 ± 0.0007	364.51	1503.5	1502.9 ± 0.7	0.9888 ± 0.0008	0.9929 ± 0.0005	1.00 ± 0.00	4.45 ± 0.04
0.5150 ± 0.0055	0.0109 ± 0.0004	0.9792 ± 0.0009	364.51	1496.4	1495.4 ± 0.7	0.9787 ± 0.0010	0.9869 ± 0.0007	1.00 ± 0.00	4.27 ± 0.04
0.5150 ± 0.0055	0.0160 ± 0.0004	0.9698 ± 0.0011	364.52	1489.5	1487.9 ± 0.8	0.9689 ± 0.0011	0.9816 ± 0.0008	1.00 ± 0.00	4.11 ± 0.03
0.5150 ± 0.0055	0.0271 ± 0.0005	0.9500 ± 0.0015	364.51	1474.5	1472.0 ± 0.9	0.9485 ± 0.0015	0.9717 ± 0.0010	1.01 ± 0.00	3.80 ± 0.02
0.5150 ± 0.0055	0.0583 ± 0.0009	0.8984 ± 0.0023	364.51	1437.0	1430.9 ± 1.1	0.8952 ± 0.0025	0.9515 ± 0.0015	1.02 ± 0.00	3.14 ± 0.01
0.5150 ± 0.0055	0.0923 ± 0.0012	0.8480 ± 0.0031	364.51	1402.4	1392.7 ± 1.2	0.8434 ± 0.0033	0.9375 ± 0.0017	1.05 ± 0.00	2.67 ± 0.01
0.5150 ± 0.0055	0.1303 ± 0.0016	0.7981 ± 0.0037	364.51	1369.0	1357.3 ± 1.2	0.7925 ± 0.0039	0.9273 ± 0.0018	1.08 ± 0.00	2.31 ± 0.01
0.5150 ± 0.0055	0.1730 ± 0.0020	0.7485 ± 0.0042	364.51	1335.8	1324.0 ± 1.2	0.7424 ± 0.0044	0.9193 ± 0.0019	1.12 ± 0.01	2.03 ± 0.01
0.5150 ± 0.0055	0.2226 ± 0.0025	0.6982 ± 0.0047	364.51	1301.4	1291.1 ± 1.0	0.6921 ± 0.0049	0.9127 ± 0.0019	1.17 ± 0.01	1.82 ± 0.01
0.5150 ± 0.0055	0.2790 ± 0.0031	0.6486 ± 0.0050	364.51	1266.1	1258.7 ± 0.8	0.6430 ± 0.0052	0.9069 ± 0.0019	1.23 ± 0.01	1.65 ± 0.01
0.5150 ± 0.0055	0.3449 ± 0.0038	0.5989 ± 0.0052	364.51	1228.7	1225.0 ± 0.6	0.5942 ± 0.0053	0.9014 ± 0.0018	1.30 ± 0.01	1.51 ± 0.01
0.5150 ± 0.0055	0.4235 ± 0.0046	0.5487 ± 0.0053	364.51	1188.6	1188.6 ± 0.4	0.5453 ± 0.0054	0.8958 ± 0.0017	1.38 ± 0.01	1.40 ± 0.01
0.5150 ± 0.0055	0.5166 ± 0.0055	0.4992 ± 0.0053	364.52	1145.8	1148.9 ± 0.9	0.4974 ± 0.0054	0.8898 ± 0.0016	1.46 ± 0.01	1.31 ± 0.01
0.5151 ± 0.0055	0.5195 ± 0.0055	0.4979 ± 0.0053	364.51	1145.3	1148.0 ± 0.9	0.4961 ± 0.0054	0.8896 ± 0.0016	1.46 ± 0.02	1.31 ± 0.01
0.4220 ± 0.0045	0.5195 ± 0.0055	0.4482 ± 0.0053	364.50	1092.4	1098.2 ± 1.4	0.4438 ± 0.0054	0.8821 ± 0.0015	1.57 ± 0.02	1.23 ± 0.00
0.3439 ± 0.0037	0.5195 ± 0.0055	0.3983 ± 0.0052	364.50	1032.5	1039.8 ± 2.0	0.3913 ± 0.0052	0.8730 ± 0.0014	1.68 ± 0.02	1.17 ± 0.00
0.2788 ± 0.0031	0.5195 ± 0.0055	0.3492 ± 0.0049	364.51	965.8	972.4 ± 2.5	0.3397 ± 0.0050	0.8616 ± 0.0012	1.81 ± 0.03	1.12 ± 0.00
0.2243 ± 0.0025	0.5195 ± 0.0055	0.3015 ± 0.0046	364.51	891.7	896.0 ± 2.9	0.2899 ± 0.0046	0.8473 ± 0.0014	1.95 ± 0.03	1.09 ± 0.00
0.1745 ± 0.0020	0.5195 ± 0.0055	0.2514 ± 0.0042	364.51	802.7	803.0 ± 3.1	0.2383 ± 0.0041	0.8268 ± 0.0016	2.11 ± 0.04	1.06 ± 0.00
0.1314 ± 0.0016	0.5195 ± 0.0055	0.2019 ± 0.0037	364.51	702.2	697.7 ± 3.3	0.1883 ± 0.0036	0.7979 ± 0.0019	2.28 ± 0.05	1.03 ± 0.00
0.0938 ± 0.0012	0.5195 ± 0.0055	0.1529 ± 0.0030	364.51	589.0	580.5 ± 3.4	0.1401 ± 0.0029	0.7544 ± 0.0024	2.46 ± 0.06	1.02 ± 0.00
0.0599 ± 0.0008	0.5195 ± 0.0055	0.1033 ± 0.0023	364.51	460.2	449.6 ± 3.3	0.0928 ± 0.0022	0.6803 ± 0.0032	2.66 ± 0.07	1.01 ± 0.00
0.0298 ± 0.0005	0.5195 ± 0.0055	0.0543 ± 0.0015	364.51	318.2	309.7 ± 2.8	0.0478 ± 0.0013	0.5337 ± 0.0047	2.86 ± 0.09	1.00 ± 0.00
0.0187 ± 0.0004	0.5195 ± 0.0055	0.0347 ± 0.0011	364.52	257.3	251.2 ± 2.4	0.0303 ± 0.0010	0.4246 ± 0.0057	2.94 ± 0.09	1.00 ± 0.00
0.0080 ± 0.0003	0.5195 ± 0.0055	0.0153 ± 0.0007	364.52	195.0	191.9 ± 2.0	0.0132 ± 0.0007	0.2468 ± 0.0072	3.03 ± 0.10	1.00 ± 0.00
0.0000 ± 0.0000	0.5195 ± 0.0055	0.0000 ± 0.0000	364.51	144.5	144.5 ± 0.4	0.0000 ± 0.0000	0.0000 ± 0.0000	3.09 ± 0.10	1.00 ± 0.00

of experimental variation for p, T, n_1, and n_2. These four variables are entered at their upper or lower levels to produce 16 combinations for each binary pair. This computation was done automatically in the VLEFIT code. The errors of p, T, n_1, and n_2 presented are the average absolute value of these 16 combinations. The errors of p_{calcd}, x_1, y_1, γ_1, and γ_2 are calculated similarly but are a consequence of regression. In general, this method assumes four systematic errors simultaneously from the experiments, which is highly unlikely. The approximate confidence limit of the parameters of different models was also calculated. A detailed description of the calculation process is presented by Pokki.[22]

Results and Discussion

The VLE measurements and the Barker data reduction are presented from Table 3 to Table 7. Also, the error estimations are presented. In Figure 1, the pressure as a function of liquid and vapor composition is presented.

In Table 8, the fitted parameters of the Legendre polynomial and also the parameters for Wilson, NRTL, and UNIQUAC models are presented. Also the 95 % confidence limits are presented. From the confidence limits, it can be seen that the limits for the last parameters in the Legendre polynomial are greater than the parameters itself. It indicates that the necessity

Table 6. VLE Data for 1-Butene (1) + 2-Butanol (2) at 364.5 K

				p_{exptl}	p_{calcd}				
n_1	n_2	z_1	T/K	kPa	kPa	x_1	y_1	γ_1	γ_2
0.4714 ± 0.0051	0.0000 ± 0.0000	1.0000 ± 0.0000	364.51	1510.5	1510.5 ± 0.4	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	4.42 ± 0.17
0.4714 ± 0.0051	0.0046 ± 0.0003	0.9903 ± 0.0007	364.51	1496.0	1496.4 ± 0.9	0.9897 ± 0.0007	0.9964 ± 0.0004	1.00 ± 0.00	4.19 ± 0.13
0.4714 ± 0.0051	0.0101 ± 0.0003	0.9790 ± 0.0009	364.51	1479.4	1480.4 ± 0.9	0.9777 ± 0.0009	0.9927 ± 0.0005	1.00 ± 0.00	3.95 ± 0.11
0.4714 ± 0.0051	0.0150 ± 0.0004	0.9692 ± 0.0011	364.51	1466.1	1467.2 ± 0.9	0.9675 ± 0.0012	0.9898 ± 0.0006	1.00 ± 0.00	3.76 ± 0.09
0.4714 ± 0.0051	0.0249 ± 0.0005	0.9499 ± 0.0014	364.51	1439.8	1442.0 ± 1.0	0.9471 ± 0.0015	0.9848 ± 0.0008	1.01 ± 0.00	3.42 ± 0.06
0.4714 ± 0.0051	0.0527 ± 0.0008	0.8995 ± 0.0023	364.51	1383.4	1384.9 ± 1.0	0.8943 ± 0.0025	0.9749 ± 0.0009	1.03 ± 0.00	2.78 ± 0.02
0.4714 ± 0.0051	0.0837 ± 0.0011	0.8492 ± 0.0030	364.52	1335.5	1335.7 ± 0.9	0.8424 ± 0.0033	0.9680 ± 0.0009	1.05 ± 0.00	2.34 ± 0.01
0.4714 ± 0.0051	0.1184 ± 0.0014	0.7993 ± 0.0037	364.51	1291.7	1291.3 ± 0.8	0.7916 ± 0.0039	0.9626 ± 0.0009	1.09 ± 0.01	2.03 ± 0.00
0.4714 ± 0.0051	0.1580 ± 0.0018	0.7490 ± 0.0042	364.51	1249.0	1248.5 ± 0.7	0.7410 ± 0.0045	0.9579 ± 0.0010	1.12 ± 0.01	1.81 ± 0.00
0.4714 ± 0.0051	0.2027 ± 0.0023	0.6993 ± 0.0046	364.51	1206.6	1206.4 ± 0.6	0.6916 ± 0.0049	0.9537 ± 0.0010	1.17 ± 0.01	1.64 ± 0.00
0.4714 ± 0.0051	0.2549 ± 0.0028	0.6491 ± 0.0050	364.51	1163.2	1163.2 ± 0.4	0.6422 ± 0.0052	0.9496 ± 0.0010	1.22 ± 0.01	1.51 ± 0.00
0.4714 ± 0.0051	0.3158 ± 0.0034	0.5989 ± 0.0052	364.51	1117.9	1118.1 ± 0.5	0.5933 ± 0.0053	0.9455 ± 0.0010	1.27 ± 0.01	1.40 ± 0.00
0.4714 ± 0.0051	0.3879 ± 0.0042	0.5486 ± 0.0053	364.52	1070.1	1070.2 ± 0.6	0.5446 ± 0.0054	0.9411 ± 0.0010	1.33 ± 0.01	1.32 ± 0.00
0.4733 ± 0.0051	0.4770 ± 0.0051	0.4980 ± 0.0053	364.51	1019.4	1018.9 ± 0.6	0.4961 ± 0.0054	0.9363 ± 0.0011	1.40 ± 0.01	1.25 ± 0.00
0.4714 ± 0.0050	0.4737 ± 0.0050	0.4988 ± 0.0053	364.51	1019.3	1019.5 ± 0.6	0.4967 ± 0.0054	0.9364 ± 0.0011	1.40 ± 0.01	1.25 ± 0.00
0.3875 ± 0.0042	0.4770 ± 0.0051	0.4483 ± 0.0053	364.51	958.8	958.6 ± 0.6	0.4439 ± 0.0053	0.9304 ± 0.0011	1.48 ± 0.02	1.19 ± 0.00
0.3168 ± 0.0035	0.4770 ± 0.0051	0.3991 ± 0.0052	364.51	893.1	893.1 ± 0.5	0.3924 ± 0.0052	0.9235 ± 0.0011	1.57 ± 0.02	1.15 ± 0.00
0.2566 ± 0.0028	0.4770 ± 0.0051	0.3498 ± 0.0050	364.51	820.8	820.9 ± 0.5	0.3410 ± 0.0049	0.9151 ± 0.0011	1.66 ± 0.02	1.11 ± 0.00
0.2045 ± 0.0023	0.4770 ± 0.0051	0.3001 ± 0.0046	364.51	740.6	740.6 ± 0.6	0.2895 ± 0.0046	0.9042 ± 0.0012	1.77 ± 0.03	1.07 ± 0.00
0.1600 ± 0.0019	0.4770 ± 0.0051	0.2512 ± 0.0042	364.52	653.8	653.7 ± 0.6	0.2395 ± 0.0041	0.8899 ± 0.0012	1.89 ± 0.03	1.05 ± 0.00
0.1208 ± 0.0015	0.4770 ± 0.0051	0.2021 ± 0.0037	364.52	558.2	558.3 ± 0.5	0.1902 ± 0.0036	0.8695 ± 0.0013	2.02 ± 0.04	1.03 ± 0.00
0.0863 ± 0.0011	0.4770 ± 0.0051	0.1532 ± 0.0031	364.52	454.5	454.5 ± 0.5	0.1420 ± 0.0029	0.8382 ± 0.0014	2.16 ± 0.04	1.02 ± 0.00
0.0556 ± 0.0008	0.4770 ± 0.0051	0.1044 ± 0.0023	364.51	342.4	342.4 ± 0.7	0.0952 ± 0.0022	0.7837 ± 0.0015	2.32 ± 0.06	1.01 ± 0.00
0.0279 ± 0.0005	0.4770 ± 0.0051	0.0553 ± 0.0015	364.52	221.2	221.0 ± 0.6	0.0495 ± 0.0014	0.6633 ± 0.0020	2.49 ± 0.07	1.00 ± 0.00
0.0175 ± 0.0004	0.4770 ± 0.0051	0.0354 ± 0.0011	364.52	169.3	169.5 ± 0.8	0.0315 ± 0.0011	0.5605 ± 0.0029	2.56 ± 0.08	1.00 ± 0.00
0.0071 ± 0.0003	0.4770 ± 0.0051	0.0146 ± 0.0007	364.52	114.4	114.3 ± 1.2	0.0129 ± 0.0007	0.3479 ± 0.0063	2.64 ± 0.09	1.00 ± 0.00
0.0000 ± 0.0000	0.4770 ± 0.0051	0.0000 ± 0.0000	364.51	74.5	74.5 ± 0.4	0.0000 ± 0.0000	0.0000 ± 0.0000	2.69 ± 0.10	1.00 ± 0.00

Table 7. VLE Data for 1-Butene (1) + 2-Methyl-2-propanol (2) at 364.5 K

				p_{exptl}	p_{calcd}				
n_1	n_2	z_1	T/K	kPa	kPa	x_1	y_1	γ_1	γ_2
0.4643 ± 0.0050	0.0000 ± 0.0000	1.0000 ± 0.0000	364.50	1509.8	1509.8 ± 0.4	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	3.42 ± 0.10
0.4643 ± 0.0050	0.0050 ± 0.0003	0.9894 ± 0.0007	364.50	1497.3	1497.8 ± 0.8	0.9889 ± 0.0007	0.9946 ± 0.0005	1.00 ± 0.00	3.27 ± 0.08
0.4643 ± 0.0050	0.0085 ± 0.0003	0.9821 ± 0.0008	364.51	1489.2	1489.7 ± 0.7	0.9813 ± 0.0009	0.9911 ± 0.0006	1.00 ± 0.00	3.17 ± 0.07
0.4643 ± 0.0050	0.0146 ± 0.0004	0.9695 ± 0.0011	364.50	1474.3	1475.5 ± 0.7	0.9681 ± 0.0011	0.9855 ± 0.0008	1.00 ± 0.00	3.02 ± 0.06
0.4643 ± 0.0050	0.0257 ± 0.0005	0.9476 ± 0.0015	364.51	1449.9	1451.5 ± 0.7	0.9451 ± 0.0016	0.9769 ± 0.0011	1.01 ± 0.00	2.78 ± 0.05
0.4643 ± 0.0050	0.0525 ± 0.0007	0.8985 ± 0.0023	364.51	1400.0	1401.0 ± 0.5	0.8940 ± 0.0025	0.9613 ± 0.0013	1.02 ± 0.00	2.36 ± 0.02
0.4643 ± 0.0050	0.0830 ± 0.0011	0.8483 ± 0.0030	364.51	1352.8	1352.8 ± 0.4	0.8423 ± 0.0033	0.9490 ± 0.0015	1.04 ± 0.00	2.06 ± 0.01
0.4643 ± 0.0050	0.1169 ± 0.0014	0.7989 ± 0.0037	364.51	1308.5	1307.6 ± 0.5	0.7919 ± 0.0039	0.9390 ± 0.0015	1.07 ± 0.00	1.83 ± 0.01
0.4643 ± 0.0050	0.1554 ± 0.0018	0.7493 ± 0.0042	364.51	1264.0	1263.1 ± 0.5	0.7420 ± 0.0044	0.9301 ± 0.0016	1.10 ± 0.01	1.66 ± 0.00
0.4643 ± 0.0050	0.2000 ± 0.0022	0.6989 ± 0.0046	364.51	1218.6	1218.0 ± 0.5	0.6919 ± 0.0048	0.9217 ± 0.0016	1.14 ± 0.01	1.53 ± 0.00
0.4643 ± 0.0050	0.2510 ± 0.0028	0.6491 ± 0.0050	364.52	1172.4	1172.4 ± 0.4	0.6428 ± 0.0051	0.9136 ± 0.0016	1.18 ± 0.01	1.42 ± 0.00
0.4643 ± 0.0050	0.3096 ± 0.0034	0.6000 ± 0.0052	364.51	1124.8	1125.7 ± 0.5	0.5949 ± 0.0053	0.9055 ± 0.0016	1.22 ± 0.01	1.34 ± 0.00
0.4643 ± 0.0050	0.3799 ± 0.0041	0.5500 ± 0.0053	364.51	1074.1	1075.9 ± 0.6	0.5464 ± 0.0054	0.8969 ± 0.0016	1.27 ± 0.01	1.27 ± 0.00
0.4643 ± 0.0050	0.4642 ± 0.0049	0.5001 ± 0.0053	364.51	1020.6	1023.2 ± 0.7	0.4983 ± 0.0054	0.8875 ± 0.0016	1.33 ± 0.01	1.21 ± 0.00
0.4630 ± 0.0050	0.4660 ± 0.0049	0.4984 ± 0.0053	364.51	1022.6	1022.1 ± 0.7	0.4966 ± 0.0054	0.8871 ± 0.0016	1.33 ± 0.01	1.21 ± 0.00
0.3790 ± 0.0041	0.4660 ± 0.0049	0.4485 ± 0.0053	364.51	960.9	960.8 ± 0.7	0.4445 ± 0.0053	0.8756 ± 0.0016	1.39 ± 0.02	1.16 ± 0.00
0.3097 ± 0.0034	0.4660 ± 0.0049	0.3992 ± 0.0052	364.52	895.2	895.1 ± 0.6	0.3931 ± 0.0052	0.8622 ± 0.0016	1.46 ± 0.02	1.12 ± 0.00
0.2507 ± 0.0028	0.4660 ± 0.0049	0.3498 ± 0.0050	364.52	823.7	823.8 ± 0.5	0.3419 ± 0.0050	0.8461 ± 0.0017	1.54 ± 0.02	1.09 ± 0.00
0.2009 ± 0.0023	0.4660 ± 0.0049	0.3012 ± 0.0046	364.51	747.9	747.9 ± 0.5	0.2918 ± 0.0046	0.8263 ± 0.0017	1.62 ± 0.02	1.06 ± 0.00
0.1566 ± 0.0018	0.4660 ± 0.0049	0.2515 ± 0.0042	364.51	664.2	664.2 ± 0.5	0.2411 ± 0.0041	0.8001 ± 0.0017	1.71 ± 0.03	1.04 ± 0.00
0.1182 ± 0.0014	0.4660 ± 0.0049	0.2023 ± 0.0037	364.50	575.3	575.2 ± 0.5	0.1917 ± 0.0036	0.7647 ± 0.0018	1.81 ± 0.03	1.03 ± 0.00
0.0844 ± 0.0011	0.4660 ± 0.0049	0.1533 ± 0.0031	364.50	480.4	480.5 ± 0.6	0.1435 ± 0.0029	0.7135 ± 0.0017	1.92 ± 0.04	1.01 ± 0.00
0.0543 ± 0.0008	0.4660 ± 0.0049	0.1044 ± 0.0023	364.50	379.4	379.4 ± 0.6	0.0963 ± 0.0022	0.6320 ± 0.0016	2.04 ± 0.05	1.01 ± 0.00
0.0271 ± 0.0005	0.4660 ± 0.0049	0.0551 ± 0.0015	364.51	271.2	271.2 ± 0.5	0.0500 ± 0.0014	0.4790 ± 0.0016	2.17 ± 0.06	1.00 ± 0.00
0.0170 ± 0.0004	0.4660 ± 0.0049	0.0353 ± 0.0011	364.51	226.3	226.1 ± 0.7	0.0318 ± 0.0011	0.3723 ± 0.0022	2.22 ± 0.07	1.00 ± 0.00
0.0069 ± 0.0003	0.4660 ± 0.0049	0.0147 ± 0.0007	364.51	177.8	177.8 ± 1.1	0.0132 ± 0.0007	0.1991 ± 0.0041	2.28 ± 0.07	1.00 ± 0.00
0.0000 ± 0.0000	0.4660 ± 0.0049	0.0000 ± 0.0000	364.51	142.7	142.7 ± 0.4	0.0000 ± 0.0000	0.0000 ± 0.0000	2.33 ± 0.08	1.00 ± 0.00

of the parameters is questionable. In our case, the priority was to obtain parameters that describe the system as well as possible. If one parameter was reduced, the accuracy was approximately a decade worse for the 1-butene + methanol system and 2 times worse for other investigated systems.

For NRTL and UNIQUAC models, the curve of the liquid phase Gibbs energy of mixing against the composition was checked so that no liquid−liquid split occurred with the modeled parameters at the temperature of the experiment. For NRTL parameters, the α-parameter was set to 0.4, because if the parameter was optimized the other parameters started to correlate with this parameter.

The comparison between the predictive methods and experimental results is presented in Table 9. In general, the UNIFAC-Dortmund seems to give more accurate results. In both cases, the predictive methods mainly overestimate the vapor pressure, and the residuals of the pressures were approximately 10 kPa for systems that were closer to ideal (e.g., 1-butene + 2-butanol) and (30 to 100) kPa for nonideal systems (e.g., 1-butene + methanol). An example of the

Table 8. Regressed Activity Coefficient Model Parameters for the Legendre, Wilson, NRTL, and UNIQUAC Models and the 95 % Confidence Limits of the Parameters and Pressure Residuals

	1-butene + methanol		1-butene + 1-propanol		1-butene + 2-propanol		1-butene + 2-butanol		1-butene + 2-methyl-2-propanol	
	value	95 % confidence limit	value	95 % confidence limit	value	95 % confidence limit	value	95 % confidence limit	value	95 % confidence limit
					Legendre					
Legendre $a_{1,0}$	3.01243	0.01316	1.50017	0.01329	1.34787	0.02287	1.16234	0.01748	0.98116	0.02809
Legendre $a_{2,0}$	−0.11204	0.02372	0.28651	0.02054	0.20661	0.03197	0.23122	0.01956	0.18367	0.03660
Legendre $a_{3,0}$	0.23510	0.01879	0.10123	0.01577	0.08027	0.02882	0.07757	0.01992	0.05348	0.03285
Legendre $a_{4,0}$	0.00578	0.01205	0.03100	0.01053	0.01717	0.01908	0.01804	0.01535	0.00813	0.02079
Legendre $a_{5,0}$	0.00430	0.00892	0.00511	0.00842	0.00197	0.00983	0.00393	0.01524	0.00200	0.01298
$\lvert\Delta p\rvert$/kPa	0.6		0.6		0.4		0.4		0.5	
					Wilson					
$\lambda_{2,1}$/K	339.33	26.71	204.36	6.40	198.07	3.70	176.92	4.47	130.66	6.24
$\lambda_{2,1}$/K	1730.59	11.71	1278.65	4.96	1065.66	4.20	930.31	4.58	768.99	6.40
Wilson volume ratio	2.20		1.19		1.17		0.97		0.95	
$\lvert\Delta p\rvert$/kPa	10.6		2.7		2.9		4.6		3.9	
					NRTL					
$\lambda_{2,1}$/K	532.755	4.86469	553.342	7.469	461.315	7.57596	467.744	8.41597	403.739	6.49308
$\lambda_{2,1}$/K	439.066	8.53065	157.878	7.49356	148.587	7.90777	70.7431	8.1917	38.0364	6.11544
$\alpha_{1,2} = \alpha_{2,1}$	0.4		0.4		0.4		0.4		0.4	
$\lvert\Delta p\rvert$/kPa	13.9		9.4		8.3		8.5		6.6	
					UNIQUAC					
$\lambda_{1,2}$/K	570.95	6.60	300.74	7.61	250.53	7.29	98.90	6.77	143.51	4.81
$\lambda_{2,1}$/K	24.87	4.81	−29.20	5.82	−17.42	5.97	50.98	7.25	−1.91	4.49
$\lvert\Delta p\rvert$/kPa	17.9		10.8		9.1		9.2		5.7	

Table 9. Comparison of the Results from Predictive Models and Regressed Measurements Using the Legendre Polynomial Activity Coefficient Model

	1-butene + methanol	1-butene + 1-propanol	1-butene + 2-propanol	1-butene + 2-butanol	1-butene + 2-methyl-2-propanol
			Legendre		
$\lvert\Delta p\rvert$/kPa	0.63	0.58	0.40	0.36	0.51
$\gamma_{\mathrm{inf},1}$	7.87	3.63	3.34	2.70	2.33
$\gamma_{\mathrm{inf},2}$	9.36	6.85	5.23	4.45	3.42
			UNIFAC		
$\lvert\Delta p\rvert$/kPa	101.12	37.98	14.17	13.41	31.27
$\gamma_{\mathrm{inf},1}$	7.06	4.36	3.00	2.29	2.28
$\gamma_{\mathrm{inf},2}$	14.93	7.41	5.72	4.51	4.55
			UNIFAC-Dortmund		
$\lvert\Delta p\rvert$/kPa	29.56	11.67	15.29	17.62	15.13
$\gamma_{\mathrm{inf},1}$	7.26	3.38	2.91	2.40	2.00
$\gamma_{\mathrm{inf},2}$	13.36	7.50	6.03	5.34	4.00
			Literature[a]		
$\gamma_{\mathrm{inf},1}$	7.0				

[a] Miyano et al.[4] at 374.0 K.

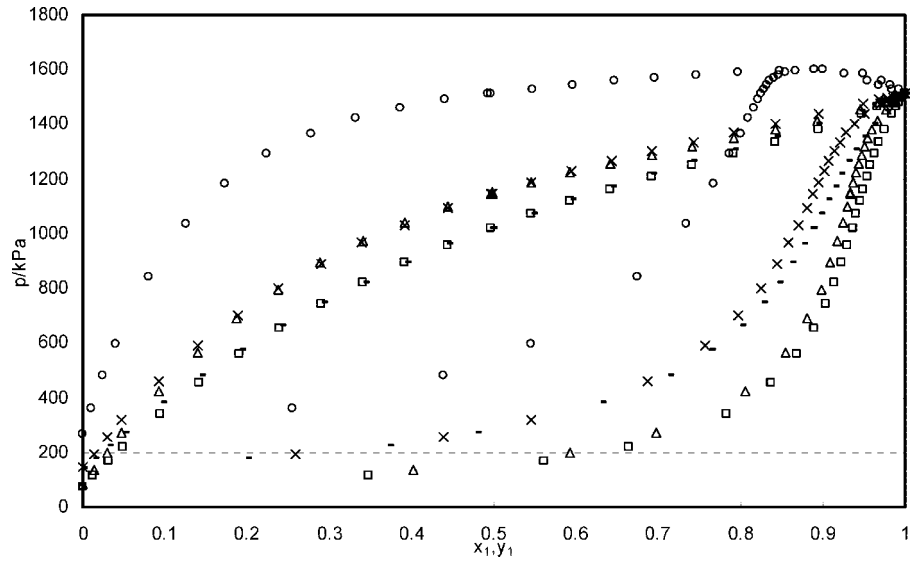

Figure 1. Pressure−composition diagram of the investigated systems. ○, 1-butene + methanol; △, 1-butene + 1-propanol; ×, 1-butene + 2-propanol; □, 1-butene + 2-butanol; −, 1-butene + 2-methyl-2-propanol.

differences is shown in Figure 2. For activity coefficients, the activity coefficient for 1-butene in infinite dilution is underestimated and for alcohols is overestimated.

The literature value in Table 9 for the 1-butene + methanol system presented by Miyano et al. is at a temperature of 374.0 K, and the activity coefficient is somewhat lower than our

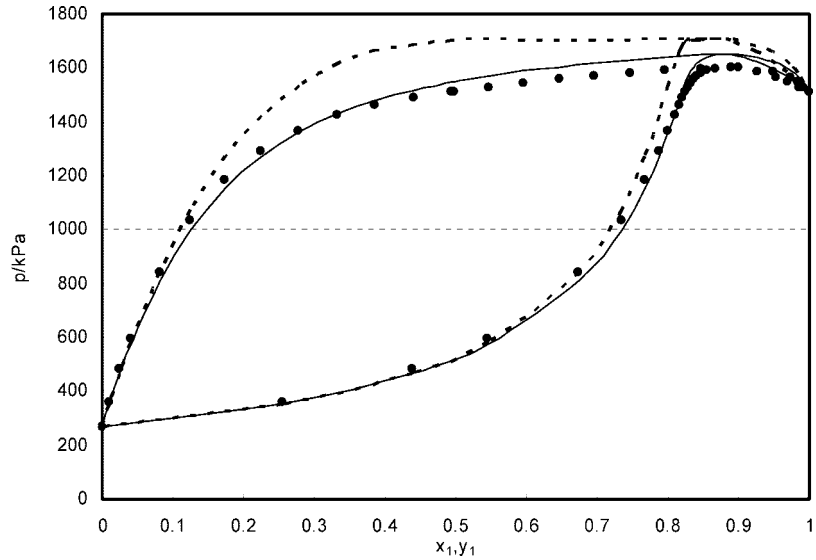

Figure 2. Comparison of the experimental results and predictive models for 1-butene+methanol. ●, experimental; —, UNIFAC-Dortmund; - -, UNIFAC.

Table 10. Calculated and Predicted Azeotropic Compositions for the 1-Butene + Methanol System

	x_1	T/K	p/kPa
Legendre	0.877	364.51	1606.2
UNIFAC	0.846	364.51	1719.8
UNIFAC-Dortmund	0.870	364.51	1656.3

results. However, other results by Miyano et al.[4,23] show that the values of the activity coefficient decrease when the temperature increases, and therefore it can be said that both results are in the same magnitude. For 1-butene+2-propanol and 1-butene + 2-butanol the activity coefficients were found at temperatures from (250 to 300) K.[24,25] For other components, the activity coefficients at infinite dilution were not found in the literature.

From the literature, there was no previous data for the azeotropic point at this temperature. Therefore, the comparison was made only with the Legendre polynomial used as the activity coefficient model and with the predictive methods (Table 10). It can be seen that the azeotropic point is almost at the same composition for each analysis, and only the vapor pressure varies. In general, the results are in good agreement. From Figure 2, the azeotropic behavior in the 1-butene + methanol system can be seen. The azeotropic point is $x_1 = 0.877$, $p_{az} =$ 1606.2 kPa, and $T = 364.51$ K, which is derived from the polynomial fit. In other investigated systems, no azeotropic points were found. Also, Laakkonen et al.[5] determined the azeotropic points with the same compounds at lower temperature, $T = 323$ K. In that case, the azeotropic point was found at higher composition point ($x_1 = 0.93$). This shows that these nonideal systems are highly temperature dependent.

Conclusions

VLE data for five binary mixtures consisting of 1-butene and alcohols were measured with a static total pressure apparatus at $T = 364.5$ K. The results were converted with the Barker method from pTz data to $pTxy$ data. In all cases, the average absolute deviation of measured and calculated pressure was less than 1 kPa. For all systems, the Wilson, NRTL, and UNIQUAC parameters were regressed, and errors for these models are within 20 kPa for the 1-butene + methanol system and within 10 kPa for other systems. The best result came with the Wilson model. The measured data were also compared with predictive UNIFAC and UNIFAC-Dortmund methods. The UNIFAC-Dortmund gives notably better predictions for when the system is more nonideal (1-butene + methanol, 1-butene + 1-propanol, 1-butene + 2-methyl-2-propanol). Otherwise, the differences of the predictions are small.

For these binary pairs, only 1-butene + methanol showed azeotropic behavior at $x_1 = 0.865$, $p_{az} = 1606.2$ kPa, and $T =$ 364.51 K.

Literature Cited

(1) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. Group-contribution estimation of activity coefficients in nonideal liquid mixtures. *AIChE J.* **1975**, *21*, 1086–1099.
(2) Weidlich, U.; Gmehling, J. A modified UNIFAC model. 1. prediction of VLE, h^E, and γ^∞. *Ind. Eng. Chem. Res.* **1987**, *26*, 1372–1381.
(3) Klamt, A.; Eckert, F. COSMO-RS: A novel and efficient method for the a priori prediction of thermophysical data of liquids. *Fluid Phase Equilib.* **2000**, *172*, 43–72.
(4) Miyano, Y.; Fujihara, I.; Sato, K. Henry's law constants of 1-butene, 2-methylpropene, trans-2-butene, and 1,3-butadiene in methanol at 374−490 K. *Fluid Phase Equilib.* **2006**, *247*, 143–148.
(5) Laakkonen, M.; Pokki, J.; Uusi.Kyyny, P.; Aittamaa, J. Vapour-liquid equilibrium for the 1-butene + methanol, + ethanol, + 2-propanol, + 2-butanol and + 2-methyl-2-propanol systems at 326 K. *Fluid Phase Equilib.* **2003**, *206*, 237–252.
(6) Uusi-Kyyny, P.; Pokki, J.; Laakkonen, M.; Aittamaa, J.; Liukkonen, S. Vapor liquid equilibrium for the binary systems 2-methylpentane + 2-butanol at 329.2 K and n-hexane + 2-butanol at 329.2 and 363.2 K with a static apparatus. *Fluid Phase Equilib.* **2002**, *201*, 343–358.
(7) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.
(8) Perry, R. H.; Green, D. W. *Perry's Chemical Engineers' Handbook*; McGraw-Hill: New York, 1997.
(9) Yaws, C. L. *Chemical Properties Handbook*; McGraw-Hill: New York, 1999.
(10) Ouni, T.; Zaytseva, A.; Uusi.Kyyny, P.; Pokki, J.; Aittamaa, J. Vapour-liquid equilibrium for the 2-methylpropane + methanol, +ethanol, +2-propanol, +2-butanol and +2-methyl-2-propanol systems at 313.15 K. *Fluid Phase Equilib.* **2005**, *232*, 90–99.
(11) Barker, J. A. Determination of activity coefficients from total static pressure measurements. *Aust. J. Chem.* **1953**, *6*, 207–210.
(12) Soave, G. Equilibrium constants from modified Redlich-Kwong equation of state. *Chem. Eng. Sci.* **1972**, *27*, 1197–1203.
(13) Rackett, H. G. Equation of state for saturated liquids. *J. Chem. Eng. Data,* **1970**, *15*, 514–517.
(14) Gmehling J.; Onken U. *Vapor−Liquid Equilibrium Data Collection*, DECHEMA Chemistry Data Series: Frankfurt/Main, 1977; Part 1, Vol. 1.
(15) BYU-DIPPR, Project 801. *Evaluated Standard Thermophysical Property Values*; American Institute of Chemical Engineers, Thermophysical Properties Laboratory, Department of Chemical Engineering, Brigham Young University: Provo, Utah, 2005.

(16) Wilson, G. M. Vapor−liquid equilibrium. XI. New expression for the excess free energy of mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127–130.

(17) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135–144.

(18) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J.* **1975**, *21*, 116–128.

(19) Zaytseva, A.; Uusi-Kyyny, P.; Pokki, J.; Pakkanen, M.; Aittamaa, J. Vapor−liquid equilibrium for the trans-2-butene + methanol, + ethanol, + 2-propanol, + 2-butanol, and + 2-methyl-2-propanol systems at 332 K. *J. Chem. Eng. Data* **2004**, *49*, 1168–1174.

(20) Daubert T. E.; Danner R. P. *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation*; Hemisphere: New York, 1989.

(21) Hynynen, K.; Uusi-Kyyny, P.; Pokki, J.; Pakkanen, M.; Aittamaa, J. 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. *J. Chem. Eng. Data* **2006**, *51*, 562–568.

(22) Pokki J. P. *Development of Vapour Liquid Equilibrium Calculation Methods for Chemical Engineering Design, Dissertation, Chemical Engineering Report Series No. 46*; Helsinki University of Technology: Espoo, 2004.

(23) Miyano, Y.; Nakanishi, K.; Fukuchi, K. Henry's constants of butane, isobutane, 1-butene and isobutene in methanol at 255−320 K. *Fluid Phase Equilib.* **2003**, *208*, 223–238.

(24) Miyano, Y. Henry's constants and infinite dilution activity coefficients of propane, propene, butane, isobutane, 1-butene, isobutene, trans-2-butene, and 1,3-butadiene in 1-butanol and 2-butanol from (250 to 330) K. *J. Chem. Eng. Data* **2004**, *49*, 1285–1289.

(25) Miyano, Y. Henry's constants and infinite dilution activity coefficients of propane, propene, butane, isobutane, 1-butene, isobutene, trans-2-butene, and 1,3-butadiene in 2-propanol at 250−330 K. *J. Chem. Eng. Data* **2004**, *49*, 368–371.

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