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Vapor–Liquid Equilibrium for Butane + Methanol, + Ethanol, + 2-Propanol, + 2-Butanol, and + 2-Methyl-2-Propanol (TBA) at 323 K

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Vapor–liquid equilibrium (VLE) data for butane + methanol, + ethanol, + 2-propanol, + 2-butanol, and + 2-methyl-2-propanol (TBA) was measured at 323 K with a static total pressure apparatus. Measured *pTz* (pressure–temperature–total composition) data was reduced to liquid- and vapor-phase compositions using Barker's method. Azeotropic points were found for butane (1) + ethanol ($x_1 = 0.970$; $T = 323.12$ K; $p = 501.1$ kPa) and + methanol ($x_1 = 0.908$; $T = 323.13$ K; $p = 528.2$ kPa). Wilson, NRTL, and UNIQUAC model parameters were calculated. The fitted Legendre polynomial was compared against predictive UNIFAC and UNIFAC–Dortmund models, and an error analysis was made.

Introduction

Vapor–liquid equilibrium (VLE) data is needed for modeling separation processes in various stages of development, design, and optimization of chemical plants. In the absence of experimental results VLE can be predicted using models like UNIFAC[1] and COSMO-RS.[2] These methods have been found to be useful in preliminary stages of process development. However, the accuracy of these predictions is seldom adequate; this is encountered frequently with azeotropic distillations. A good way to achieve accurate results for a certain operating condition is to measure VLE and fit a liquid activity coefficient model against experimental results.

Previously, we have published VLE data[3] for butane + methanol, 2-propanol, 2-butanol, and 2-methyl-2-propanol at 364.5 K; there is no additional VLE data on butane + 2-propanol in the literature. Fischer et al.[4] measured VLE data for both butane + ethanol and + methanol in various temperatures ranging from (273.2 to 373.2) K. VLE for butane + methanol has been measured by Leu et al.[5,6] at (273.2, 323.2, 372.5, and 469.9) K. Kretschmer and Wiebe[7] made a limited amount of VLE measurements from the butane + methanol system. Holderbaum et al.[8] and Deak et al.[9] have published VLE data for butane + ethanol at various temperatures ranging from (298 to 523) K. Dalhoff et al.[10] have measured VLE data for butane + ethanol at 293.2 K. Isobaric VLE data[11] is available for a butane + 2-butanol system. Melpolder has published high-pressure VLE data[12] for butane + 2-methyl-2-propanol at (333, 358, 383, 408, and 433) K. Infinite dilution activity coefficients are available for butane + methanol,[10,13] ethanol,[8,10,4] 2-propanol,[14] 2-butanol,[15] and 2-methyl-2-propanol.[16] In the literature, there are reported azeotropic points for butane + ethanol[8] and methanol[5] near the temperature of 323 K.

Experimental

Materials. Purities and suppliers of used experimental materials are presented in Table 1. The alcohols were dried over Merck 3A molecular sieves for at least 24 h before degassing. The degassing of alcohols was performed by vacuum rectification[17] with modifications.[18] Butane was degassed by evacuation in a syringe pump; the vacuum line was opened 10 times for a 10 s period. The quality of degassing was checked by comparing measured vapor pressures against correlations from the literature (Table 2). In this article, butane is always addressed as component (1) and the alcohol as component (2).

Table 1. Component, Supplier, and Component Purity (wt %)

component	supplier	purity
butane	AGA Oy	99.95
methanol	Merck	99.80
ethanol	Primalco Oy	> 99.5
2-propanol	Riedel-de Haën	99.80
2-butanol	Fluka	> 99.8
2-methyl-2-propanol	Fluka	> 99.7

Table 2. Measured Pure Component Vapor Pressures (p_i) vs Literature Correlations

		(p_i)/kPa			
component	T/K	this work	ref 31	ref 32	ref 24
butane	323.15	495.7	497.2	496.6	496.5
	323.15	495.6	497.2	496.6	496.5
	323.12	495.0	496.8	496.3	496.1
	323.13	495.3	496.9	496.4	496.2
	323.15	495.7	497.2	496.6	496.5
methanol	323.13	55.5	55.6	55.4	55.6
ethanol	323.14	29.4	29.5	29.4	29.6
2-propanol	323.19	23.6	23.8	24.1	24.1
2-butanol	323.17	10.7	10.7	11.0	11.1
2-methyl-2-propanol	323.20	23.8	23.7	23.6	23.8

Apparatus and Procedure. Details of the static total pressure device and procedure were presented in Uusi-Kyyny et al.[19] The pressure transducer was replaced by Digiquartz 31K-165-HT-CE which has a suitable pressure range [(0 to 6.9) MPa]. Stability of the water bath was ± 0.02 K. For each data point, the apparatus records the value of temperature (T) of the cell and the syringe pumps, the cell equilibrium pressure (p), and the volume of components injected to the equilibrium cell (V_1, V_2). The volume of the cell was 113.66 cm^3. The amount of moles injected to the cell and the total composition (z) was then computed. The liquid and vapor mole fractions (x,y) was calculated based on total pressure measurements through data reduction.

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Table 3. Pure Component Physical Properties: Critical Temperature T_c, Critical Pressure p_c, Acentric Factor ω, Wilson Volume Ratio V, UNIQUAC and UNIFAC/UNIFAC–Dortmund Volume R, and Area Q Parameters[a]

	T_c^b/K	p_c^b/MPa	ω^b	V^b/cm^3·mol^{-1}	$R_{UQ\&UF}^c$	$R_{UF(Dort)}^d$	$Q_{UQ\&UF}^c$	$Q_{UF(Dort)}^d$
butane	425.18 ± 4.25	3.7969 ± 0.1898	0.1993	100.4	3.151	2.53	2.776	3.5378
methanol	512.58 ± 5.12	8.0959 ± 0.2429	0.5656	40.73	1.4311	0.8585	1.432	0.9938
ethanol	516.25 ± 5.16	6.3835 ± 0.1915	0.6371	58.68	2.5755	2.4952	2.588	2.6616
2-propanol	508.31 ± 5.08	4.7643 ± 0.1429	0.6689	76.92	3.2491	2.9605	3.124	3.32344
2-butanol	536.01 ± 5.36	4.1938 ± 0.1258	0.5711	92.35	3.9235	3.593	3.664	4.03154
2-methyl-2-propanol	506.20 ± 5.06	3.9719 ± 0.1192	0.6158	94.88	3.9228	4.4497	3.744	4.9096

[a] The given errors were calculated from the maximum error percent estimated by the authors of the database. [b] Reference 33. [c] Reference 31. [d] Reference 34.

Table 4. VLE Data for Butane (1) + Methanol (2) at 323.15 K[a]

n_1/mol	n_2/mol	z_1	T/K	p_{exp}/kPa	p_{leg}/kPa	x_1	y_1	γ_1	γ_2
0.5639 ± 0.0061	0.0000 ± 0.0000	1.0000 ± 0.0000	323.13	495.3	495.3 ± 0.7	1.000 ± 0.0000	1.000 ± 0.0000	1.00 ± 0.00	31.36 ± 8.30
0.5639 ± 0.0061	0.0079 ± 0.0006	0.9862 ± 0.0010	323.13	517.4	512.5 ± 3.4	0.987 ± 0.0011	0.961 ± 0.0053	1.00 ± 0.00	24.22 ± 4.56
0.5639 ± 0.0061	0.0153 ± 0.0006	0.9736 ± 0.0011	323.13	524.3	520.5 ± 4.0	0.974 ± 0.0012	0.940 ± 0.0054	1.01 ± 0.00	19.51 ± 2.40
0.5639 ± 0.0061	0.0279 ± 0.0008	0.9529 ± 0.0012	323.13	527.6	526.2 ± 3.5	0.954 ± 0.0013	0.921 ± 0.0023	1.02 ± 0.00	14.28 ± 0.73
0.5639 ± 0.0061	0.0597 ± 0.0011	0.9043 ± 0.0016	323.13	528.2	528.4 ± 2.8	0.904 ± 0.0016	0.907 ± 0.0032	1.06 ± 0.01	8.19 ± 0.22
0.5639 ± 0.0061	0.0966 ± 0.0015	0.8537 ± 0.0019	323.13	527.3	527.8 ± 2.8	0.853 ± 0.0019	0.903 ± 0.0038	1.12 ± 0.01	5.53 ± 0.18
0.5639 ± 0.0061	0.1373 ± 0.0019	0.8042 ± 0.0022	323.13	526.1	526.7 ± 2.0	0.803 ± 0.0022	0.901 ± 0.0026	1.18 ± 0.01	4.21 ± 0.08
0.5639 ± 0.0061	0.1841 ± 0.0024	0.7538 ± 0.0024	323.13	525.0	525.4 ± 1.0	0.752 ± 0.0024	0.900 ± 0.0014	1.26 ± 0.00	3.39 ± 0.02
0.5639 ± 0.0061	0.2376 ± 0.0029	0.7035 ± 0.0026	323.14	524.0	524.0 ± 0.8	0.701 ± 0.0026	0.898 ± 0.0012	1.35 ± 0.01	2.85 ± 0.02
0.5639 ± 0.0061	0.2980 ± 0.0035	0.6542 ± 0.0027	323.14	523.1	522.8 ± 0.9	0.652 ± 0.0027	0.897 ± 0.0012	1.44 ± 0.01	2.46 ± 0.02
0.5639 ± 0.0061	0.3695 ± 0.0043	0.6041 ± 0.0028	323.15	522.1	521.9 ± 0.8	0.601 ± 0.0028	0.897 ± 0.0012	1.56 ± 0.01	2.16 ± 0.02
0.5639 ± 0.0061	0.4546 ± 0.0051	0.5537 ± 0.0028	323.15	520.9	520.9 ± 0.7	0.551 ± 0.0028	0.896 ± 0.0012	1.70 ± 0.01	1.92 ± 0.01
0.5639 ± 0.0061	0.5559 ± 0.0061	0.5035 ± 0.0028	323.15	519.6	519.8 ± 0.7	0.501 ± 0.0028	0.896 ± 0.0012	1.86 ± 0.01	1.73 ± 0.01
0.5639 ± 0.0061	0.6783 ± 0.0074	0.4540 ± 0.0027	323.15	517.7	518.0 ± 0.8	0.452 ± 0.0027	0.895 ± 0.0012	2.06 ± 0.01	1.58 ± 0.01
0.5639 ± 0.0061	0.8343 ± 0.0090	0.4033 ± 0.0026	323.15	515.0	515.4 ± 0.7	0.402 ± 0.0027	0.894 ± 0.0012	2.30 ± 0.02	1.46 ± 0.00
0.5639 ± 0.0061	1.0661 ± 0.0113	0.3460 ± 0.0024	323.14	510.5	510.5 ± 0.8	0.345 ± 0.0025	0.893 ± 0.0012	2.65 ± 0.02	1.34 ± 0.00
0.5214 ± 0.0056	0.7831 ± 0.0085	0.3997 ± 0.0026	323.13	514.9	514.8 ± 0.7	0.398 ± 0.0027	0.894 ± 0.0012	2.33 ± 0.02	1.45 ± 0.00
0.4206 ± 0.0046	0.7831 ± 0.0085	0.3494 ± 0.0025	323.14	510.6	510.6 ± 0.8	0.346 ± 0.0026	0.893 ± 0.0012	2.65 ± 0.02	1.34 ± 0.00
0.3350 ± 0.0037	0.7831 ± 0.0085	0.2996 ± 0.0023	323.13	503.7	503.6 ± 0.8	0.295 ± 0.0024	0.891 ± 0.0012	3.07 ± 0.03	1.25 ± 0.00
0.2603 ± 0.0029	0.7831 ± 0.0085	0.2495 ± 0.0021	323.13	492.0	492.0 ± 0.8	0.243 ± 0.0022	0.888 ± 0.0012	3.64 ± 0.03	1.17 ± 0.00
0.1951 ± 0.0022	0.7831 ± 0.0085	0.1994 ± 0.0018	323.14	471.4	471.6 ± 0.8	0.191 ± 0.0019	0.882 ± 0.0013	4.43 ± 0.04	1.11 ± 0.00
0.1377 ± 0.0016	0.7831 ± 0.0085	0.1495 ± 0.0015	323.14	434.5	434.6 ± 0.8	0.140 ± 0.0016	0.871 ± 0.0014	5.55 ± 0.06	1.06 ± 0.00
0.0874 ± 0.0011	0.7831 ± 0.0085	0.1004 ± 0.0011	323.14	369.2	368.9 ± 0.7	0.091 ± 0.0012	0.847 ± 0.0017	7.17 ± 0.09	1.03 ± 0.00
0.0429 ± 0.0006	0.7831 ± 0.0085	0.0520 ± 0.0007	323.14	256.5	256.5 ± 0.7	0.045 ± 0.0008	0.780 ± 0.0022	9.56 ± 0.17	1.01 ± 0.00
0.0259 ± 0.0005	0.7831 ± 0.0085	0.0320 ± 0.0006	323.14	190.9	190.9 ± 0.7	0.027 ± 0.0006	0.706 ± 0.0026	10.86 ± 0.22	1.00 ± 0.00
0.0000 ± 0.0000	0.7831 ± 0.0085	0.0000 ± 0.0000	323.13	55.5	55.5 ± 0.7	0.000 ± 0.0000	0.000 ± 0.0000	13.48 ± 0.31	1.00 ± 0.00

[a] T is the experimental temperature; n_1 and n_2 are the moles of components injected into the equilibrium cell; z_1 is the total mole fraction; x_1 and y_1 are the calculated mole fractions in the liquid and vapor phases, respectively; the experimental pressure is p_{exp}, and the pressure calculated from the Legendre-polynomial fit is p_{leg}; γ_1 and γ_2 are the calculated activity coefficients.

Table 5. VLE Data for Butane (1) + Ethanol (2) at 323.15 K[a]

n_1/mol	n_2/mol	z_1	T/K	p_{exp}/kPa	p_{leg}/kPa	x_1	y_1	γ_1	γ_2
0.6227 ± 0.0067	0.0000 ± 0.0000	1.0000 ± 0.0000	323.12	495.0	495.0 ± 0.7	1.000 ± 0.0000	1.000 ± 0.0000	1.00 ± 0.00	25.72 ± 4.94
0.6227 ± 0.0067	0.0053 ± 0.0004	0.9916 ± 0.0006	323.12	499.0	497.9 ± 1.0	0.992 ± 0.0006	0.988 ± 0.0016	1.00 ± 0.00	21.81 ± 3.54
0.6227 ± 0.0067	0.0176 ± 0.0005	0.9725 ± 0.0008	323.12	501.1	500.0 ± 1.7	0.973 ± 0.0008	0.971 ± 0.0023	1.01 ± 0.00	15.59 ± 1.58
0.6227 ± 0.0067	0.0292 ± 0.0006	0.9552 ± 0.0009	323.12	500.6	499.6 ± 1.9	0.955 ± 0.0009	0.964 ± 0.0016	1.02 ± 0.00	11.97 ± 0.72
0.6227 ± 0.0067	0.0671 ± 0.0010	0.9028 ± 0.0013	323.12	497.0	497.0 ± 2.8	0.902 ± 0.0014	0.956 ± 0.0012	1.06 ± 0.01	6.54 ± 0.07
0.6227 ± 0.0067	0.1094 ± 0.0015	0.8506 ± 0.0017	323.12	493.3	494.9 ± 3.4	0.849 ± 0.0017	0.955 ± 0.0020	1.12 ± 0.01	4.41 ± 0.10
0.6227 ± 0.0067	0.1523 ± 0.0019	0.8035 ± 0.0020	323.12	490.0	492.5 ± 3.2	0.802 ± 0.0020	0.953 ± 0.0019	1.18 ± 0.01	3.44 ± 0.07
0.6227 ± 0.0067	0.2052 ± 0.0024	0.7522 ± 0.0022	323.12	486.4	488.7 ± 2.3	0.750 ± 0.0022	0.952 ± 0.0015	1.25 ± 0.01	2.81 ± 0.04
0.6227 ± 0.0067	0.2639 ± 0.0030	0.7024 ± 0.0024	323.12	483.0	484.2 ± 1.5	0.701 ± 0.0024	0.950 ± 0.0012	1.33 ± 0.01	2.41 ± 0.02
0.6227 ± 0.0067	0.3339 ± 0.0037	0.6510 ± 0.0025	323.12	479.2	479.2 ± 1.0	0.649 ± 0.0025	0.948 ± 0.0011	1.42 ± 0.01	2.10 ± 0.01
0.6227 ± 0.0067	0.4153 ± 0.0046	0.5999 ± 0.0026	323.12	475.1	474.4 ± 1.0	0.599 ± 0.0027	0.947 ± 0.0011	1.52 ± 0.01	1.87 ± 0.01
0.6227 ± 0.0067	0.5078 ± 0.0055	0.5509 ± 0.0027	323.12	470.5	469.8 ± 0.9	0.550 ± 0.0027	0.946 ± 0.0012	1.64 ± 0.01	1.69 ± 0.01
0.6227 ± 0.0067	0.6228 ± 0.0067	0.5000 ± 0.0027	323.12	464.7	464.4 ± 0.7	0.499 ± 0.0027	0.944 ± 0.0012	1.79 ± 0.01	1.54 ± 0.00
0.6671 ± 0.0072	0.5491 ± 0.0059	0.5485 ± 0.0027	323.12	470.4	469.6 ± 0.9	0.548 ± 0.0027	0.946 ± 0.0012	1.65 ± 0.01	1.68 ± 0.01
0.5311 ± 0.0057	0.5491 ± 0.0059	0.4917 ± 0.0027	323.12	463.3	463.2 ± 0.7	0.490 ± 0.0028	0.944 ± 0.0012	1.82 ± 0.01	1.51 ± 0.00
0.4397 ± 0.0048	0.5491 ± 0.0059	0.4447 ± 0.0027	323.13	455.9	456.4 ± 0.6	0.441 ± 0.0028	0.943 ± 0.0013	1.99 ± 0.01	1.40 ± 0.00
0.3607 ± 0.0040	0.5491 ± 0.0059	0.3965 ± 0.0026	323.13	445.8	446.5 ± 0.7	0.392 ± 0.0027	0.941 ± 0.0014	2.19 ± 0.02	1.31 ± 0.00
0.2918 ± 0.0032	0.5491 ± 0.0059	0.3471 ± 0.0025	323.14	432.1	432.4 ± 0.6	0.341 ± 0.0026	0.938 ± 0.0014	2.44 ± 0.02	1.23 ± 0.00
0.2329 ± 0.0026	0.5491 ± 0.0059	0.2979 ± 0.0024	323.14	413.3	412.9 ± 0.7	0.290 ± 0.0025	0.934 ± 0.0015	2.74 ± 0.02	1.16 ± 0.00
0.1776 ± 0.0021	0.5491 ± 0.0059	0.2444 ± 0.0021	323.14	384.8	383.8 ± 0.8	0.235 ± 0.0022	0.928 ± 0.0016	3.15 ± 0.03	1.11 ± 0.00
0.1366 ± 0.0016	0.5491 ± 0.0059	0.1993 ± 0.0019	323.14	351.8	351.0 ± 0.8	0.189 ± 0.0020	0.920 ± 0.0017	3.58 ± 0.04	1.07 ± 0.00
0.0978 ± 0.0012	0.5491 ± 0.0059	0.1512 ± 0.0016	323.14	304.4	304.4 ± 0.7	0.141 ± 0.0017	0.907 ± 0.0020	4.15 ± 0.05	1.04 ± 0.00
0.0636 ± 0.0009	0.5491 ± 0.0059	0.1038 ± 0.0013	323.14	241.8	242.3 ± 0.6	0.095 ± 0.0013	0.881 ± 0.0026	4.86 ± 0.07	1.02 ± 0.00
0.0312 ± 0.0005	0.5491 ± 0.0059	0.0537 ± 0.0009	323.14	153.8	153.8 ± 0.7	0.048 ± 0.0009	0.811 ± 0.0038	5.77 ± 0.11	1.00 ± 0.00
0.0189 ± 0.0004	0.5491 ± 0.0059	0.0333 ± 0.0007	323.14	110.7	110.0 ± 0.7	0.029 ± 0.0007	0.734 ± 0.0046	6.18 ± 0.14	1.00 ± 0.00
0.0000 ± 0.0000	0.5491 ± 0.0059	0.0000 ± 0.0000	323.14	29.4	29.4 ± 0.7	0.000 ± 0.0000	0.000 ± 0.0000	6.87 ± 0.21	1.00 ± 0.00

[a] T is the experimental temperature; n_1 and n_2 are the moles of components injected into the equilibrium cell; z_1 is the total mole fraction; x_1 and y_1 are the calculated mole fractions in the liquid and vapor phases, respectively; the experimental pressure is p_{exp}, and the pressure calculated from the Legendre-polynomial fit is p_{leg}; γ_1 and γ_2 are the calculated activity coefficients.

Each binary pair measurement was done by approaching the equimolar composition from each end of the composition scale. If the pressure curves intercepted, the measurement was considered successful. The vapor volume in the cell was kept to a minimum to improve the accuracy of experiments. The measurements were started from pure component 1, and

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

n_1/mol	n_2/mol	z_1	T/K	p_{exp}/kPa	p_{leg}/kPa	x_1	y_1	γ_1	γ_2
0.5644 ± 0.0061	0.0000 ± 0.0000	1.0000 ± 0.0000	323.15	495.6	495.6 ± 0.7	1.000 ± 0.0000	1.000 ± 0.0000	1.00 ± 0.00	13.21 ± 2.61
0.5644 ± 0.0061	0.0078 ± 0.0003	0.9863 ± 0.0006	323.15	494.7	493.6 ± 1.1	0.986 ± 0.0006	0.991 ± 0.0012	1.00 ± 0.00	11.15 ± 1.65
0.5644 ± 0.0061	0.0193 ± 0.0005	0.9670 ± 0.0008	323.15	492.5	490.2 ± 1.5	0.967 ± 0.0008	0.983 ± 0.0015	1.01 ± 0.00	8.96 ± 0.84
0.5644 ± 0.0061	0.0318 ± 0.0006	0.9467 ± 0.0009	323.14	489.9	486.6 ± 1.9	0.946 ± 0.0010	0.977 ± 0.0013	1.02 ± 0.00	7.30 ± 0.41
0.5644 ± 0.0061	0.0640 ± 0.0009	0.8982 ± 0.0013	323.15	483.7	479.7 ± 2.8	0.897 ± 0.0013	0.971 ± 0.0007	1.05 ± 0.01	4.89 ± 0.05
0.5644 ± 0.0061	0.1005 ± 0.0013	0.8489 ± 0.0017	323.15	477.3	474.4 ± 3.7	0.847 ± 0.0017	0.968 ± 0.0012	1.10 ± 0.01	3.61 ± 0.05
0.5644 ± 0.0061	0.1417 ± 0.0017	0.7994 ± 0.0019	323.15	470.6	469.4 ± 4.1	0.797 ± 0.0020	0.966 ± 0.0014	1.15 ± 0.01	2.86 ± 0.05
0.5644 ± 0.0061	0.1879 ± 0.0022	0.7502 ± 0.0022	323.15	463.7	464.0 ± 3.8	0.748 ± 0.0022	0.964 ± 0.0014	1.22 ± 0.01	2.39 ± 0.04
0.5644 ± 0.0061	0.2411 ± 0.0027	0.7007 ± 0.0024	323.16	456.5	457.6 ± 3.0	0.699 ± 0.0024	0.962 ± 0.0014	1.28 ± 0.01	2.07 ± 0.03
0.5644 ± 0.0061	0.3027 ± 0.0034	0.6509 ± 0.0025	323.16	448.8	449.9 ± 2.0	0.649 ± 0.0025	0.960 ± 0.0013	1.36 ± 0.01	1.84 ± 0.01
0.5644 ± 0.0061	0.3740 ± 0.0041	0.6014 ± 0.0026	323.16	440.6	441.3 ± 1.1	0.600 ± 0.0027	0.958 ± 0.0013	1.44 ± 0.01	1.67 ± 0.01
0.5644 ± 0.0061	0.4598 ± 0.0050	0.5511 ± 0.0027	323.17	431.4	431.5 ± 0.7	0.550 ± 0.0027	0.956 ± 0.0012	1.54 ± 0.01	1.53 ± 0.00
0.5644 ± 0.0061	0.5617 ± 0.0061	0.5012 ± 0.0027	323.17	421.0	420.6 ± 1.0	0.501 ± 0.0028	0.954 ± 0.0012	1.65 ± 0.01	1.42 ± 0.00
0.4957 ± 0.0054	0.5000 ± 0.0054	0.4978 ± 0.0027	323.18	420.3	419.7 ± 1.0	0.496 ± 0.0028	0.954 ± 0.0012	1.66 ± 0.01	1.41 ± 0.00
0.4062 ± 0.0044	0.5000 ± 0.0054	0.4483 ± 0.0027	323.18	407.3	406.7 ± 1.0	0.445 ± 0.0028	0.951 ± 0.0013	1.79 ± 0.01	1.31 ± 0.00
0.3305 ± 0.0036	0.5000 ± 0.0054	0.3979 ± 0.0026	323.18	391.4	391.1 ± 0.8	0.394 ± 0.0027	0.948 ± 0.0014	1.95 ± 0.01	1.24 ± 0.00
0.2677 ± 0.0030	0.5000 ± 0.0054	0.3487 ± 0.0025	323.19	372.3	372.5 ± 0.8	0.343 ± 0.0026	0.944 ± 0.0016	2.13 ± 0.02	1.17 ± 0.00
0.2134 ± 0.0024	0.5000 ± 0.0054	0.2991 ± 0.0024	323.19	348.5	348.9 ± 0.9	0.293 ± 0.0025	0.939 ± 0.0017	2.35 ± 0.02	1.12 ± 0.00
0.1656 ± 0.0019	0.5000 ± 0.0054	0.2488 ± 0.0022	323.19	318.3	318.6 ± 0.9	0.241 ± 0.0022	0.932 ± 0.0020	2.60 ± 0.02	1.08 ± 0.00
0.1249 ± 0.0015	0.5000 ± 0.0054	0.1999 ± 0.0019	323.19	281.6	281.6 ± 0.7	0.192 ± 0.0020	0.922 ± 0.0022	2.88 ± 0.03	1.05 ± 0.00
0.0906 ± 0.0011	0.5000 ± 0.0054	0.1534 ± 0.0016	323.19	238.6	238.1 ± 0.8	0.146 ± 0.0017	0.906 ± 0.0025	3.19 ± 0.04	1.03 ± 0.00
0.0560 ± 0.0008	0.5000 ± 0.0054	0.1007 ± 0.0013	323.19	178.4	177.9 ± 0.9	0.094 ± 0.0013	0.871 ± 0.0032	3.61 ± 0.06	1.01 ± 0.00
0.0277 ± 0.0005	0.5000 ± 0.0054	0.0525 ± 0.0009	323.19	111.2	111.3 ± 0.8	0.048 ± 0.0009	0.791 ± 0.0047	4.06 ± 0.08	1.00 ± 0.00
0.0173 ± 0.0004	0.5000 ± 0.0054	0.0335 ± 0.0007	323.19	81.5	81.5 ± 0.7	0.031 ± 0.0007	0.713 ± 0.0059	4.27 ± 0.09	1.00 ± 0.00
0.0000 ± 0.0000	0.5000 ± 0.0054	0.0000 ± 0.0000	323.19	23.6	23.6 ± 0.7	0.000 ± 0.0000	0.000 ± 0.0000	4.68 ± 0.12	1.00 ± 0.00

[a] T is the experimental temperature; n_1 and n_2 are the moles of components injected into the equilibrium cell; z_1 is the total mole fraction; x_1 and y_1 are the calculated mole fractions in the liquid and vapor phases, respectively; the experimental pressure is p_{exp}, and the pressure calculated from the Legendre-polynomial fit is p_{leg}; γ_1 and γ_2 are the calculated activity coefficients.

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

n_1/mol	n_2/mol	z_1	T/K	p_{exp}/kPa	p_{leg}/kPa	x_1	y_1	γ_1	γ_2
0.5143 ± 0.0056	0.0000 ± 0.0000	1.0000 ± 0.0000	323.15	495.7	495.7 ± 0.7	1.000 ± 0.0000	1.000 ± 0.0000	1.00 ± 0.00	11.17 ± 1.49
0.5143 ± 0.0056	0.0050 ± 0.0003	0.9904 ± 0.0005	323.15	491.9	492.0 ± 0.8	0.990 ± 0.0005	0.997 ± 0.0003	1.00 ± 0.00	9.86 ± 1.03
0.5143 ± 0.0056	0.0164 ± 0.0004	0.9690 ± 0.0007	323.15	485.8	484.9 ± 1.1	0.969 ± 0.0007	0.993 ± 0.0006	1.01 ± 0.00	7.68 ± 0.43
0.5143 ± 0.0056	0.0276 ± 0.0005	0.9491 ± 0.0009	323.15	481.6	479.5 ± 1.6	0.948 ± 0.0009	0.991 ± 0.0006	1.01 ± 0.00	6.27 ± 0.17
0.5143 ± 0.0056	0.0574 ± 0.0008	0.8996 ± 0.0013	323.15	472.5	469.6 ± 2.6	0.898 ± 0.0013	0.988 ± 0.0007	1.05 ± 0.01	4.19 ± 0.05
0.5143 ± 0.0056	0.0907 ± 0.0012	0.8501 ± 0.0016	323.15	463.9	462.1 ± 3.1	0.848 ± 0.0016	0.986 ± 0.0008	1.09 ± 0.01	3.13 ± 0.06
0.5143 ± 0.0056	0.1282 ± 0.0015	0.8005 ± 0.0019	323.16	455.2	454.9 ± 2.8	0.798 ± 0.0019	0.985 ± 0.0009	1.15 ± 0.01	2.53 ± 0.04
0.5143 ± 0.0056	0.1704 ± 0.0020	0.7511 ± 0.0022	323.16	446.2	446.9 ± 2.0	0.748 ± 0.0022	0.984 ± 0.0009	1.20 ± 0.01	2.15 ± 0.02
0.5143 ± 0.0056	0.2191 ± 0.0025	0.7012 ± 0.0024	323.17	436.6	437.7 ± 1.3	0.699 ± 0.0023	0.983 ± 0.0010	1.26 ± 0.00	1.89 ± 0.01
0.5143 ± 0.0056	0.2750 ± 0.0030	0.6516 ± 0.0025	323.17	426.5	427.2 ± 0.9	0.649 ± 0.0025	0.982 ± 0.0011	1.33 ± 0.01	1.70 ± 0.00
0.5143 ± 0.0056	0.3404 ± 0.0037	0.6017 ± 0.0026	323.17	415.5	415.6 ± 0.8	0.600 ± 0.0026	0.981 ± 0.0012	1.40 ± 0.01	1.55 ± 0.00
0.5143 ± 0.0056	0.4175 ± 0.0045	0.5519 ± 0.0027	323.18	403.4	403.1 ± 0.7	0.551 ± 0.0027	0.980 ± 0.0013	1.48 ± 0.01	1.44 ± 0.00
0.5143 ± 0.0056	0.4583 ± 0.0049	0.5288 ± 0.0027	323.18	397.3	396.8 ± 0.7	0.528 ± 0.0027	0.979 ± 0.0014	1.52 ± 0.01	1.39 ± 0.00
0.4270 ± 0.0047	0.4362 ± 0.0047	0.4947 ± 0.0027	323.22	387.0	386.9 ± 0.7	0.492 ± 0.0028	0.978 ± 0.0014	1.59 ± 0.01	1.33 ± 0.00
0.3578 ± 0.0039	0.4362 ± 0.0047	0.4506 ± 0.0027	323.21	372.5	372.3 ± 0.7	0.447 ± 0.0028	0.976 ± 0.0015	1.69 ± 0.01	1.26 ± 0.00
0.2886 ± 0.0032	0.4362 ± 0.0047	0.3982 ± 0.0026	323.21	352.5	352.4 ± 0.8	0.393 ± 0.0027	0.974 ± 0.0016	1.83 ± 0.01	1.19 ± 0.00
0.2390 ± 0.0027	0.4362 ± 0.0047	0.3540 ± 0.0025	323.20	332.9	332.9 ± 0.8	0.348 ± 0.0026	0.972 ± 0.0017	1.95 ± 0.02	1.15 ± 0.00
0.1906 ± 0.0022	0.4362 ± 0.0047	0.3041 ± 0.0024	323.20	306.8	306.8 ± 0.7	0.297 ± 0.0025	0.969 ± 0.0019	2.12 ± 0.02	1.10 ± 0.00
0.1513 ± 0.0018	0.4362 ± 0.0047	0.2575 ± 0.0022	323.20	278.1	278.1 ± 0.7	0.250 ± 0.0023	0.965 ± 0.0022	2.29 ± 0.02	1.07 ± 0.00
0.1125 ± 0.0014	0.4362 ± 0.0047	0.2050 ± 0.0020	323.18	239.7	239.4 ± 0.7	0.197 ± 0.0020	0.959 ± 0.0026	2.51 ± 0.03	1.04 ± 0.00
0.0820 ± 0.0011	0.4362 ± 0.0047	0.1583 ± 0.0017	323.18	199.2	198.9 ± 0.7	0.151 ± 0.0017	0.949 ± 0.0031	2.73 ± 0.03	1.03 ± 0.00
0.0528 ± 0.0007	0.4362 ± 0.0047	0.1081 ± 0.0014	323.17	148.5	148.2 ± 0.7	0.102 ± 0.0014	0.930 ± 0.0042	3.00 ± 0.04	1.01 ± 0.00
0.0328 ± 0.0005	0.4362 ± 0.0047	0.0700 ± 0.0011	323.16	104.6	104.6 ± 0.7	0.065 ± 0.0011	0.900 ± 0.0059	3.22 ± 0.06	1.00 ± 0.00
0.0132 ± 0.0003	0.4362 ± 0.0047	0.0293 ± 0.0007	323.16	52.0	52.2 ± 0.7	0.027 ± 0.0007	0.797 ± 0.0109	3.50 ± 0.09	1.00 ± 0.00
0.0000 ± 0.0000	0.4362 ± 0.0047	0.0000 ± 0.0000	323.17	10.7	10.7 ± 0.7	0.000 ± 0.0000	0.000 ± 0.0000	3.72 ± 0.14	1.00 ± 0.00

[a] T is the experimental temperature; n_1 and n_2 are the moles of components injected into the equilibrium cell; z_1 is the total mole fraction; x_1 and y_1 are the calculated mole fractions in the liquid and vapor phases, respectively; the experimental pressure is p_{exp}, and the pressure calculated from the Legendre-polynomial fit is p_{leg}; γ_1 and γ_2 are the calculated activity coefficients.

then, a predetermined amount of component 2 was added. The cell was continuously mixed and monitored until the pressure stabilized; then, another dose of component 2 was added. The procedure was repeated until equimolar concentration was reached. The cell was then emptied and vacuumed. Then, the procedure was repeated starting with pure component 2 where component 1 was added in a similar manner as described above. It took approximately 35 min to achieve equilibrium after the addition of a component.

Data Reduction. The compositions of the vapor and liquid phases were calculated from the total pressure data with Barker's method[20] using VLEFIT[21] software. Barker's method is based on the least-squares method and calculates the activity coefficients for a solution from total pressure measurements. The basic equation for VLE is

$$\frac{y_i}{x_i} = \frac{\gamma_i \varphi_i^{s} p_i^{s}}{\varphi_i p} \exp \int_{p_i^{s}}^{p} \frac{V_i^{L}}{RT}\, dp \qquad (1)$$

The measured data was reduced by Legendre polynomials[22] as the liquid activity coefficient model and the cubic SRK[23] (Soave–Redlich–Kwong) equation of state; the binary interaction parameters were set at 0. The scheme of data reduction is reported at detail in Uusi-Kyyny et al.[19] Critical properties, acentric factor, Wilson volume ratio, and UNIFAC/UNIQUAC parameters for pure components used in data reduction and model fitting are presented in Table 3.

Table 8. VLE Data for Butane (1) + TBA (2) at 323.15 K[a]

n_1/mol	n_2/mol	z_1	T/K	p_{exp}/kPa	p_{leg}/kPa	x_1	y_1	γ_1	γ_2
0.5111 ± 0.0055	0.0000 ± 0.0000	1.0000 ± 0.0000	323.15	495.7	495.7 ± 0.7	1.000 ± 0.0000	1.000 ± 0.0000	1.00 ± 0.00	10.28 ± 9.10
0.5111 ± 0.0055	0.0058 ± 0.0003	0.9888 ± 0.0005	323.15	493.0	493.1 ± 2.0	0.989 ± 0.0005	0.994 ± 0.0032	1.00 ± 0.00	8.67 ± 5.31
0.5111 ± 0.0055	0.0159 ± 0.0004	0.9699 ± 0.0007	323.17	488.8	489.0 ± 3.3	0.970 ± 0.0007	0.988 ± 0.0034	1.01 ± 0.00	6.72 ± 2.15
0.5111 ± 0.0055	0.0271 ± 0.0005	0.9496 ± 0.0009	323.17	484.8	484.8 ± 4.4	0.949 ± 0.0009	0.984 ± 0.0021	1.02 ± 0.01	5.34 ± 0.82
0.5111 ± 0.0055	0.0563 ± 0.0008	0.9008 ± 0.0012	323.17	475.5	476.4 ± 7.9	0.899 ± 0.0013	0.979 ± 0.0011	1.05 ± 0.02	3.52 ± 0.05
0.5111 ± 0.0055	0.0896 ± 0.0011	0.8508 ± 0.0016	323.18	466.0	468.4 ± 10.4	0.849 ± 0.0016	0.975 ± 0.0023	1.09 ± 0.03	2.66 ± 0.14
0.5111 ± 0.0055	0.1274 ± 0.0015	0.8005 ± 0.0019	323.19	456.1	459.1 ± 9.9	0.798 ± 0.0019	0.972 ± 0.0026	1.14 ± 0.03	2.19 ± 0.12
0.5111 ± 0.0055	0.1708 ± 0.0020	0.7495 ± 0.0021	323.19	445.3	447.9 ± 7.5	0.747 ± 0.0021	0.969 ± 0.0023	1.19 ± 0.02	1.91 ± 0.07
0.5111 ± 0.0055	0.2191 ± 0.0024	0.6999 ± 0.0023	323.19	434.0	435.5 ± 4.5	0.697 ± 0.0023	0.966 ± 0.0018	1.24 ± 0.02	1.72 ± 0.04
0.5111 ± 0.0055	0.2741 ± 0.0030	0.6509 ± 0.0025	323.21	422.1	422.6 ± 2.1	0.649 ± 0.0025	0.963 ± 0.0013	1.29 ± 0.01	1.57 ± 0.01
0.5111 ± 0.0055	0.3396 ± 0.0037	0.6008 ± 0.0026	323.21	408.6	408.5 ± 1.0	0.599 ± 0.0027	0.960 ± 0.0011	1.35 ± 0.01	1.46 ± 0.00
0.5111 ± 0.0055	0.4166 ± 0.0045	0.5509 ± 0.0027	323.21	393.9	393.7 ± 1.0	0.550 ± 0.0027	0.956 ± 0.0011	1.42 ± 0.01	1.36 ± 0.00
0.5111 ± 0.0055	0.5093 ± 0.0054	0.5009 ± 0.0027	323.20	377.6	377.6 ± 0.9	0.500 ± 0.0028	0.953 ± 0.0012	1.49 ± 0.01	1.29 ± 0.00
0.5151 ± 0.0056	0.4139 ± 0.0044	0.5545 ± 0.0027	323.25	396.2	395.3 ± 1.0	0.553 ± 0.0027	0.957 ± 0.0011	1.41 ± 0.01	1.37 ± 0.00
0.4206 ± 0.0046	0.4139 ± 0.0044	0.5040 ± 0.0027	323.24	378.9	378.5 ± 0.9	0.502 ± 0.0028	0.953 ± 0.0012	1.49 ± 0.01	1.29 ± 0.00
0.3444 ± 0.0038	0.4139 ± 0.0044	0.4542 ± 0.0027	323.23	359.9	360.0 ± 0.7	0.451 ± 0.0028	0.948 ± 0.0014	1.58 ± 0.01	1.22 ± 0.00
0.2804 ± 0.0031	0.4139 ± 0.0044	0.4039 ± 0.0027	323.23	338.6	339.0 ± 0.8	0.399 ± 0.0028	0.944 ± 0.0016	1.68 ± 0.01	1.17 ± 0.00
0.2271 ± 0.0026	0.4139 ± 0.0044	0.3542 ± 0.0026	323.23	315.0	315.3 ± 0.8	0.349 ± 0.0027	0.937 ± 0.0018	1.79 ± 0.01	1.12 ± 0.00
0.1811 ± 0.0021	0.4139 ± 0.0044	0.3044 ± 0.0024	323.22	288.3	288.2 ± 0.7	0.298 ± 0.0025	0.929 ± 0.0020	1.91 ± 0.01	1.09 ± 0.00
0.1409 ± 0.0017	0.4139 ± 0.0044	0.2539 ± 0.0022	323.22	257.6	257.3 ± 0.8	0.247 ± 0.0023	0.918 ± 0.0022	2.05 ± 0.02	1.06 ± 0.00
0.1056 ± 0.0013	0.4139 ± 0.0044	0.2033 ± 0.0020	323.22	222.5	222.3 ± 0.8	0.196 ± 0.0020	0.903 ± 0.0025	2.22 ± 0.02	1.04 ± 0.00
0.0758 ± 0.0010	0.4139 ± 0.0044	0.1548 ± 0.0017	323.21	184.4	184.4 ± 0.6	0.148 ± 0.0017	0.880 ± 0.0032	2.40 ± 0.03	1.02 ± 0.00
0.0216 ± 0.0004	0.4139 ± 0.0044	0.0495 ± 0.0009	323.21	82.6	82.6 ± 0.7	0.046 ± 0.0009	0.717 ± 0.0061	2.88 ± 0.06	1.00 ± 0.00
0.0155 ± 0.0004	0.4139 ± 0.0044	0.0360 ± 0.0008	323.21	67.2	67.3 ± 0.7	0.033 ± 0.0008	0.651 ± 0.0064	2.95 ± 0.07	1.00 ± 0.00
0.0000 ± 0.0000	0.4139 ± 0.0044	0.0000 ± 0.0000	323.20	23.8	23.8 ± 0.7	0.000 ± 0.0000	0.000 ± 0.0000	3.12 ± 0.12	1.00 ± 0.00

[a] T is the experimental temperature; n_1 and n_2 are the moles of components injected into the equilibrium cell; z_1 is the total mole fraction; x_1 and y_1 are the calculated mole fractions in the liquid and vapor phases, respectively; the experimental pressure is p_{exp}, and the pressure calculated from the Legendre-polynomial fit is p_{leg}; γ_1 and γ_2 are the calculated activity coefficients.

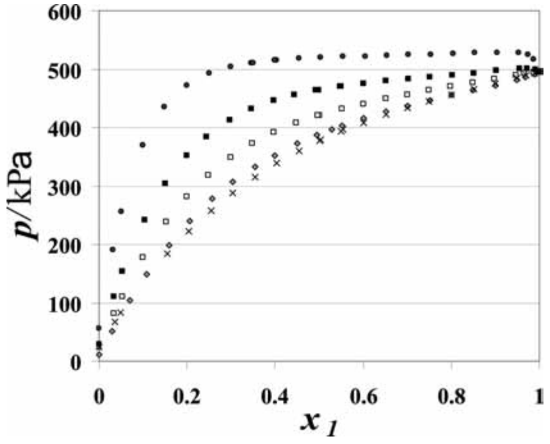

Figure 1. Pressure–composition diagram of butane (1) ●, + methanol; ■, + ethanol; □, + 2-propanol; ♦, + 2-butanol; ×, + TBA at 323 K.

Error Analysis. The overall uncertainty in the temperature measurements was ± 0.02 K for the water bath and ± 0.1 K for the syringe pumps. The pressure transducer used for pressure measurement from the cell had an uncertainty of ± 0.7 kPa, and the pressure meters in the syringe pumps ± 20 kPa. The uncertainty in injected volumes was ± 0.02 cm^3, which was obtained from calibrations with distilled water. The liquid density of pure components was estimated by a correlation.[24] Uncertainty from the density correlation was considered to be < 1.0 %. Mixing was assumed ideal, due to small excess volumes[25] of these solutions.

The error analysis procedure is presented in Laakkonen et al.,[26] and it was improved by Hynynen et al.[27] In short, this factorial method approximates the maximum error by first calculating the upper and lower limits for a range 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 different combinations for each binary pair; the computation is done automatically with in-house code VLEFIT. The error presented in Tables 4 to 8 is the average of the absolute error values from the 16 combinations. This approach is reliable in indicating the scale of maximum possible error, because it assumes four simultaneous systematic maximum errors which remain constant for the entire length of the experiment which is highly unlikely. This is an improvement to our previous approach, where all the variables were either at their upper or lower level (only two combinations).

Results and Discussion

In all the measurements, the pressure coincided (Figure 1) when the different sides of the binaries met. The pure component vapor pressure agrees with the pressure predicted by correlations (Table 2). The experimental data was regressed with Barker's method, and the liquid activity coefficient was fitted with Legendre polynomials. The results are shown in Tables 4 to 8, together with estimated maximum errors. In Figure 1 the pressure–composition diagram is shown. It can be seen that butane + methanol and + ethanol behave differently; the maximum cell vapor pressure is not with pure butane ($x_1 = 1$).

Parameters for four different liquid activity coefficient models are presented in Table 9. The models used are the following: Legendre[22] polynomials, NRTL,[28] Wilson,[29] and UNIQUAC.[30] With all binary pairs, the Legendre polynomials give the best fit and UNIQUAC performs poorest. Wilson and NRTL also give good fits but do not perform as well as Legendre. The results are inline with expectations; a model with more parameters to fit is likely to give a better result. The predictive models are based on a fit of many different binary pairs at different measurement conditions, whereas our Legendre fit is made in constant temperature for one set of binary pair experiments, resulting in increased accuracy for the specific case.

The predictive UNIFAC models are compared against the fitted Legendre polynomial in Table 10. Again, the Legendre gives the best fit; the error is an order of magnitude smaller than with UNIFAC models. The modified UNIFAC–Dortmund performs better than the standard UNIFAC with all the binary pairs. The infinite dilution activity coefficients are similar with the UNIFAC and Legendre fitting, with the exception of butane + methanol where Legendre has a higher activity coefficient. UNIFAC–Dortmund seems to overpredict the activity coefficients for alcohols; values are categorically higher (from (+

Table 9. Liquid Activity Coefficient Model Parameters for Legendre, Wilson, NRTL, and UNIQUAC[a]

butane (1)	+ methanol	+ ethanol	+ 2-propanol	+ 2-butanol	+ TBA
Legendre, $a_{1,0}$	2.52794	2.17442	1.80356	1.60352	1.41955
Legendre, $a_{2,0}$	0.28490	0.480847	0.43339	0.45228	0.453305
Legendre, $a_{3,0}$	0.41524	0.346875	0.23186	0.22777	0.262891
Legendre, $a_{4,0}$	0.11522	0.154356	0.08524	0.09348	0.124309
Legendre, $a_{5,0}$	0.07233	0.066291	0.02729	0.03202	0.051663
Legendre, $a_{6,0}$	0.02209	0.024669		0.00436	0.018690
Legendre, $a_{7,0}$	0.00793				
$\|\Delta p\|$/kPa	0.55	0.74	0.88	0.54	0.58
Wilson $\lambda_{1,2}$/K	273.83	164.25	116.26	100.01	77.67
Wilson $\lambda_{2,1}$/K	1187.44	1009.03	781.34	701.15	557.06
Wilson volume ratio	2.465	1.711	1.305	1.087	1.058
$\|\Delta p\|$/kPa	3.06	0.91	2.14	2.82	3.03
NRTL, $g_{1,2}–g_{1,1}$/K	763.93	714.10	568.01	566.72	539.07
NRTL, $g_{2,1}–g_{2,2}$/K	570.92	382.64	254.96	212.03	201.48
NRTL $\alpha_{12} = \alpha_{21}$	0.4408	0.4667	0.4837	0.5560	0.6818
$\|\Delta p\|$/kPa	2.47	2.46	2.95	1.96	1.10
UNIQUAC, $u_{12}–u_{11}$/K	592.24	267.14	138.74	191.36	130.98
UNIQUAC, $u_{12}–u_{11}$/K	50.984	22.192	33.307	20.435	15.139
$\|\Delta p\|$/kPa	14.03	10.78	5.70	7.00	5.29

[a] The Legendre model parameters were obtained with data reduction from measured values; Wilson, NRTL, and UNIQUAC parameters were fit from regressed values, Wilson volume ratios, and absolute average pressure residual $|\Delta p|$ for butane (1) + methanol, + ethanol, + 2-propanol, + 2-butanol, and + TBA.

Table 10. Comparison between the VLE Data Generated with the Predictive Methods UNIFAC and UNIFAC–Dortmund against the Fitted Legendre Polynomial

butane (1)	+ methanol	+ ethanol	+ 2-propanol	+ 2-butanol	+ TBA
		Legendre			
$\|\Delta p\|$/kPa	0.55	0.74	0.88	0.54	0.58
$\gamma_{\mathrm{inf},1}$	13.48	6.87	4.68	3.72	3.12
$\gamma_{\mathrm{inf},2}$	31.36	25.72	13.21	11.17	10.28
		UNIFAC			
$\|\Delta p\|$/kPa	15.04	15.94	13.13	14.07	10.71
$\gamma_{\mathrm{inf},1}$	9.99	4.43	3.14	2.45	2.44
$\gamma_{\mathrm{inf},2}$	19.56	21.80	16.68	13.05	13.09
		UNIFAC–Dortmund			
$\|\Delta p\|$/kPa	8.33	13.53	9.22	10.66	8.52
$\gamma_{\mathrm{inf},1}$	12.68	6.59	3.78	3.07	2.32
$\gamma_{\mathrm{inf},2}$	54.66	37.76	23.77	21.33	13.35
$\gamma_{\mathrm{inf},1}$	9.39[b], 13.8[f]	6.95[a], 6.12[g], 5.07[b]	4.7[c]	3.6[e]	3.11[d]
$\gamma_{\mathrm{inf},2}$	17.48[b]	26.12[a], 17.03[g], 19.33[b]			

[a] Reference 8. [b] Reference 4. [c] Reference 14. [d] Reference 16. [e] Reference 15. [f] Reference 13.

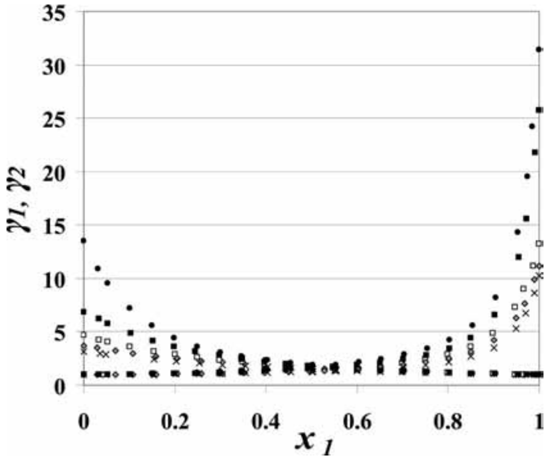

Figure 2. Activity coefficient–composition diagram of butane (1) ●, + methanol; ■, + ethanol; □, + 2-propanol; ♦, + 2-butanol; ×, + TBA at 323 K.

30 to + 91) % at infinite dilution). The comparison with literature (Table 10) shows that activity coefficients in infinite dilution are in line with literature, with the exception of butane + methanol[4] where our fit has higher activity coefficients. The activity coefficient graphs are presented in Figure 2.

Table 11. Measured Azeotropic Compositions of Butane + Alcohols Compared with UNIFAC and UNIFAC–Dortmund Model Predictions and Literature Values

	x_1	T/K	p/kPa
butane (1) + methanol			
this work (experiment)	0.908	323.13	528.2
UNIFAC	0.905	323.13	519.9
UNIFAC–Dortmund	0.908	323.13	535.4
Leu et al.[5]	0.913	323.2	525.8
butane (1) + ethanol			
this work (experiment)	0.970	323.12	501.1
UNIFAC	0.985	323.12	489.1
UNIFAC–Dortmund	0.965	323.12	504.6
Holderbaum et al.[8]	0.962	323.75	511.5

This work confirms the previous findings that there are azeotropic points with *n*-butane + methanol[5] and + ethanol[8] at 323 K, both by experimental work and by predictive modeling (Table 11; Figure 3). The azeotropic points are for butane (1) + methanol ($x_1 = 0.908$; $T = 323.13$ K; $p = 528.2$ kPa) and for butane (1) + ethanol ($x_1 = 0.970$; $T = 323.12$ K; $p = 501.1$ kPa). The values were calculated from measurements near the azeotropic point by polynomial interpolation. The agreement between different sources for the locatioyn of the azeotropic points is good; the variation for methanol is from $x_1 = 0.905$ to 0.913, and for ethanol, it is from $x_1 = 0.962$ to 0.985.

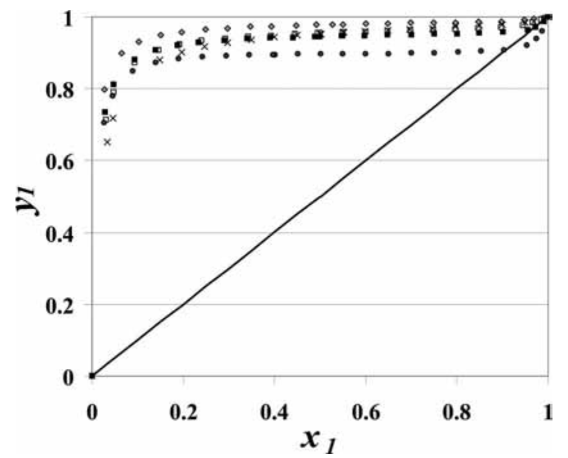

Figure 3. Composition diagram of butane (1) ●, + methanol; ■, + ethanol; □, + 2-propanol; ♦, + 2-butanol; ×, + TBA at 323 K.

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