Vapor–Liquid Equilibrium for the Systems *trans*-2-Butene + Methanol, + 1-Propanol, + 2-Propanol, + 2-Butanol, and + 2-Methyl-2-propanol at 364.5 K

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Vapor–liquid equilibrium (VLE) data for *trans*-2-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 $p-T-z$ (pressure−temperature−total composition) data were reduced to liquid and vapor phase compositions using Barker's method. An azeotropic point was found for *trans*-2-butene + methanol ($x_1 = 0.854$; $T = 364.52$; $p = 1385.1$ kPa). Wilson 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 are needed for modeling separation processes in various stages of development, design, and optimization of chemical plants. In the absence of experimental data, vapor–liquid equilibrium can be predicted using group contribution methods like UNIFAC[1] or UNIFAC−Dortmund.[2] Although these models are useful in preliminary process design, their accuracy is often inadequate for modeling separation processes that are sensitive to vapor–liquid equilibrium. Development of these predictive models also requires accurate measured data.

We have previously published VLE data for *trans*-2-butene + methanol, + 2-propanol, + 2-butanol, and + 2-methyl-2-propanol at 332 K.[3] Infinite dilution activity coefficients have been reported for *trans*-2-butene in methanol at (255 to 320) K[4] and (374 to 490) K,[5] 1-propanol at (260 to 340) K,[6] 2-propanol at (250 to 330) K,[7] 2-butanol at (250 to 330) K,[8] and 2-methyl-2-propanol at (300 to 330) K.[9]

Experimental

Materials. Purities and suppliers of used 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 the alcohols was performed by vacuum rectification[10] with modifications.[11] *trans*-2-Butene was degassed by evacuation in a syringe pump. The vacuum line was opened 10 times for a period of 10 s. The quality of the degassing procedure was checked by comparing measured vapor pressures to values from literature correlations (Table 2). In this article, *trans*-2-butene is always addressed as component (1) and the alcohol as component (2).

Apparatus and Procedure. The static total pressure apparatus is described in detail in Uusi-Kyyny et al.[12] The pressure transducer was replaced by a Digiquartz 2300A-101 with a pressure range of (0 to 2) MPa. The volume of the cell was 112.68 cm^3 for all systems except *trans*-2-butene + 2-butanol, for which a 113.10 cm^3 cell was used. The stability of the water bath was ± 0.02 K.

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Table 1. Material Purities and Suppliers

component	supplier	purity (wt %)
trans-2-butene	Messer Finland Oy	99.4
methanol	Merck	99.8
1-propanol	Riedel-de-Haën	99.8
2-propanol	Riedel-de-Haën	99.8
2-butanol	Fluka	>99.8
2-methyl-2-propanol	Fluka	>99.7

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

		(p_i)/kPa			
component	T/K	this work	ref 25	ref 26	ref 18
trans-2-butene	364.52	1268.9		1278.0	1274.9
	364.52	1268.0		1278.0	1274.9
	364.52	1270.9		1278.0	1274.9
	364.52	1270.1		1278.0	1274.9
	364.52	1269.7		1278.0	1274.9
methanol	364.52	267.6	267.7	266.9	267.5
1-propanol	364.53	81.2	81.5	81.5	80.8
2-propanol	364.51	144.1	144.8	142.1	142.7
2-butanol	364.52	75.4	73.7	75.0	74.9
2-methyl-2-propanol	364.52	143.3	142.3	141.7	143.1

[a] The vapor pressure values for *trans*-2-butene were obtained from five different experiments.

Table 3. Pure Component Critical Properties:[a] Critical Temperature T_c, Critical Pressure P_c, Acentric Factor ω[b]

component	T_c/K	p_c/MPa	ω
trans-2-butene	428.63 ± 4.29	4.1024 ± 0.0410	0.2128
methanol	512.58 ± 5.13	8.0959 ± 0.2429	0.5656
1-propanol	536.71 ± 5.37	5.1696 ± 0.1551	0.6279
2-propanol	508.31 ± 5.08	4.7643 ± 0.1429	0.6689
2-butanol	536.01 ± 5.36	4.1938 ± 0.1258	0.5711
2-methyl-2-propanol	506.20 ± 5.06	3.9719 ± 0.1192	0.6158

[a] Ref 27. [b] The given errors are calculated from the maximum error percent estimated by the authors of the database.

At each equilibrium point, the temperatures of the cell and the syringe pumps, the cell pressure, and the total volume of components fed into the cell were recorded. The total number of moles and the total composition were then calculated from the volumes of the components. The liquid and vapor mole fractions were calculated from the total pressure measurements

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Table 4. VLE Data for *trans*-2-Butene (1) + Methanol (2) at 364.5 K[a]

n_1/mol	n_2/mol	z_1	T/K	p_{exptl}/kPa	p_{leg}/kPa	x_1	y_1	γ_1	γ_2
0.6592 ± 0.0070	0.0000 ± 0.0000	1.0000 ± 0.0000	364.52	1268.9	1268.9 ± 0.4	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	10.27 ± 0.19
0.6592 ± 0.0070	0.0080 ± 0.0006	0.9880 ± 0.0010	364.51	1296.8	1296.4 ± 1.7	0.9886 ± 0.0009	0.9736 ± 0.0018	1.00 ± 0.00	9.40 ± 0.19
0.6592 ± 0.0070	0.0160 ± 0.0007	0.9764 ± 0.0012	364.52	1320.6	1318.5 ± 1.5	0.9772 ± 0.0012	0.9523 ± 0.0018	1.00 ± 0.00	8.65 ± 0.14
0.6592 ± 0.0070	0.0219 ± 0.0007	0.9678 ± 0.0013	364.53	1335.2	1331.9 ± 1.3	0.9688 ± 0.0013	0.9389 ± 0.0017	1.00 ± 0.00	8.15 ± 0.13
0.6592 ± 0.0070	0.0364 ± 0.0009	0.9477 ± 0.0017	364.52	1358.1	1354.9 ± 1.0	0.9489 ± 0.0017	0.9134 ± 0.0016	1.01 ± 0.00	7.13 ± 0.11
0.6592 ± 0.0070	0.0760 ± 0.0013	0.8966 ± 0.0025	364.52	1379.5	1380.3 ± 0.8	0.8974 ± 0.0026	0.8730 ± 0.0016	1.03 ± 0.00	5.28 ± 0.07
0.6592 ± 0.0070	0.1194 ± 0.0017	0.8467 ± 0.0032	364.52	1381.0	1383.8 ± 0.8	0.8465 ± 0.0033	0.8514 ± 0.0018	1.07 ± 0.00	4.14 ± 0.05
0.6592 ± 0.0070	0.1680 ± 0.0022	0.7969 ± 0.0038	364.53	1376.8	1379.6 ± 1.0	0.7959 ± 0.0039	0.8383 ± 0.0020	1.12 ± 0.00	3.38 ± 0.03
0.6592 ± 0.0070	0.2221 ± 0.0028	0.7480 ± 0.0043	364.52	1370.4	1372.5 ± 1.1	0.7462 ± 0.0045	0.8295 ± 0.0020	1.18 ± 0.00	2.86 ± 0.02
0.6592 ± 0.0070	0.2854 ± 0.0034	0.6979 ± 0.0047	364.52	1362.8	1363.9 ± 1.2	0.6956 ± 0.0049	0.8230 ± 0.0020	1.25 ± 0.01	2.46 ± 0.02
0.6592 ± 0.0070	0.3579 ± 0.0041	0.6481 ± 0.0050	364.52	1354.4	1354.6 ± 1.1	0.6456 ± 0.0052	0.8178 ± 0.0019	1.33 ± 0.01	2.16 ± 0.01
0.6592 ± 0.0070	0.4431 ± 0.0050	0.5980 ± 0.0052	364.53	1345.3	1344.6 ± 0.9	0.5956 ± 0.0054	0.8135 ± 0.0018	1.42 ± 0.01	1.93 ± 0.01
0.6592 ± 0.0070	0.5431 ± 0.0060	0.5483 ± 0.0054	364.52	1334.7	1333.7 ± 0.8	0.5462 ± 0.0055	0.8096 ± 0.0016	1.54 ± 0.01	1.75 ± 0.01
0.6592 ± 0.0070	0.6612 ± 0.0072	0.4992 ± 0.0054	364.52	1322.7	1321.7 ± 0.7	0.4978 ± 0.0055	0.8060 ± 0.0014	1.67 ± 0.02	1.60 ± 0.01
0.6581 ± 0.0070	0.6703 ± 0.0073	0.4954 ± 0.0054	364.52	1321.8	1320.7 ± 0.7	0.4940 ± 0.0054	0.8057 ± 0.0014	1.68 ± 0.02	1.59 ± 0.01
0.5384 ± 0.0057	0.6703 ± 0.0073	0.4454 ± 0.0053	364.52	1305.1	1304.6 ± 1.0	0.4414 ± 0.0054	0.8015 ± 0.0012	1.85 ± 0.02	1.45 ± 0.01
0.4387 ± 0.0047	0.6703 ± 0.0073	0.3956 ± 0.0052	364.52	1283.5	1283.6 ± 1.0	0.3884 ± 0.0053	0.7965 ± 0.0012	2.07 ± 0.03	1.35 ± 0.01
0.3543 ± 0.0038	0.6703 ± 0.0073	0.3458 ± 0.0049	364.52	1254.0	1254.7 ± 0.9	0.3352 ± 0.0050	0.7899 ± 0.0012	2.34 ± 0.03	1.26 ± 0.00
0.2825 ± 0.0031	0.6703 ± 0.0073	0.2965 ± 0.0046	364.52	1213.1	1213.8 ± 0.6	0.2823 ± 0.0046	0.7810 ± 0.0013	2.68 ± 0.04	1.18 ± 0.00
0.2203 ± 0.0025	0.6703 ± 0.0073	0.2473 ± 0.0041	364.53	1154.3	1154.6 ± 1.0	0.2300 ± 0.0041	0.7679 ± 0.0014	3.11 ± 0.05	1.12 ± 0.00
0.1666 ± 0.0019	0.6703 ± 0.0073	0.1991 ± 0.0036	364.52	1071.0	1070.9 ± 1.1	0.1797 ± 0.0035	0.7480 ± 0.0015	3.66 ± 0.07	1.08 ± 0.00
0.1181 ± 0.0014	0.6703 ± 0.0073	0.1498 ± 0.0029	364.52	950.5	949.8 ± 0.8	0.1300 ± 0.0028	0.7145 ± 0.0013	4.38 ± 0.09	1.04 ± 0.00
0.0765 ± 0.0010	0.6703 ± 0.0073	0.1025 ± 0.0022	364.52	790.9	790.4 ± 1.0	0.0851 ± 0.0021	0.6566 ± 0.0009	5.28 ± 0.13	1.02 ± 0.00
0.0384 ± 0.0006	0.6703 ± 0.0073	0.0541 ± 0.0014	364.52	575.5	575.9 ± 1.1	0.0427 ± 0.0013	0.5305 ± 0.0007	6.44 ± 0.20	1.00 ± 0.00
0.0241 ± 0.0005	0.6703 ± 0.0073	0.0346 ± 0.0010	364.52	472.9	473.3 ± 0.6	0.0267 ± 0.0009	0.4304 ± 0.0008	6.99 ± 0.24	1.00 ± 0.00
0.0104 ± 0.0003	0.6703 ± 0.0073	0.0153 ± 0.0006	364.52	362.3	361.9 ± 1.4	0.0115 ± 0.0006	0.2578 ± 0.0026	7.60 ± 0.29	1.00 ± 0.00
0.0000 ± 0.0000	0.6703 ± 0.0073	0.0000 ± 0.0000	364.52	267.6	267.6 ± 0.4	0.0000 ± 0.0000	0.0000 ± 0.0000	8.11 ± 0.32	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_{exptl}; 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 *trans*-2-Butene (1) + 1-Propanol (2) at 364.5 K[a]

n_1/mol	n_2/mol	z_1	T/K	p_{exptl}/kPa	p_{leg}/kPa	x_1	y_1	γ_1	γ_2
0.5314 ± 0.0057	0.0000 ± 0.0000	1.0000 ± 0.0000	364.52	1268.0	1268.0 ± 0.4	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	6.90 ± 0.18
0.5314 ± 0.0057	0.0061 ± 0.0003	0.9887 ± 0.0007	364.53	1259.9	1260.4 ± 0.7	0.9885 ± 0.0008	0.9933 ± 0.0006	1.00 ± 0.00	6.35 ± 0.12
0.5314 ± 0.0057	0.0102 ± 0.0004	0.9811 ± 0.0009	364.52	1254.1	1255.1 ± 0.7	0.9806 ± 0.0009	0.9892 ± 0.0007	1.00 ± 0.00	6.02 ± 0.10
0.5314 ± 0.0057	0.0170 ± 0.0004	0.9691 ± 0.0011	364.52	1245.2	1246.6 ± 0.7	0.9682 ± 0.0012	0.9837 ± 0.0008	1.00 ± 0.00	5.56 ± 0.07
0.5314 ± 0.0057	0.0286 ± 0.0006	0.9490 ± 0.0015	364.52	1231.2	1232.9 ± 0.7	0.9476 ± 0.0015	0.9761 ± 0.0009	1.01 ± 0.00	4.90 ± 0.04
0.5314 ± 0.0057	0.0595 ± 0.0009	0.8993 ± 0.0023	364.51	1200.8	1201.4 ± 0.7	0.8963 ± 0.0024	0.9633 ± 0.0010	1.03 ± 0.00	3.74 ± 0.01
0.5314 ± 0.0057	0.0947 ± 0.0012	0.8488 ± 0.0030	364.52	1173.9	1173.5 ± 0.6	0.8446 ± 0.0032	0.9553 ± 0.0010	1.07 ± 0.00	2.99 ± 0.01
0.5314 ± 0.0057	0.1340 ± 0.0016	0.7986 ± 0.0037	364.52	1149.2	1148.4 ± 0.6	0.7936 ± 0.0039	0.9498 ± 0.0010	1.11 ± 0.00	2.49 ± 0.01
0.5314 ± 0.0057	0.1782 ± 0.0021	0.7489 ± 0.0042	364.53	1125.3	1124.7 ± 0.5	0.7435 ± 0.0044	0.9455 ± 0.0010	1.16 ± 0.01	2.15 ± 0.01
0.5314 ± 0.0057	0.2284 ± 0.0026	0.6994 ± 0.0046	364.52	1100.8	1100.8 ± 0.5	0.6940 ± 0.0048	0.9418 ± 0.0010	1.22 ± 0.01	1.90 ± 0.01
0.5314 ± 0.0057	0.2865 ± 0.0032	0.6497 ± 0.0049	364.52	1075.7	1075.8 ± 0.6	0.6448 ± 0.0051	0.9383 ± 0.0010	1.28 ± 0.01	1.71 ± 0.00
0.5314 ± 0.0057	0.3543 ± 0.0039	0.5999 ± 0.0052	364.52	1048.7	1048.9 ± 0.6	0.5958 ± 0.0053	0.9348 ± 0.0011	1.36 ± 0.01	1.56 ± 0.00
0.5314 ± 0.0057	0.4351 ± 0.0047	0.5498 ± 0.0053	364.52	1019.0	1019.2 ± 0.5	0.5467 ± 0.0054	0.9311 ± 0.0010	1.44 ± 0.01	1.44 ± 0.00
0.5314 ± 0.0057	0.5306 ± 0.0057	0.5004 ± 0.0053	364.52	986.3	986.4 ± 0.5	0.4986 ± 0.0054	0.9272 ± 0.0010	1.53 ± 0.02	1.35 ± 0.00
0.5326 ± 0.0057	0.5345 ± 0.0057	0.4991 ± 0.0053	364.51	985.6	985.6 ± 0.5	0.4975 ± 0.0054	0.9271 ± 0.0010	1.53 ± 0.02	1.35 ± 0.00
0.4367 ± 0.0047	0.5345 ± 0.0057	0.4496 ± 0.0053	364.52	945.3	945.2 ± 0.6	0.4457 ± 0.0054	0.9223 ± 0.0010	1.64 ± 0.02	1.27 ± 0.00
0.3564 ± 0.0039	0.5345 ± 0.0057	0.4001 ± 0.0052	364.52	898.1	897.9 ± 0.6	0.3938 ± 0.0052	0.9166 ± 0.0010	1.77 ± 0.02	1.20 ± 0.00
0.2903 ± 0.0032	0.5345 ± 0.0057	0.3519 ± 0.0050	364.52	844.0	843.8 ± 0.5	0.3434 ± 0.0050	0.9097 ± 0.0010	1.92 ± 0.03	1.15 ± 0.00
0.2327 ± 0.0026	0.5345 ± 0.0057	0.3033 ± 0.0046	364.53	779.4	779.4 ± 0.4	0.2928 ± 0.0046	0.9006 ± 0.0011	2.08 ± 0.03	1.10 ± 0.00
0.1819 ± 0.0021	0.5345 ± 0.0057	0.2539 ± 0.0042	364.52	702.0	702.1 ± 0.6	0.2420 ± 0.0042	0.8881 ± 0.0011	2.27 ± 0.04	1.07 ± 0.00
0.1379 ± 0.0016	0.5345 ± 0.0057	0.2051 ± 0.0037	364.52	612.7	612.7 ± 0.6	0.1926 ± 0.0036	0.8703 ± 0.0012	2.48 ± 0.04	1.04 ± 0.00
0.0994 ± 0.0012	0.5345 ± 0.0057	0.1569 ± 0.0031	364.52	510.4	510.4 ± 0.5	0.1448 ± 0.0030	0.8428 ± 0.0013	2.71 ± 0.05	1.02 ± 0.00
0.0654 ± 0.0009	0.5345 ± 0.0057	0.1090 ± 0.0024	364.51	395.0	395.0 ± 0.6	0.0989 ± 0.0023	0.7956 ± 0.0013	2.96 ± 0.07	1.01 ± 0.00
0.0326 ± 0.0006	0.5345 ± 0.0057	0.0575 ± 0.0015	364.51	255.3	255.2 ± 0.5	0.0510 ± 0.0014	0.6822 ± 0.0015	3.26 ± 0.09	1.00 ± 0.00
0.0231 ± 0.0005	0.5345 ± 0.0057	0.0415 ± 0.0012	364.52	208.5	208.6 ± 0.5	0.0365 ± 0.0011	0.6108 ± 0.0019	3.36 ± 0.10	1.00 ± 0.00
0.0000 ± 0.0000	0.5345 ± 0.0057	0.0000 ± 0.0000	364.53	81.2	81.2 ± 0.4	0.0000 ± 0.0000	0.0000 ± 0.0000	3.63 ± 0.13	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_{exptl}; and the pressure calculated from the Legendre polynomial fit is p_{leg}; γ_1 and γ_2 are the calculated activity coefficients.

with Barker[13] data reduction. A detailed description of the procedure is given in Uusi-Kyyny et al.[12]

The composition range for each measured binary pair was covered by approaching the point of equimolar mixture from both ends of the composition scale. The quality of the measurements was verified by the coincidence of the curves at equimolar composition. The vapor volume in the cell was kept to a minimum to improve the accuracy of the measurements. The measurements were started by injecting pure component 1 into the cell and measuring the vapor pressure. Then, a predetermined amount of component 2 was added, and the pressure was allowed to stabilize. Then, another dose of component 2 was added, and the procedure was repeated until equimolar concentration was reached. Then, the cell was emptied and evacuated, and the second part of the run was performed, starting with component 2.

Table 6. VLE Data for *trans*-2-Butene (1) + 2-Propanol (2) at 364.5 K[a]

n_1/mol	n_2/mol	z_1	T/K	p_{exptl}/kPa	p_{leg}/kPa	x_1	y_1	γ_1	γ_2
0.5271 ± 0.0056	0.0000 ± 0.0000	1.0000 ± 0.0000	364.52	1268.7	1268.7 ± 0.4	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	5.29 ± 0.12
0.5271 ± 0.0056	0.0060 ± 0.0003	0.9887 ± 0.0007	364.53	1264.5	1264.8 ± 0.6	0.9885 ± 0.0007	0.9911 ± 0.0007	1.00 ± 0.00	4.96 ± 0.08
0.5271 ± 0.0056	0.0117 ± 0.0004	0.9783 ± 0.0009	364.52	1259.9	1260.7 ± 0.6	0.9780 ± 0.0009	0.9838 ± 0.0009	1.00 ± 0.00	4.68 ± 0.07
0.5271 ± 0.0056	0.0172 ± 0.0004	0.9684 ± 0.0011	364.52	1255.3	1256.3 ± 0.7	0.9678 ± 0.0011	0.9775 ± 0.0011	1.00 ± 0.00	4.44 ± 0.05
0.5271 ± 0.0056	0.0281 ± 0.0005	0.9493 ± 0.0014	364.52	1246.0	1247.3 ± 0.7	0.9484 ± 0.0015	0.9670 ± 0.0012	1.01 ± 0.00	4.03 ± 0.03
0.5271 ± 0.0056	0.0605 ± 0.0009	0.8971 ± 0.0023	364.52	1219.3	1220.2 ± 0.7	0.8947 ± 0.0024	0.9460 ± 0.0014	1.03 ± 0.00	3.19 ± 0.01
0.5271 ± 0.0056	0.0948 ± 0.0012	0.8475 ± 0.0030	364.52	1194.5	1194.3 ± 0.6	0.8441 ± 0.0032	0.9325 ± 0.0015	1.06 ± 0.00	2.65 ± 0.00
0.5271 ± 0.0056	0.1331 ± 0.0016	0.7984 ± 0.0036	364.53	1169.4	1168.7 ± 0.5	0.7942 ± 0.0039	0.9224 ± 0.0015	1.09 ± 0.00	2.28 ± 0.00
0.5271 ± 0.0056	0.1772 ± 0.0021	0.7485 ± 0.0042	364.52	1143.0	1142.5 ± 0.5	0.7438 ± 0.0044	0.9139 ± 0.0016	1.13 ± 0.01	2.00 ± 0.00
0.5271 ± 0.0056	0.2270 ± 0.0026	0.6990 ± 0.0046	364.52	1116.4	1116.0 ± 0.6	0.6943 ± 0.0048	0.9065 ± 0.0016	1.18 ± 0.01	1.80 ± 0.00
0.5271 ± 0.0056	0.2845 ± 0.0032	0.6495 ± 0.0049	364.52	1088.4	1088.3 ± 0.7	0.6451 ± 0.0051	0.8995 ± 0.0016	1.24 ± 0.01	1.64 ± 0.00
0.5271 ± 0.0056	0.3517 ± 0.0038	0.5998 ± 0.0052	364.52	1058.5	1058.5 ± 0.6	0.5961 ± 0.0053	0.8925 ± 0.0016	1.30 ± 0.01	1.51 ± 0.00
0.5271 ± 0.0056	0.4314 ± 0.0046	0.5500 ± 0.0053	364.52	1025.8	1026.1 ± 0.5	0.5472 ± 0.0054	0.8853 ± 0.0016	1.37 ± 0.01	1.41 ± 0.00
0.5271 ± 0.0056	0.5265 ± 0.0056	0.5003 ± 0.0053	364.52	990.5	990.9 ± 0.5	0.4989 ± 0.0054	0.8777 ± 0.0015	1.45 ± 0.01	1.32 ± 0.00
0.5280 ± 0.0056	0.5313 ± 0.0057	0.4984 ± 0.0053	364.52	989.6	989.6 ± 0.5	0.4970 ± 0.0054	0.8774 ± 0.0015	1.46 ± 0.01	1.32 ± 0.00
0.4329 ± 0.0047	0.5313 ± 0.0057	0.4489 ± 0.0053	364.52	947.5	947.4 ± 0.6	0.4455 ± 0.0053	0.8683 ± 0.0015	1.55 ± 0.02	1.25 ± 0.00
0.3555 ± 0.0039	0.5313 ± 0.0057	0.4009 ± 0.0052	364.52	901.0	901.0 ± 0.7	0.3954 ± 0.0052	0.8581 ± 0.0015	1.66 ± 0.02	1.19 ± 0.00
0.2885 ± 0.0032	0.5313 ± 0.0057	0.3519 ± 0.0050	364.52	847.0	846.9 ± 0.6	0.3444 ± 0.0050	0.8456 ± 0.0015	1.78 ± 0.02	1.14 ± 0.00
0.2316 ± 0.0026	0.5313 ± 0.0057	0.3036 ± 0.0046	364.52	785.9	785.8 ± 0.4	0.2944 ± 0.0046	0.8302 ± 0.0015	1.92 ± 0.03	1.10 ± 0.00
0.1814 ± 0.0021	0.5313 ± 0.0057	0.2545 ± 0.0042	364.52	714.1	714.1 ± 0.6	0.2440 ± 0.0042	0.8096 ± 0.0016	2.08 ± 0.03	1.07 ± 0.00
0.1380 ± 0.0016	0.5313 ± 0.0057	0.2061 ± 0.0037	364.52	632.9	632.9 ± 0.7	0.1950 ± 0.0036	0.7817 ± 0.0017	2.26 ± 0.04	1.04 ± 0.00
0.0998 ± 0.0012	0.5313 ± 0.0057	0.1581 ± 0.0031	364.52	540.7	540.7 ± 0.6	0.1474 ± 0.0030	0.7409 ± 0.0017	2.47 ± 0.05	1.02 ± 0.00
0.0661 ± 0.0009	0.5313 ± 0.0057	0.1107 ± 0.0024	364.52	437.0	437.0 ± 0.6	0.1014 ± 0.0023	0.6758 ± 0.0015	2.69 ± 0.06	1.01 ± 0.00
0.0352 ± 0.0006	0.5313 ± 0.0057	0.0621 ± 0.0016	364.52	317.6	317.5 ± 0.7	0.0558 ± 0.0015	0.5496 ± 0.0011	2.95 ± 0.08	1.00 ± 0.00
0.0222 ± 0.0004	0.5313 ± 0.0057	0.0401 ± 0.0012	364.52	258.3	258.6 ± 0.5	0.0357 ± 0.0011	0.4453 ± 0.0012	3.08 ± 0.10	1.00 ± 0.00
0.0128 ± 0.0003	0.5313 ± 0.0057	0.0235 ± 0.0009	364.52	212.7	212.4 ± 0.7	0.0208 ± 0.0008	0.3231 ± 0.0022	3.18 ± 0.11	1.00 ± 0.00
0.0000 ± 0.0000	0.5313 ± 0.0057	0.0000 ± 0.0000	364.51	144.1	144.1 ± 0.4	0.0000 ± 0.0000	0.0000 ± 0.0000	3.33 ± 0.13	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_{exptl}; 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 *trans*-2-Butene (1) + 2-Butanol (2) at 364.5 K[a]

n_1/mol	n_2/mol	z_1	T/K	p_{exptl}/kPa	p_{leg}/kPa	x_1	y_1	γ_1	γ_2
0.4826 ± 0.0052	0.0000 ± 0.0000	1.0000 ± 0.0000	364.52	1270.1	1270.1 ± 0.4	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	4.27 ± 0.09
0.4826 ± 0.0052	0.0050 ± 0.0003	0.9898 ± 0.0006	364.53	1258.5	1258.9 ± 0.9	0.9894 ± 0.0007	0.9961 ± 0.0003	1.00 ± 0.00	4.05 ± 0.07
0.4826 ± 0.0052	0.0098 ± 0.0003	0.9801 ± 0.0008	364.52	1247.5	1248.4 ± 0.9	0.9792 ± 0.0009	0.9927 ± 0.0005	1.00 ± 0.00	3.87 ± 0.06
0.4826 ± 0.0052	0.0149 ± 0.0004	0.9701 ± 0.0010	364.52	1237.0	1238.1 ± 1.0	0.9688 ± 0.0011	0.9895 ± 0.0006	1.00 ± 0.00	3.69 ± 0.06
0.4826 ± 0.0052	0.0254 ± 0.0005	0.9500 ± 0.0014	364.52	1216.7	1218.1 ± 1.1	0.9478 ± 0.0015	0.9837 ± 0.0007	1.01 ± 0.00	3.38 ± 0.05
0.4826 ± 0.0052	0.0537 ± 0.0008	0.8999 ± 0.0022	364.51	1172.7	1173.4 ± 1.3	0.8959 ± 0.0024	0.9728 ± 0.0010	1.02 ± 0.00	2.77 ± 0.03
0.4826 ± 0.0052	0.0850 ± 0.0011	0.8502 ± 0.0030	364.52	1135.6	1134.9 ± 1.2	0.8449 ± 0.0032	0.9650 ± 0.0011	1.05 ± 0.00	2.35 ± 0.02
0.4826 ± 0.0052	0.1204 ± 0.0014	0.8004 ± 0.0036	364.51	1100.5	1099.5 ± 1.0	0.7943 ± 0.0039	0.9589 ± 0.0012	1.08 ± 0.00	2.04 ± 0.01
0.4826 ± 0.0052	0.1602 ± 0.0018	0.7508 ± 0.0041	364.52	1066.8	1065.9 ± 0.9	0.7444 ± 0.0044	0.9538 ± 0.0012	1.12 ± 0.01	1.82 ± 0.01
0.4826 ± 0.0052	0.2065 ± 0.0023	0.7003 ± 0.0046	364.52	1032.2	1031.9 ± 0.7	0.6941 ± 0.0048	0.9490 ± 0.0011	1.16 ± 0.01	1.64 ± 0.00
0.4826 ± 0.0052	0.2593 ± 0.0029	0.6505 ± 0.0049	364.52	997.1	997.5 ± 0.6	0.6449 ± 0.0051	0.9444 ± 0.0011	1.21 ± 0.01	1.51 ± 0.00
0.4826 ± 0.0052	0.3210 ± 0.0035	0.6005 ± 0.0052	364.53	960.6	961.2 ± 0.8	0.5959 ± 0.0053	0.9398 ± 0.0011	1.27 ± 0.01	1.40 ± 0.00
0.4826 ± 0.0052	0.3936 ± 0.0042	0.5508 ± 0.0053	364.52	921.5	922.4 ± 0.9	0.5475 ± 0.0054	0.9349 ± 0.0011	1.33 ± 0.01	1.32 ± 0.00
0.4826 ± 0.0052	0.4815 ± 0.0051	0.5005 ± 0.0053	364.52	880.0	880.1 ± 0.8	0.4988 ± 0.0054	0.9294 ± 0.0011	1.39 ± 0.02	1.25 ± 0.00
0.4856 ± 0.0052	0.4860 ± 0.0052	0.4998 ± 0.0053	364.52	880.1	879.6 ± 0.8	0.4982 ± 0.0053	0.9293 ± 0.0011	1.39 ± 0.02	1.25 ± 0.00
0.4005 ± 0.0043	0.4860 ± 0.0052	0.4518 ± 0.0053	364.52	831.8	831.6 ± 0.7	0.4483 ± 0.0053	0.9229 ± 0.0011	1.47 ± 0.02	1.19 ± 0.00
0.3262 ± 0.0036	0.4860 ± 0.0052	0.4017 ± 0.0052	364.52	776.1	776.3 ± 0.5	0.3963 ± 0.0052	0.9150 ± 0.0012	1.55 ± 0.02	1.15 ± 0.00
0.2645 ± 0.0029	0.4860 ± 0.0052	0.3524 ± 0.0050	364.52	716.1	716.2 ± 0.7	0.3453 ± 0.0050	0.9055 ± 0.0013	1.65 ± 0.02	1.11 ± 0.00
0.2119 ± 0.0024	0.4860 ± 0.0052	0.3036 ± 0.0046	364.52	650.6	650.5 ± 0.9	0.2950 ± 0.0046	0.8935 ± 0.0014	1.75 ± 0.02	1.08 ± 0.00
0.1663 ± 0.0019	0.4860 ± 0.0052	0.2549 ± 0.0042	364.52	578.8	578.4 ± 0.9	0.2454 ± 0.0042	0.8778 ± 0.0015	1.86 ± 0.03	1.05 ± 0.00
0.1268 ± 0.0015	0.4860 ± 0.0052	0.2070 ± 0.0037	364.52	500.4	500.2 ± 0.7	0.1971 ± 0.0036	0.8563 ± 0.0015	1.98 ± 0.03	1.03 ± 0.00
0.0912 ± 0.0012	0.4860 ± 0.0052	0.1580 ± 0.0031	364.52	412.9	412.9 ± 0.5	0.1486 ± 0.0030	0.8232 ± 0.0015	2.12 ± 0.04	1.02 ± 0.00
0.0600 ± 0.0008	0.4860 ± 0.0052	0.1099 ± 0.0024	364.52	319.2	319.4 ± 0.8	0.1020 ± 0.0023	0.7685 ± 0.0014	2.27 ± 0.05	1.01 ± 0.00
0.0304 ± 0.0005	0.4860 ± 0.0052	0.0589 ± 0.0016	364.51	211.0	211.3 ± 0.7	0.0538 ± 0.0015	0.6462 ± 0.0015	2.44 ± 0.07	1.00 ± 0.00
0.0198 ± 0.0004	0.4860 ± 0.0052	0.0391 ± 0.0012	364.52	167.1	167.1 ± 0.5	0.0355 ± 0.0012	0.5509 ± 0.0017	2.51 ± 0.08	1.00 ± 0.00
0.0092 ± 0.0003	0.4860 ± 0.0052	0.0185 ± 0.0008	364.52	119.7	119.5 ± 0.8	0.0167 ± 0.0008	0.3702 ± 0.0041	2.59 ± 0.09	1.00 ± 0.00
0.0000 ± 0.0000	0.4860 ± 0.0052	0.0000 ± 0.0000	364.52	75.4	75.4 ± 0.4	0.0000 ± 0.0000	0.0000 ± 0.0000	2.66 ± 0.10	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_{exptl}; and the pressure calculated from the Legendre polynomial fit is p_{leg}; γ_1 and γ_2 are the calculated activity coefficients.

Data Reduction. The compositions of the vapor and liquid phases were calculated from the total pressure data with Barker's method[13] by using VLEFIT[14] software. Barker's method is based on the least-squares method and calculates the activity coefficients for the liquid phase from total pressure measurements. By equating fugacities in vapor and liquid phases, the following relationship for VLE can be found:

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

where x_i and y_i are the liquid and vapor phase mole fractions for component i, respectively; γ_i is the activity coefficient for component i; φ_i^S is the saturated liquid fugacity coefficient for pure component i at system temperature; φ_i is the fugacity

Table 8. VLE Data for *trans*-2-Butene (1) + 2-Methyl-2-propanol (2) at 364.5 K[a]

n_1/mol	n_2/mol	z_1	T/K	p_{expt}/kPa	p_{leg}/kPa	x_1	y_1	γ_1	γ_2
0.4675 ± 0.0050	0.0000 ± 0.0000	1.0000 ± 0.0000	364.52	1268.1	1268.1 ± 0.4	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	3.45 ± 0.07
0.4675 ± 0.0050	0.0047 ± 0.0003	0.9902 ± 0.0006	364.53	1260.5	1260.5 ± 0.7	0.9898 ± 0.0007	0.9945 ± 0.0005	1.00 ± 0.00	3.31 ± 0.06
0.4675 ± 0.0050	0.0096 ± 0.0003	0.9798 ± 0.0008	364.52	1251.8	1252.3 ± 0.7	0.9792 ± 0.0009	0.9891 ± 0.0006	1.00 ± 0.00	3.17 ± 0.05
0.4675 ± 0.0050	0.0143 ± 0.0004	0.9704 ± 0.0010	364.52	1244.3	1244.8 ± 0.7	0.9694 ± 0.0011	0.9846 ± 0.0008	1.00 ± 0.00	3.06 ± 0.05
0.4675 ± 0.0050	0.0243 ± 0.0005	0.9506 ± 0.0014	364.53	1228.7	1229.4 ± 0.7	0.9488 ± 0.0015	0.9759 ± 0.0010	1.01 ± 0.00	2.83 ± 0.04
0.4675 ± 0.0050	0.0521 ± 0.0007	0.8997 ± 0.0022	364.53	1190.5	1190.8 ± 0.8	0.8963 ± 0.0024	0.9581 ± 0.0015	1.02 ± 0.00	2.39 ± 0.02
0.4675 ± 0.0050	0.0831 ± 0.0011	0.8491 ± 0.0030	364.52	1154.4	1154.1 ± 0.8	0.8444 ± 0.0032	0.9445 ± 0.0017	1.04 ± 0.00	2.07 ± 0.02
0.4675 ± 0.0050	0.1171 ± 0.0014	0.7997 ± 0.0036	364.52	1119.7	1119.3 ± 0.7	0.7941 ± 0.0038	0.9336 ± 0.0017	1.07 ± 0.00	1.84 ± 0.01
0.4675 ± 0.0050	0.1559 ± 0.0018	0.7500 ± 0.0041	364.51	1084.8	1084.5 ± 0.6	0.7440 ± 0.0044	0.9238 ± 0.0018	1.10 ± 0.00	1.66 ± 0.01
0.4675 ± 0.0050	0.2001 ± 0.0022	0.7003 ± 0.0046	364.52	1049.5	1049.3 ± 0.5	0.6945 ± 0.0048	0.9147 ± 0.0018	1.14 ± 0.01	1.53 ± 0.00
0.4675 ± 0.0050	0.2521 ± 0.0028	0.6497 ± 0.0049	364.52	1011.9	1012.1 ± 0.5	0.6445 ± 0.0051	0.9055 ± 0.0017	1.18 ± 0.01	1.42 ± 0.00
0.4675 ± 0.0050	0.3119 ± 0.0034	0.5999 ± 0.0052	364.52	973.3	973.5 ± 0.6	0.5955 ± 0.0053	0.8963 ± 0.0017	1.23 ± 0.01	1.33 ± 0.00
0.4675 ± 0.0050	0.3825 ± 0.0041	0.5500 ± 0.0053	364.52	932.4	932.6 ± 0.6	0.5469 ± 0.0054	0.8865 ± 0.0017	1.27 ± 0.01	1.27 ± 0.00
0.4675 ± 0.0050	0.4669 ± 0.0050	0.5003 ± 0.0053	364.52	889.1	889.0 ± 0.6	0.4987 ± 0.0054	0.8759 ± 0.0017	1.33 ± 0.01	1.21 ± 0.00
0.4721 ± 0.0051	0.4688 ± 0.0050	0.5017 ± 0.0053	364.51	890.3	890.3 ± 0.6	0.5002 ± 0.0054	0.8762 ± 0.0017	1.33 ± 0.01	1.21 ± 0.00
0.3873 ± 0.0042	0.4688 ± 0.0050	0.4524 ± 0.0053	364.51	840.3	840.5 ± 0.5	0.4491 ± 0.0053	0.8636 ± 0.0018	1.39 ± 0.01	1.16 ± 0.00
0.3168 ± 0.0035	0.4688 ± 0.0050	0.4033 ± 0.0052	364.51	786.7	786.7 ± 0.5	0.3983 ± 0.0052	0.8489 ± 0.0018	1.45 ± 0.02	1.12 ± 0.00
0.2571 ± 0.0029	0.4688 ± 0.0050	0.3542 ± 0.0050	364.51	728.4	728.3 ± 0.6	0.3476 ± 0.0050	0.8315 ± 0.0019	1.53 ± 0.02	1.09 ± 0.00
0.2065 ± 0.0023	0.4688 ± 0.0050	0.3058 ± 0.0047	364.52	666.2	666.1 ± 0.7	0.2979 ± 0.0046	0.8103 ± 0.0020	1.61 ± 0.02	1.07 ± 0.00
0.1619 ± 0.0019	0.4688 ± 0.0050	0.2567 ± 0.0043	364.52	597.8	597.7 ± 0.6	0.2480 ± 0.0042	0.7829 ± 0.0020	1.69 ± 0.03	1.04 ± 0.00
0.1232 ± 0.0015	0.4688 ± 0.0050	0.2081 ± 0.0037	364.52	524.7	524.6 ± 0.5	0.1992 ± 0.0037	0.7467 ± 0.0020	1.79 ± 0.03	1.03 ± 0.00
0.0891 ± 0.0011	0.4688 ± 0.0050	0.1597 ± 0.0031	364.52	445.6	445.7 ± 0.5	0.1511 ± 0.0031	0.6955 ± 0.0018	1.89 ± 0.04	1.02 ± 0.00
0.0592 ± 0.0008	0.4688 ± 0.0050	0.1121 ± 0.0025	364.52	362.5	362.6 ± 0.7	0.1049 ± 0.0024	0.6186 ± 0.0015	2.01 ± 0.04	1.01 ± 0.00
0.0321 ± 0.0005	0.4688 ± 0.0050	0.0641 ± 0.0017	364.52	272.7	272.7 ± 0.6	0.0592 ± 0.0016	0.4842 ± 0.0013	2.13 ± 0.06	1.00 ± 0.00
0.0230 ± 0.0005	0.4688 ± 0.0050	0.0467 ± 0.0014	364.52	238.8	238.7 ± 0.4	0.0430 ± 0.0013	0.4074 ± 0.0015	2.17 ± 0.06	1.00 ± 0.00
0.0125 ± 0.0003	0.4688 ± 0.0050	0.0259 ± 0.0010	364.52	196.8	196.8 ± 0.7	0.0237 ± 0.0009	0.2768 ± 0.0024	2.23 ± 0.07	1.00 ± 0.00
0.0000 ± 0.0000	0.4688 ± 0.0050	0.0000 ± 0.0000	364.52	143.3	143.3 ± 0.7	0.0000 ± 0.0000	0.0000 ± 0.0000	2.30 ± 0.08	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_{expt}; and the pressure calculated from the Legendre polynomial fit is p_{leg}; γ_1 and γ_2 are the calculated activity coefficients.

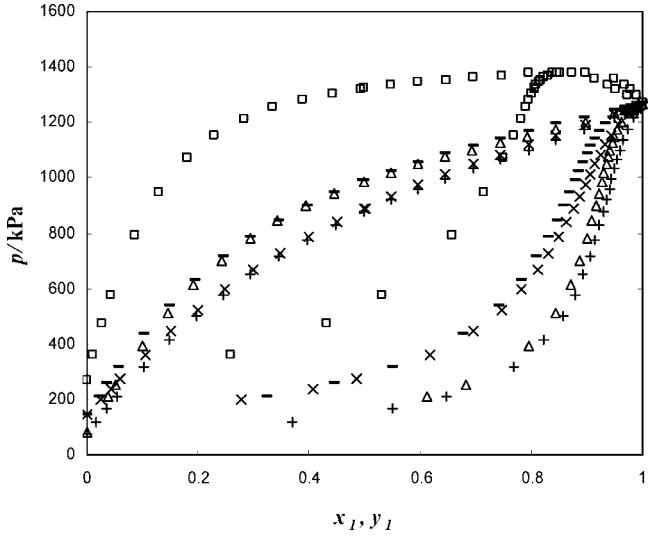

Figure 1. Pressure−composition diagram for *trans*-2-butene (1) + alcohol (2) at 364.5 K: □, *trans*-2-butene + methanol; Δ, + 1-propanol; −, + 2-propanol; +, + 2-butanol; ×, + 2-methyl-2-propanol.

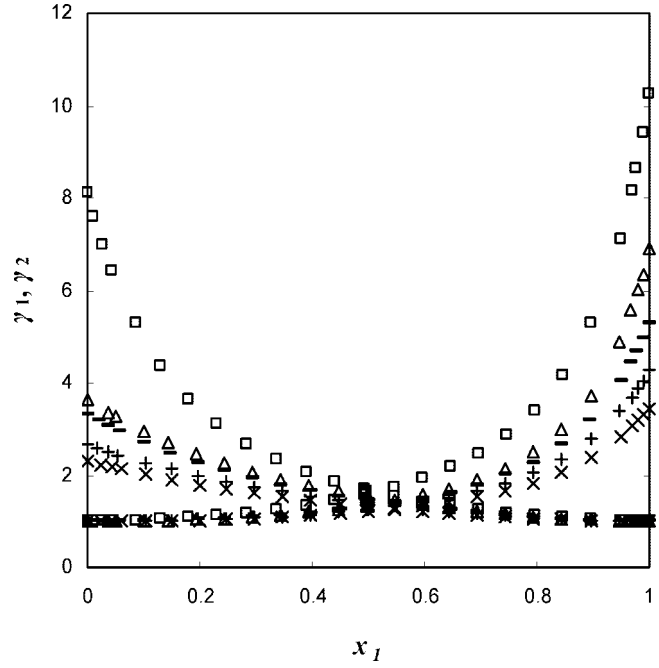

Figure 2. Activity coefficient−composition diagram with the values from the Legendre polynomial expression for *trans*-2-butene (1) + alcohol (2) at 364.5 K: □, *trans*-2-butene + methanol; Δ, + 1-propanol; −, + 2-propanol; +, + 2-butanol; ×, + 2-methyl-2-propanol.

coefficient in the vapor phase for component i; p_i^s is the vapor pressure of pure component i at system temperature; p is the total pressure; V_i^L is the molar volume of pure component i in the liquid phase at system temperature and pressure; R is the universal gas constant; and T is the system temperature.

The fugacities were calculated using the Soave−Redlich−Kwong equation of state[15] with the binary interaction parameters set at 0. The liquid molar volume in the Poynting correction was calculated with the Rackett equation.[16] The liquid phase activity coefficients were obtained by optimizing the parameters of Legendre polynomials.[17] The number of parameters was chosen separately for each system to obtain the best results without overfitting. The data reduction scheme is presented in detail in Uusi-Kyyny et al.[12] The critical properties used in the data reduction are presented in Table 3.

Error Analysis. The overall uncertainty in the temperature measurements was ± 0.03 K in the water bath. The overall uncertainty in the pressure measurements was ± 0.4 kPa in the cell and ± 20 kPa in the syringe pumps. The uncertainty in the injected volumes was ± 0.02 cm^3, obtained from calibrations with distilled water. Liquid densities of pure components were calculated from a correlation.[18] The error in the calculated density was considered less than 1.0 %. Volume change due to

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

trans-2-butene (1)	+ methanol	+ 1-propanol	+ 2-propanol	+ 2-butanol	+ 2-methyl-2-propanol
Legendre, $a_{1,0}$	2.0361	1.5003	1.3462	1.1471	0.97813
Legendre, $a_{2,0}$	0.099906	0.28931	0.21169	0.22579	0.19329
Legendre, $a_{3,0}$	0.16322	0.10418	0.085275	0.067553	0.057770
Legendre, $a_{4,0}$	0.018438	0.031086	0.019417	0.0099763	0.010070
Legendre, $a_{5,0}$	0.011995	0.0059960	0.0032925	0	0
Δp/kPa	0.10	−0.15	−0.11	−0.10	−0.04
$\lvert\Delta p\rvert$/kPa	1.02	0.33	0.30	0.44	0.18
Wilson $\lambda_{1,2}$/K	182.8	110.5	99.94	93.45	60.71
Wilson $\lambda_{2,1}$/K	896.7	639.8	540.3	449.3	395
Wilson volume ratio[b]	2.197	1.193	1.165	0.971	0.943
Δp/kPa	−3.16	0.08	1.49	−0.52	1.14
$\lvert\Delta p\rvert$/kPa	5.10	1.17	2.12	1.40	1.69

[a] The Legendre model parameters were obtained with data reduction from measured values. Wilson parameters were fit from regressed values, Wilson volume ratios, average pressure residual Δp, and absolute average pressure residual $\lvert\Delta p\rvert$ for *trans*-2-butene (1) + methanol, + 1-propanol, + 2-propanol, + 2-butanol, and + 2-methyl-2-propanol. [b] Defined as v_1/v_2, where v_i is the liquid molar volume of component i at the normal boiling point (ref 27).

Table 10. Comparison between the VLE Data Generated by the Predictive Methods UNIFAC and UNIFAC−Dortmund against the Fitted Legendre Polynomial for *trans*-2-Butene (1) + Alcohols (2)

trans-2-Butene (1)	+ methanol	+ 1-propanol	+ 2-propanol	+ 2-butanol	+ 2-methyl-2-propanol
			Legendre		
Δp/kPa	0.10	−0.15	−0.11	−0.10	−0.04
$\lvert\Delta p\rvert$/kPa	1.02	0.33	0.30	0.44	0.18
γ^{∞}_1	8.11	3.63	3.33	2.66	2.30
γ^{∞}_2	10.27	6.90	5.29	4.27	3.45
			UNIFAC		
Δp/kPa	69.89	−25.09	8.14	−3.56	27.43
$\lvert\Delta p\rvert$/kPa	72.86	25.34	16.93	13.12	27.89
γ^{∞}_1	7.20	2.88	2.88	2.22	2.21
γ^{∞}_2	14.57	6.36	6.36	4.99	5.02
			UNIFAC−Dortmund		
Δp/kPa	13.23	3.58	0.86	7.38	−2.06
$\lvert\Delta p\rvert$/kPa	24.38	11.46	14.27	14.60	12.84
γ^{∞}_1	7.43	3.29	2.84	2.35	1.96
γ^{∞}_2	14.56	7.94	6.36	5.63	4.20

mixing was neglected. Because of the small excess volumes of the solutions, the error caused by this assumption was considered negligible.[19]

The procedure used to calculate the maximum error for the number of injected moles (n_i) and the total composition (z_i) is the same as in Laakkonen et al.[20] with improvements by Hynynen et al.[21] The maximum errors for the reduced variables x_i, y_i, p_{leg}, and γ_i were calculated by conducting the Barker data reduction with the upper and lower errors of the measured variables n_i, z_i, T, and p_{exptl} and considering the maximum deviation from the original reduction results as the theoretical maximum error for the reduced variables. The calculated uncertainties gave an estimate of the error scale of the reduced variable.

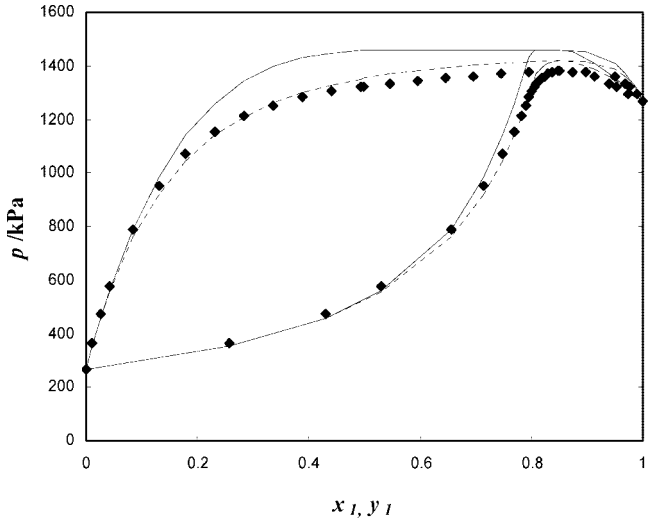

Figure 3. Pressure−composition diagram for the *trans*-2-butene (1) + methanol (2) system at 364.5 K: ♦, experimental values; —, UNIFAC results; ···, UNIFAC−Dortmund results.

Table 11. Measured Azeotropic Composition of *trans*-2-Butene (1) + Methanol (2), Compared with UNIFAC and UNIFAC−Dortmund Model Predictions

	T/K	x_1	p/kPa
this work	364.52	0.854	1385.1
UNIFAC	364.52	0.829	1460.1
UNIFAC−Dortmund	364.52	0.854	1419.6
ref 3	332.07	0.988	607.9

Results and Discussion

The VLE measurements and the results of the Barker regressions are presented in Tables 4 to 8, together with the estimated maximum errors. The injected amounts of moles are presented in the tables with more digits than their error estimates would require; this is done to permit the repetition of our calculations. The experimental pressure as a function of vapor and liquid composition is shown in Figure 1. The activity coefficients from Tables 4 to 8 as functions of liquid composition are shown in Figure 2. The system *trans*-2-butene + methanol showed azeotropic behavior at x(*trans*-2-butene) = 0.854, p_{leg} = 1385.1 kPa, and T = 364.52 K, calculated with the Legendre polynomial (experimental pressure maximum of 1381.0 kPa at 364.52 K). The Legendre[17] parameters obtained

by data reduction and Wilson[24] activity coefficient model parameters are presented in Table 9.

The predictive UNIFAC models are compared to the fitted Legendre polynomial in Table 10. The UNIFAC and UNIFAC−Dortmund parameters used for the predictions included the revisions by Wittig et al.[22] and Gmehling et al.[23] For the methanol molecule, the UNIFAC models provide a predetermined methanol group, or the molecule can be assembled from a CH_3- and an OH− (primary) group. In this case, it was surprising to find that the prediction was actually better with the assembled methanol molecule. However, the predetermined methanol group was used in further comparisons since most estimation method users will probably use the predetermined methanol group by default. When using the assembled methanol molecule, the pressure residuals and infinite dilution activity coefficients were $\Delta p = 23.82$ kPa, $|\Delta p| = 27.79$ kPa, $\gamma^{\infty}{}_1 = 7.28$, and $\gamma^{\infty}{}_2 = 11.24$ for UNIFAC, and $\Delta p = 2.60$ kPa, $|\Delta p| = 9.18$ kPa, $\gamma^{\infty}{}_1 = 7.29$, and $\gamma^{\infty}{}_2 = 11.06$ for UNIFAC–Dortmund.

The UNIFAC−Dortmund model performs better compared to UNIFAC in all the systems except *trans*-2-butene + 2-butanol; especially for the systems *trans*-2-butene + methanol and + 2-methyl-2-propanol, the pressure residuals are substantially smaller with UNIFAC−Dortmund than with UNIFAC. The predictive methods seem to overestimate the infinite dilution activity coefficients for all the alcohols except 1-propanol and underestimate the infinite dilution activity coefficients for *trans*-2-butene. Figure 3 shows a comparison in terms of vapor pressures between experimental data and predictions by UNIFAC and UNIFAC−Dortmund for the system *trans*-2-butene + methanol. Both UNIFAC and UNIFAC−Dortmund predict an azeotrope in the *trans*-2-butene + methanol system, and UNIFAC−Dortmund also predicts the position of the azeotrope quite accurately. Zaytseva et al.[3] also observed an azeotrope at x(*trans*-2-butene) = 0.988 at 332.07 K. In Table 11, the measured azeotrope is compared with the values predicted by the UNIFAC models. In Figure 3 and Table 11, the values were calculated using the predetermined methanol group.

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