Vapor Liquid Equilibrium for Six Binary Systems of C_4-Hydrocarbons + 2-Propanone

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Isothermal vapor−liquid equilibrium of the six binary systems 2-propanone + *n*-butane, + 2-methylpropane, + 1-butene, + *cis*-2-butene, + 2-methylpropene, + *trans*-2-butene were measured from (364.1 to 365.46) K with an automated static total pressure apparatus. Measured *pTz* data was reduced into *pTxy* data using the Barker method. Error analysis was conducted for all measured and calculated data. All measured systems exhibited positive deviation from Raoult's law, and an azeotropic point was found for the *n*-butane + 2-propanone system. Parameters of Wilson and UNIQUAC activity coefficient models were regressed with the experimental VLE data. Results obtained with two predictive methods, UNIFAC and COSMO-RS, were compared with measured data.

Introduction

Accurate vapor−liquid equilibrium (VLE) data are essential in simulation and design of industrial chemical separation processes such as distillation. The static total pressure apparatus used in this work provides a reliable method for determination of VLE based on measured total pressures and initial concentrations of components. The advantages of the method include the absence of sample withdrawal and the effective time utilization in measurements. The importance of the studied components in chemical industry is manifested through the fact that they are used in production processes of tertiary ethers. As the economically negative effects of increased emissions in energy production become more pronounced, the role of additive components that contribute the cleaner combustion processes continues to grow in importance.

Younghun et al.[1] have measured *n*-butane + 2-methylpropane at 330.2 K, 2-methylpropane + 2-propanone at 318.6 K, 1-butene + 2-propanone at 323.3 K, *cis*-2-butene + 2-propanone at 331.9 K, 2-methylpropene + 2-propanone at 323.1 K, and *trans*-2-butene + 2-propanone at 332.1 K. *n*-Butane + 2-propanone have also been previously measured[2] in temperature range of (273.2 to 313.2) K. Excess enthalpies for *n*-butane + 2-propene have been reported[3] at 233.15, 253.15, and 263.15 K. Solubilities of *trans*-2-butene in 2-propanone were found in the literature[4] at 298.15 and 323.15 K. Solubilities of 2-methylpropane and 2-methylpropene in 2-propanone have been measured[5] at 278.15, 298.15, and 318.15 K.

COSMO-RS[16] has appeared as an alternative method to structure-interpolating group contribution methods (GCMs), which have been widely used by chemical engineers to predict thermophysical properties of liquid solutions for which adequate experimental data are not available. COSMO-RS is unlike GCMs able to produce the necessary information about the molecular interactions without extensive use of experimental data, which makes it more suitable for predictive purposes.

Table 1. Vapor Pressure p^{l+g} Measured and Calculated from Literature Correlations

		p^{l+g}/kPa			
component	*T*/K	this work	Reid et al.[23]	Yaws[24]	Perry and Green[25]
2-propanone	364.52	296.80	296.31	296.73	296.65
	365.43	302.56	303.69	304.14	304.07
	364.51	294.30	296.23	296.65	296.57
	364.51	296.40			
	364.51	297.10			
	364.51	297.10			
n-butane	364.51	1284.70	1289.10	1286.16	1286.54
2-methylpropane	364.50	1685.60	1675.64	1682.98	1685.11
1-butene	364.51	1510.50	1514.12	1526.04	1511.61
cis-2-butene	365.43	1213.01	1210.45	1202.27	1218.13
2-methylpropene	364.51	1546.20	1541.40	1556.90	1543.12
trans-2-butene	364.50	1269.20		1277.59	1274.53

Experimental Section

Materials. 2-Propanone (99.5 mass %, purity determined by gas chromatography) was provided by Merck. *n*-Butane (99.95 mass %) and 2-methylpropane (99.95 mass %) were purchased from AGA Oy. 1-Butene (99.6 mass %), *cis*-2-butene (99.4 mass %), 2-methylpropene (99.8 mass %), and *trans*-2-butene (99.4 mass %) were acquired from Messer Finland Oy. 2-Propanone was dried over molecular sieves (Merck, 3 Å) before the degassing procedure. The degassing procedure was conducted with a distillation method comparable to the one described by Fischer and Gmehling.[6] All other components were degassed in syringe pumps by opening the vacuum line valve 10 times for a period of 10 s. The success of the degassing procedure was tested by comparing the measured vapor pressures with the values calculated from literature correlations presented in Table 1.

Apparatus and Procedure. The main principles of the static total pressure apparatus and experimental setup are discussed thoroughly in recent publications.[7−9] The temperature of the water bath, syringe pumps, and equilibrium cell were measured with Pt-100 probes connected to a Systemteknik S2541 temperature meter. The temperature probes were calibrated at the

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Finnish National Standards Laboratory. The resolution of the temperature measurement system was 0.005 K, and the calibration uncertainty was ± 0.015 K. The overall uncertainty of the temperature measurement was estimated to be ± 0.03 K.

The pressure was measured with Digiquartz 2100A-101-CE pressure transducer (kPa) equipped with a Digiquartz 740 intelligent display unit. The calibration of the pressure measurement system was conducted at the Finnish National Standards Laboratory. To avoid the condensation effects in pressure measurement line, the pressure transducer and the tube connecting the pressure transducer to the equilibrium cell were electrically heated. The uncertainty of the display unit of the pressure measurement was ± 0.069 kPa. The overall accuracy of the pressure measurement system was ± 0.2 kPa including the uncertainty of pressure transducer, the heated pressure measurement line, and the equilibrium cell. The components were injected to the cell with syringe pumps (Isco 260 D and Isco 100 DM). The temperatures and the pressures of the barrels of syringe pumps were controlled. The temperatures of the syringe pumps were measured with temperature probes located in contact with the syringe pump barrels. The pressures of the syringe pump barrels were measured with built-in strain gauge pressure meters. The injection volumes of the pumps were calibrated gravimetrically prior to the measurements with distilled water.

The total volume of the equilibrium cell was 113.10 cm^3. The volume was determined by injecting degassed distilled water to the cell at 298.15 K. The estimated uncertainty of cell volume measurement was ± 0.05 cm^3. The valves for filling and evacuation the cell and the fitting for emptying the cell were welded the cell lid. The pressure measurement line tube was soldered to the cell lid. The cell content was mixed with a magnetic stirred, and small baffles were installed to the cell in order to reduce the equilibration time. The cell was immersed in a water bath, which was built of an insulated cylindrical vessel with a volume of approximately 70 dm^3. The temperature of the water bath was maintained constant with a heating coil located on the inside wall of the bath. The temperature stability of the bath was estimated to be ± 0.02 K as discussed in our earlier paper.[9]

A similar measurement procedure was used for all of the investigated systems. The composition range of the investigated systems was measured in two parts: measurements were started from both ends of the composition scale and continued to approximately equimolar mixture. Injected volumes were optimized so that the equilibrium cell became nearly filled with mixture in both steps of the measurement in order to improve the measurement accuracy of the overall compositions in equilibrium cell. Pure component vapor pressures and from 26 to 27 points were measured for each investigated binaries. The syringe pumps were operated in constant pressure mode (2000 kPa) to ensure the accuracy of the volume measurement and to prevent contamination of the degassed components. The amount of injected component was calculated from the displacement of the piston of the syringe pump, temperature and pressure of the pump were measured, and liquid densities were calculated from a literature pressure correlation. The Hankinson−Brobst−Thomson method[10] was used to take the effect of pressure syringe pump on liquid densities into account. The cell and bath contents were mixed continuously during the measurements.

In the measurements component 1 was first introduced into the cell, and its vapor pressure was measured. The procedure was repeated in order to preclude the possibility of incomplete degassing. Increased vapor pressure would indicate incomplete degassing due to the dissolved gases. After the pure component vapor pressure measurement, a predetermined amount of component 2 was added to the equilibrium cell. The cell content was mixed with a magnetic mixer, and the cell was allowed to equilibrate for 20 min. The additions of component 2 were continued until the target composition was reached. A similar procedure was used to measure the other side of the isotherm beginning with injection of component 2 into the equilibrium cell and checking its vapor pressure. The equilibrium cell was emptied and evacuated between the measurements. The overall success of the run could be verified by comparing the measured pressures when the different sides of the isotherm meet at the mole fraction of approximately 0.5. The run was considered as successful when the difference between measured pressures at isotherm end points was lower than the measurement accuracy.

Table 2. Pure Component Physical Properties[a]

component	T_c/K	p_c/MPa	ω	υ^b/cm^3	R_{UNIQ}[d]	Q_{UNIQ}[d]
2-propanone[11]	508.2	4.7015	0.3064	73.93[c]	2.574	2.336
n-butane[11]	425.18	3.7969	0.1993	96.553	3.151	2.776
2-methylpropene[11]	408.14	3.648	0.1770	97.704	3.150	2.772
1-butene[11]	419.59	4.019	0.1867	89.621	2.921	2.564
cis-2-butene[11]	435.58	4.2058	2.2030	87.45	2.919	2.563
2-methylpropene[11]	417.9	3.999	0.1893	89.424	2.920	2.684
trans-2-butene[11]	428.63	4.1024	0.2182	89.415	2.919	2.563

[a] T_c, critical temperature; p_c, critical pressure; ω, acentric factor; υ, liquid molar volume; R_{NUIQ}, at normal boiling point, UNIQUAC volume parameter; Q_{UNIQ}, UNIQUAC area paremeter. [b] At normal boiling point. [c] At 298.15 and 0.101325 MPa. [d] Reid et al.[23]

The data transfer between the water bath, temperature and pressure meters, stepping motors and syringe pumps, and the PC were operated via SmartIO C168H/8 ports card at a PCI bus. The actual run was planned in a spreadsheet program and transferred into the automation control system. Once the program was started, the proceedings of the measurements was followed with trend plots. Data written in a file as a function of time allowed the detailed analysis of the measurement and further analysis of the final results.

Error Analysis. Error estimates for the total mole fractions in the equilibrium cell were obtained with a total differentiation method from absolute errors of measured variables, which have been reported above. The uncertainty of overall composition depends on the uncertainty of injected amounts of components. The estimated inaccuracy of injected volumes $\Delta V_1 \pm 0.02$ cm^3 was obtained from calibration experiments with distilled water. The reported uncertainties for temperature and pressure measurement of the pumps were $\Delta T \pm 0.1$K and $\Delta P \pm 20$ kPa, respectively. Component liquid densities were calculated from correlations with reported uncertainties,[11] which were less than 1.0 % for 1-butene, *n*-butane, and 2-methylpropane and less than 3.0 % for *cis*-2-butene, 2-methylpropene, *trans*-2-butene, and 2-propanone. Mathematical treatment of the error analysis is presented elsewhere.[7] Uncertainties for the reduced variables were obtained by conducting the Barker data reduction with upper and lower limits of the measured n_i, T, and P values and taking the maximum deviation from the original reduction results as the theoretical maximum error for the corresponding reduced variables. The calculated uncertainties were considered to give some estimate of the error scale of the reduced variables even though the maximum errors do not necessarily occur at the upper or lower limits of the measured variables.

Data Reduction. The Barker[12] method was used to convert the measured pressures and injected molar amounts of components into composition of vapor and liquid phases. The method requires use of an activity coefficient model, which can predict

Table 3. VLE Data for the *n*-Butane (1) + 2-Propanone (2) System at 364.51 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
0.5036 ± 0.0054	0.0	1.0	364.51	1284.50	1284.50 ± 0.03	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	3.44 ± 0.01
0.5036 ± 0.0054	0.0059 ± 0.0003	0.9884 ± 0.0008	364.51	1285.40	1284.97 ± 0.06	0.9884 ± 0.0006	0.9884 ± 0.0006	1.00 ± 0.01	3.33 ± 0.01
0.5036 ± 0.0054	0.0113 ± 0.0004	0.9781 ± 0.001	364.51	1285.40	1284.77 ± 0.07	0.9781 ± 0.0006	0.9787 ± 0.0006	1.00 ± 0.01	3.24 ± 0.01
0.5036 ± 0.0054	0.0162 ± 0.0004	0.9688 ± 0.0011	364.51	1284.80	1284.13 ± 0.08	0.9687 ± 0.0005	0.9704 ± 0.0005	1.00 ± 0.01	3.15 ± 0.01
0.5036 ± 0.0054	0.0272 ± 0.0006	0.9488 ± 0.0015	364.51	1282.00	1281.47 ± 0.08	0.9485 ± 0.0005	0.9537 ± 0.0005	1.00 ± 0.01	2.99 ± 0.01
0.5036 ± 0.0054	0.0583 ± 0.0009	0.8963 ± 0.0024	364.50	1268.40	1268.38 ± 0.09	0.8952 ± 0.0004	0.9171 ± 0.0003	1.02 ± 0.01	2.61 ± 0.01
0.5036 ± 0.0054	0.0904 ± 0.0012	0.8478 ± 0.0031	364.50	1250.50	1250.87 ± 0.11	0.8459 ± 0.0003	0.8901 ± 0.0001	1.03 ± 0.01	2.33 ± 0.01
0.5036 ± 0.0054	0.1276 ± 0.0016	0.7978 ± 0.0037	364.51	1229.70	1229.80 ± 0.11	0.7951 ± 0.0003	0.8674 ± 0.0003	1.06 ± 0.01	2.09 ± 0.01
0.5036 ± 0.0054	0.1698 ± 0.002	0.7478 ± 0.0042	364.51	1206.40	1206.53 ± 0.10	0.7446 ± 0.0002	0.8481 ± 0.0004	1.09 ± 0.01	1.90 ± 0.01
0.5036 ± 0.0054	0.2182 ± 0.0025	0.6977 ± 0.0046	364.51	1181.80	1181.80 ± 0.07	0.6943 ± 0.0001	0.8313 ± 0.0004	1.13 ± 0.01	1.74 ± 0.01
0.5036 ± 0.0054	0.2736 ± 0.0031	0.648 ± 0.005	364.52	1156.20	1155.98 ± 0.06	0.6446 ± 0.0001	0.8162 ± 0.0004	1.17 ± 0.01	1.61 ± 0.01
0.5036 ± 0.0054	0.338 ± 0.0037	0.5984 ± 0.0052	364.53	1129.00	1128.70 ± 0.07	0.5954 ± 0.0001	0.8020 ± 0.0004	1.22 ± 0.01	1.49 ± 0.01
0.5036 ± 0.0054	0.4145 ± 0.0045	0.5485 ± 0.0053	364.50	1099.00	1099.22 ± 0.14	0.5462 ± 0.0002	0.7881 ± 0.0004	1.29 ± 0.01	1.40 ± 0.01
0.5076 ± 0.0054	0.5133 ± 0.0055	0.4972 ± 0.0053	364.51	1067.00	1066.75 ± 0.19	0.4960 ± 0.0002	0.7735 ± 0.0004	1.36 ± 0.01	1.32 ± 0.01
0.5036 ± 0.0054	0.5103 ± 0.0055	0.4967 ± 0.0053	364.50	1065.70	1066.15 ± 0.17	0.4954 ± 0.0002	0.7733 ± 0.0004	1.36 ± 0.01	1.32 ± 0.01
0.4149 ± 0.0045	0.5133 ± 0.0055	0.447 ± 0.0053	364.51	1029.30	1029.17 ± 0.28	0.4439 ± 0.0003	0.7574 ± 0.0004	1.44 ± 0.01	1.25 ± 0.01
0.338 ± 0.0037	0.5133 ± 0.0055	0.397 ± 0.0052	364.51	986.80	986.80 ± 0.12	0.3919 ± 0.0005	0.7394 ± 0.0006	1.54 ± 0.01	1.19 ± 0.01
0.273 ± 0.003	0.5133 ± 0.0055	0.3472 ± 0.0049	364.52	938.40	938.38 ± 0.10	0.3401 ± 0.0003	0.7187 ± 0.0007	1.66 ± 0.01	1.14 ± 0.01
0.2178 ± 0.0024	0.5133 ± 0.0055	0.2979 ± 0.0046	364.51	883.00	883.02 ± 0.10	0.2890 ± 0.0004	0.6939 ± 0.0007	1.80 ± 0.01	1.10 ± 0.01
0.1697 ± 0.0019	0.5133 ± 0.0055	0.2484 ± 0.0042	364.51	818.40	818.41 ± 0.68	0.2381 ± 0.0009	0.6625 ± 0.0012	1.96 ± 0.01	1.07 ± 0.01
0.1283 ± 0.0015	0.5133 ± 0.0055	0.1999 ± 0.0036	364.51	744.90	744.72 ± 0.27	0.1889 ± 0.0007	0.6220 ± 0.0010	2.14 ± 0.01	1.04 ± 0.01
0.0917 ± 0.0011	0.5133 ± 0.0055	0.1515 ± 0.003	364.51	659.00	659.00 ± 0.06	0.1408 ± 0.0008	0.5656 ± 0.0008	2.35 ± 0.01	1.02 ± 0.01
0.0586 ± 0.0008	0.5133 ± 0.0055	0.1025 ± 0.0023	364.51	558.60	558.57 ± 2.37	0.0935 ± 0.0005	0.4799 ± 0.0020	2.59 ± 0.02	1.01 ± 0.01
0.0293 ± 0.0005	0.5133 ± 0.0055	0.0539 ± 0.0014	364.51	443.70	443.70 ± 0.18	0.0481 ± 0.0009	0.3372 ± 0.0008	2.88 ± 0.05	1.00 ± 0.01
0.0184 ± 0.0004	0.5133 ± 0.0055	0.0345 ± 0.0011	364.51	393.00	393.33 ± 0.61	0.0305 ± 0.0009	0.2493 ± 0.0019	3.00 ± 0.06	1.00 ± 0.01
0.0	0.5133 ± 0.0055	0.0	364.51	297.10	297.10 ± 0.01	0.0000 ± 0.0000	0.0000 ± 0.0000	3.24 ± 0.08	1.00 ± 0.01

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

Table 4. VLE Data for the 2-Methylpropane (1) + 2-Propanone (2) System at 364.51 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
0.4864 ± 0.0053	0.0	1.0	364.50	1685.60	1685.60 ± 0.03	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	3.41 ± 0.02
0.4864 ± 0.0053	0.0049 ± 0.0003	0.9899 ± 0.0008	364.51	1682.10	1681.91 ± 0.17	0.9898 ± 0.0006	0.9914 ± 0.0005	1.00 ± 0.01	3.32 ± 0.02
0.4864 ± 0.0053	0.0099 ± 0.0004	0.9801 ± 0.0009	364.50	1678.00	1677.76 ± 0.21	0.9798 ± 0.0006	0.9832 ± 0.0005	1.00 ± 0.01	3.24 ± 0.01
0.4864 ± 0.0053	0.015 ± 0.0004	0.9701 ± 0.0011	364.51	1673.40	1673.14 ± 0.24	0.9697 ± 0.0005	0.9754 ± 0.0005	1.00 ± 0.01	3.16 ± 0.01
0.4864 ± 0.0053	0.0256 ± 0.0005	0.9501 ± 0.0015	364.51	1662.50	1662.50 ± 0.27	0.9492 ± 0.0005	0.9607 ± 0.0004	1.00 ± 0.01	3.01 ± 0.01
0.4864 ± 0.0053	0.0544 ± 0.0008	0.8994 ± 0.0023	364.50	1629.40	1630.20 ± 0.25	0.8972 ± 0.0004	0.9289 ± 0.0002	1.01 ± 0.01	2.66 ± 0.01
0.4864 ± 0.0053	0.0872 ± 0.0012	0.8479 ± 0.0031	364.50	1592.60	1593.19 ± 0.20	0.8444 ± 0.0003	0.9031 ± 0.0001	1.03 ± 0.01	2.37 ± 0.01
0.4864 ± 0.0053	0.1231 ± 0.0015	0.7981 ± 0.0037	364.51	1555.30	1555.44 ± 0.22	0.7934 ± 0.0002	0.8828 ± 0.0003	1.06 ± 0.01	2.13 ± 0.01
0.4864 ± 0.0053	0.1631 ± 0.0019	0.7489 ± 0.0043	364.51	1517.70	1517.55 ± 0.22	0.7437 ± 0.0002	0.8661 ± 0.0003	1.09 ± 0.01	1.93 ± 0.01
0.4864 ± 0.0053	0.2091 ± 0.0024	0.6994 ± 0.0047	364.51	1479.40	1479.10 ± 0.32	0.6939 ± 0.0003	0.8517 ± 0.0004	1.13 ± 0.01	1.77 ± 0.01
0.4864 ± 0.0053	0.2632 ± 0.003	0.6489 ± 0.005	364.51	1439.80	1439.53 ± 0.34	0.6437 ± 0.0003	0.8385 ± 0.0005	1.17 ± 0.01	1.63 ± 0.01
0.4864 ± 0.0053	0.3254 ± 0.0036	0.5992 ± 0.0053	364.51	1399.40	1399.57 ± 0.24	0.5947 ± 0.0004	0.8265 ± 0.0005	1.23 ± 0.01	1.52 ± 0.01
0.4864 ± 0.0053	0.3986 ± 0.0043	0.5496 ± 0.0054	364.52	1358.00	1358.32 ± 0.09	0.5462 ± 0.0004	0.8149 ± 0.0004	1.29 ± 0.01	1.42 ± 0.01
0.4864 ± 0.0053	0.4871 ± 0.0052	0.4997 ± 0.0054	364.51	1313.00	1314.03 ± 0.20	0.4977 ± 0.0005	0.8030 ± 0.0003	1.36 ± 0.01	1.34 ± 0.01
0.4731 ± 0.0052	0.4926 ± 0.0053	0.4899 ± 0.0054	364.51	1305.50	1305.09 ± 0.48	0.4877 ± 0.0003	0.8005 ± 0.0003	1.38 ± 0.01	1.32 ± 0.01
0.402 ± 0.0044	0.4926 ± 0.0053	0.4494 ± 0.0054	364.51	1262.40	1262.10 ± 0.71	0.4448 ± 0.0004	0.7892 ± 0.0004	1.45 ± 0.01	1.26 ± 0.01
0.3273 ± 0.0036	0.4926 ± 0.0053	0.3992 ± 0.0052	364.51	1203.00	1203.00 ± 0.51	0.3916 ± 0.0005	0.7737 ± 0.0004	1.56 ± 0.01	1.20 ± 0.01
0.2665 ± 0.003	0.4926 ± 0.0053	0.3511 ± 0.005	364.50	1138.80	1138.82 ± 0.09	0.3407 ± 0.0009	0.7563 ± 0.0005	1.68 ± 0.01	1.15 ± 0.01
0.2131 ± 0.0024	0.4926 ± 0.0053	0.302 ± 0.0047	364.50	1063.90	1063.97 ± 0.50	0.2890 ± 0.0010	0.7348 ± 0.0005	1.82 ± 0.01	1.11 ± 0.01
0.1672 ± 0.0019	0.4926 ± 0.0053	0.2535 ± 0.0043	364.51	978.90	978.90 ± 0.11	0.2386 ± 0.0006	0.7077 ± 0.0005	1.99 ± 0.01	1.07 ± 0.01
0.1266 ± 0.0015	0.4926 ± 0.0053	0.2045 ± 0.0037	364.51	880.00	880.00 ± 0.45	0.1888 ± 0.0006	0.6711 ± 0.0006	2.18 ± 0.01	1.05 ± 0.01
0.0913 ± 0.0012	0.4926 ± 0.0053	0.1564 ± 0.0031	364.52	768.90	768.60 ± 0.67	0.1412 ± 0.0006	0.6202 ± 0.0004	2.40 ± 0.01	1.03 ± 0.01
0.0593 ± 0.0008	0.4926 ± 0.0053	0.1075 ± 0.0024	364.51	639.10	639.17 ± 0.25	0.0946 ± 0.0006	0.5406 ± 0.0004	2.67 ± 0.02	1.01 ± 0.01
0.0305 ± 0.0005	0.4926 ± 0.0053	0.0584 ± 0.0015	364.51	492.00	492.02 ± 0.10	0.0500 ± 0.0005	0.4014 ± 0.0005	2.97 ± 0.03	1.00 ± 0.01
0.0201 ± 0.0004	0.4926 ± 0.0053	0.0393 ± 0.0012	364.50	430.00	430.00 ± 3.12	0.0332 ± 0.0013	0.3149 ± 0.0058	3.09 ± 0.04	1.00 ± 0.01
0.0095 ± 0.0003	0.4926 ± 0.0053	0.019 ± 0.0008	364.51	361.40	361.29 ± 1.84	0.0159 ± 0.0007	0.1848 ± 0.0048	3.24 ± 0.05	1.00 ± 0.01
0.0	0.4926 ± 0.0053	0.0	364.51	294.30	294.30 ± 0.01	0.0000 ± 0.0000	0.0000 ± 0.0000	3.38 ± 0.05	1.00 ± 0.00

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

the bubble point pressure with higher accuracy than that with which the pressure is measured. The vapor-phase fugacities were calculated with the Soave−Redlich−Kwong equation of state[13] with a quadratic mixing rule for the attractive parameter and a linear mixing rule for the co-volume parameter. The binary interaction parameter in the quadratic mixing rule was set to the value of zero. The Legendre[14] polynomial was chosen as an activity coefficient model due to its flexible nature, which allows them to accurately represent the liquid-phase nonidealities. The binary interaction parameters in the attraction term of the equation of state were set to the value of zero. The number of terms in the Legendre polynomial was minimized in order to avoid overfitting. The scheme used in data reduction is presented in detail in earlier publications.[9] Physical properties needed in Barker data reduction are presented in Table 2. Data reduction was conducted with VLEFIT software.[15]

COSMO-RS Calculations. All Cosmo-RS calculations were conducted using a continuum model with density functional

Table 5. VLE Data for the 1-Butene (1) + 2-Propanone (2) System at 364.52 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
0.5205 ± 0.0056	0.0	1.0	364.51	1510.50	1510.50 ± 0.07	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	2.70 ± 0.01
0.5205 ± 0.0056	0.0055 ± 0.0003	0.9895 ± 0.0007	364.53	1505.00	1504.39 ± 0.69	0.9893 ± 0.0006	0.9924 ± 0.0004	1.00 ± 0.01	2.63 ± 0.01
0.5205 ± 0.0056	0.011 ± 0.0004	0.9793 ± 0.0009	364.52	1498.00	1497.75 ± 0.32	0.9789 ± 0.0005	0.9853 ± 0.0004	1.00 ± 0.01	2.57 ± 0.01
0.5205 ± 0.0056	0.0165 ± 0.0004	0.9693 ± 0.0011	364.52	1491.40	1491.19 ± 0.28	0.9686 ± 0.0005	0.9786 ± 0.0004	1.00 ± 0.01	2.51 ± 0.01
0.5205 ± 0.0056	0.0276 ± 0.0006	0.9496 ± 0.0015	364.53	1478.00	1477.81 ± 0.26	0.9485 ± 0.0005	0.9662 ± 0.0003	1.00 ± 0.01	2.39 ± 0.01
0.5205 ± 0.0056	0.0592 ± 0.0009	0.8978 ± 0.0023	364.52	1440.10	1440.27 ± 0.11	0.8955 ± 0.0004	0.9378 ± 0.0002	1.01 ± 0.01	2.14 ± 0.01
0.5205 ± 0.0056	0.094 ± 0.0012	0.847 ± 0.0031	364.52	1401.90	1401.91 ± 0.06	0.8436 ± 0.0003	0.9145 ± 0.0001	1.03 ± 0.01	1.93 ± 0.01
0.5205 ± 0.0056	0.1318 ± 0.0016	0.7979 ± 0.0037	364.52	1364.10	1364.06 ± 0.12	0.7939 ± 0.0002	0.8950 ± 0.0002	1.05 ± 0.01	1.77 ± 0.01
0.5205 ± 0.0056	0.1747 ± 0.002	0.7487 ± 0.0042	364.51	1325.50	1325.56 ± 0.14	0.7443 ± 0.0001	0.8775 ± 0.0002	1.07 ± 0.01	1.64 ± 0.01
0.5205 ± 0.0056	0.2247 ± 0.0026	0.6985 ± 0.0046	364.51	1285.80	1285.75 ± 0.14	0.6940 ± 0.0001	0.8610 ± 0.0003	1.10 ± 0.01	1.52 ± 0.01
0.5205 ± 0.0056	0.2817 ± 0.0031	0.6488 ± 0.005	364.51	1245.40	1245.43 ± 0.10	0.6447 ± 0.0001	0.8454 ± 0.0003	1.14 ± 0.01	1.43 ± 0.01
0.5205 ± 0.0056	0.349 ± 0.0038	0.5986 ± 0.0052	364.52	1203.30	1203.30 ± 0.08	0.5951 ± 0.0002	0.8299 ± 0.0003	1.18 ± 0.01	1.35 ± 0.01
0.5205 ± 0.0056	0.4274 ± 0.0046	0.5491 ± 0.0053	364.52	1159.80	1159.86 ± 0.04	0.5466 ± 0.0002	0.8143 ± 0.0003	1.23 ± 0.01	1.28 ± 0.01
0.5205 ± 0.0056	0.5219 ± 0.0056	0.4993 ± 0.0053	364.52	1113.50	1113.62 ± 0.06	0.4979 ± 0.0002	0.7978 ± 0.0003	1.28 ± 0.01	1.23 ± 0.01
0.5211 ± 0.0056	0.5252 ± 0.0056	0.498 ± 0.0053	364.52	1112.90	1112.56 ± 0.42	0.4967 ± 0.0002	0.7973 ± 0.0003	1.28 ± 0.01	1.22 ± 0.01
0.4267 ± 0.0046	0.5252 ± 0.0056	0.4483 ± 0.0053	364.52	1059.80	1059.59 ± 0.28	0.4450 ± 0.0003	0.7782 ± 0.0004	1.34 ± 0.01	1.17 ± 0.01
0.3488 ± 0.0038	0.5252 ± 0.0056	0.3991 ± 0.0052	364.51	1002.70	1002.70 ± 0.08	0.3940 ± 0.0003	0.7568 ± 0.0004	1.41 ± 0.01	1.13 ± 0.01
0.2828 ± 0.0031	0.5252 ± 0.0056	0.35 ± 0.005	364.51	940.70	940.75 ± 0.11	0.3431 ± 0.0004	0.7321 ± 0.0005	1.48 ± 0.01	1.10 ± 0.01
0.2258 ± 0.0025	0.5252 ± 0.0056	0.3006 ± 0.0046	364.52	872.50	872.50 ± 0.13	0.2922 ± 0.0004	0.7022 ± 0.0005	1.57 ± 0.01	1.07 ± 0.01
0.1764 ± 0.002	0.5252 ± 0.0056	0.2514 ± 0.0042	364.51	797.90	797.96 ± 0.10	0.2420 ± 0.0004	0.6652 ± 0.0006	1.66 ± 0.01	1.05 ± 0.01
0.1324 ± 0.0016	0.5252 ± 0.0056	0.2013 ± 0.0036	364.52	714.90	714.83 ± 0.15	0.1916 ± 0.0005	0.6166 ± 0.0006	1.77 ± 0.01	1.03 ± 0.01
0.0946 ± 0.0012	0.5252 ± 0.0056	0.1527 ± 0.003	364.52	626.70	626.47 ± 0.31	0.1434 ± 0.0005	0.5524 ± 0.0005	1.89 ± 0.01	1.02 ± 0.01
0.0607 ± 0.0008	0.5252 ± 0.0056	0.1036 ± 0.0023	364.51	529.40	529.42 ± 0.15	0.0960 ± 0.0005	0.4594 ± 0.0004	2.02 ± 0.01	1.01 ± 0.01
0.0306 ± 0.0005	0.5252 ± 0.0056	0.055 ± 0.0015	364.51	425.00	425.00 ± 0.08	0.0501 ± 0.0005	0.3141 ± 0.0005	2.16 ± 0.02	1.00 ± 0.01
0.0193 ± 0.0004	0.5252 ± 0.0056	0.0355 ± 0.0011	364.51	380.60	380.66 ± 0.29	0.0321 ± 0.0005	0.2291 ± 0.0010	2.22 ± 0.02	1.00 ± 0.01
0.0088 ± 0.0003	0.5252 ± 0.0056	0.0165 ± 0.0007	364.51	336.40	336.32 ± 0.60	0.0148 ± 0.0005	0.1220 ± 0.0019	2.28 ± 0.03	1.00 ± 0.01
0.0	0.5252 ± 0.0056	0.0	364.52	296.80	296.80 ± 0.00	0.0000 ± 0.0000	0.0000 ± 0.0000	2.34 ± 0.00	1.00 ± 0.00

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

Table 6. VLE Data for the *cis*-2-Butene (1) + 2-Propanone (2) System at 365.46 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
0.5286 ± 0.0056	0.0	1.0	365.43	1213.01	1213.01 ± 0.08	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	2.69 ± 0.03
0.5286 ± 0.0056	0.0011 ± 0.0003	0.9979 ± 0.0006	365.44	1212.01	1212.36 ± 0.43	0.9979 ± 0.0007	0.9983 ± 0.0006	1.00 ± 0.01	2.67 ± 0.03
0.5286 ± 0.0056	0.0062 ± 0.0003	0.9884 ± 0.0007	365.44	1209.61	1209.80 ± 0.26	0.9883 ± 0.0006	0.9904 ± 0.0006	1.00 ± 0.01	2.60 ± 0.02
0.5286 ± 0.0056	0.0174 ± 0.0005	0.9681 ± 0.0011	365.43	1203.51	1203.51 ± 0.07	0.9677 ± 0.0005	0.9747 ± 0.0004	1.00 ± 0.01	2.47 ± 0.01
0.5286 ± 0.0056	0.0287 ± 0.0006	0.9485 ± 0.0015	365.43	1196.61	1196.59 ± 0.06	0.9479 ± 0.0005	0.9608 ± 0.0004	1.00 ± 0.01	2.36 ± 0.01
0.5286 ± 0.0056	0.0603 ± 0.0009	0.8977 ± 0.0023	365.38	1174.81	1175.52 ± 0.79	0.8962 ± 0.0004	0.9295 ± 0.0003	1.01 ± 0.01	2.10 ± 0.02
0.5286 ± 0.0056	0.0685 ± 0.001	0.8853 ± 0.0025	365.43	1170.21	1170.20 ± 0.09	0.8836 ± 0.0007	0.9227 ± 0.0004	1.02 ± 0.01	2.04 ± 0.02
0.5286 ± 0.0056	0.094 ± 0.0012	0.849 ± 0.003	365.43	1153.21	1153.16 ± 0.11	0.8467 ± 0.0008	0.9045 ± 0.0004	1.03 ± 0.01	1.90 ± 0.02
0.5286 ± 0.0056	0.1336 ± 0.0016	0.7983 ± 0.0037	365.44	1127.71	1127.80 ± 0.17	0.7954 ± 0.0007	0.8820 ± 0.0003	1.05 ± 0.01	1.74 ± 0.01
0.5286 ± 0.0056	0.1773 ± 0.0021	0.7488 ± 0.0042	365.45	1101.71	1101.71 ± 0.10	0.7455 ± 0.0006	0.8624 ± 0.0002	1.07 ± 0.01	1.60 ± 0.01
0.5286 ± 0.0056	0.227 ± 0.0026	0.6995 ± 0.0046	365.45	1074.42	1074.41 ± 0.07	0.6962 ± 0.0006	0.8443 ± 0.0002	1.10 ± 0.01	1.50 ± 0.01
0.5286 ± 0.0056	0.2849 ± 0.0032	0.6497 ± 0.0049	365.46	1045.02	1045.19 ± 0.25	0.6465 ± 0.0005	0.8267 ± 0.0002	1.14 ± 0.01	1.40 ± 0.01
0.5286 ± 0.0056	0.3529 ± 0.0039	0.5997 ± 0.0052	365.48	1014.12	1014.06 ± 0.02	0.5969 ± 0.0005	0.8090 ± 0.0002	1.18 ± 0.01	1.33 ± 0.01
0.5286 ± 0.0056	0.4329 ± 0.0047	0.5498 ± 0.0053	365.49	981.22	980.83 ± 0.33	0.5476 ± 0.0004	0.7909 ± 0.0002	1.22 ± 0.01	1.26 ± 0.01
0.5286 ± 0.0056	0.5291 ± 0.0056	0.4998 ± 0.0053	365.49	945.52	944.92 ± 0.54	0.4985 ± 0.0001	0.7716 ± 0.0002	1.27 ± 0.01	1.21 ± 0.01
0.5305 ± 0.0057	0.5316 ± 0.0057	0.4995 ± 0.0053	365.48	943.82	944.45 ± 0.71	0.4982 ± 0.0004	0.7715 ± 0.0002	1.27 ± 0.01	1.21 ± 0.01
0.4361 ± 0.0047	0.5316 ± 0.0057	0.4506 ± 0.0053	365.47	904.13	904.59 ± 0.54	0.4480 ± 0.0004	0.7501 ± 0.0004	1.33 ± 0.01	1.16 ± 0.01
0.3569 ± 0.0039	0.5316 ± 0.0057	0.4017 ± 0.0052	365.46	860.73	860.97 ± 0.32	0.3977 ± 0.0004	0.7260 ± 0.0004	1.39 ± 0.01	1.12 ± 0.01
0.2888 ± 0.0032	0.5316 ± 0.0057	0.352 ± 0.005	365.46	812.53	812.53 ± 0.08	0.3467 ± 0.0003	0.6980 ± 0.0004	1.46 ± 0.01	1.09 ± 0.01
0.2314 ± 0.0026	0.5316 ± 0.0057	0.3033 ± 0.0046	365.46	760.43	760.43 ± 0.08	0.2969 ± 0.0003	0.6656 ± 0.0004	1.54 ± 0.01	1.07 ± 0.01
0.1815 ± 0.0021	0.5316 ± 0.0057	0.2545 ± 0.0042	365.46	703.24	703.16 ± 0.49	0.2473 ± 0.0008	0.6261 ± 0.0008	1.62 ± 0.01	1.04 ± 0.01
0.1378 ± 0.0016	0.5316 ± 0.0057	0.2058 ± 0.0037	365.47	640.24	640.24 ± 0.53	0.1983 ± 0.0002	0.5765 ± 0.0002	1.72 ± 0.01	1.03 ± 0.01
0.0995 ± 0.0012	0.5316 ± 0.0057	0.1577 ± 0.0031	365.46	571.74	571.93 ± 0.45	0.1505 ± 0.0008	0.5122 ± 0.0009	1.82 ± 0.01	1.02 ± 0.01
0.0651 ± 0.0009	0.5316 ± 0.0057	0.1091 ± 0.0024	365.46	496.45	496.37 ± 0.16	0.1029 ± 0.0005	0.4225 ± 0.0006	1.92 ± 0.01	1.01 ± 0.01
0.0287 ± 0.0005	0.5316 ± 0.0057	0.0513 ± 0.0014	365.45	397.65	397.66 ± 0.39	0.0477 ± 0.0003	0.2573 ± 0.0008	2.07 ± 0.01	1.00 ± 0.01
0.0206 ± 0.0004	0.5316 ± 0.0057	0.0374 ± 0.0012	365.45	372.65	372.59 ± 0.13	0.0347 ± 0.0003	0.2020 ± 0.0007	2.10 ± 0.01	1.00 ± 0.01
0.0	0.5316 ± 0.0057	0.0	365.43	302.56	302.56 ± 0.07	0.0000 ± 0.0000	0.0000 ± 0.0000	2.20 ± 0.03	1.00 ± 0.00

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

theory (RI-DFT) using a BF functional with TZVP basis set as it was implemented in the Turbomole program[19] (version 5.7). Geometry optimization for the investigated molecules was performed with the Turbomole software as well. Subsequent COSMO calculations were conducted with the Cosmotherm program[20] (COSMOtherm-C21-0104). Despite the ability of COSMO to predict vapor pressures, experimentally determined pure component vapor pressures were used in calculations to avoid any additional errors. For 1-butene several conformers were taking into account in COSMO-RS calculations. Only one optimized geometry was taken into account for all other investigated components in property calculations.

Results and Discussion

VLE Measurements. Measured *PTz* data and results from Barker data reduction for studied systems are presented in Tables

Table 7. VLE Data for the 2-Methylpropene (1) + 2-Propanone (2) System at 365.46 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
0.518 ± 0.0055	0.0	1.0	364.51	1546.20	1546.20 ± 0.02	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	2.57 ± 0.03
0.518 ± 0.0055	0.0059 ± 0.0003	0.9887 ± 0.0007	364.50	1537.70	1537.87 ± 0.17	0.9884 ± 0.0005	0.9923 ± 0.0003	1.00 ± 0.01	2.51 ± 0.02
0.518 ± 0.0055	0.0099 ± 0.0004	0.9813 ± 0.0009	364.50	1532.30	1532.34 ± 0.22	0.9808 ± 0.0006	0.9873 ± 0.0004	1.00 ± 0.01	2.47 ± 0.02
0.518 ± 0.0055	0.0169 ± 0.0004	0.9684 ± 0.0011	364.49	1522.30	1522.48 ± 0.20	0.9676 ± 0.0006	0.9791 ± 0.0004	1.00 ± 0.01	2.40 ± 0.02
0.518 ± 0.0055	0.028 ± 0.0006	0.9486 ± 0.0015	364.50	1506.90	1507.07 ± 0.10	0.9473 ± 0.0006	0.9672 ± 0.0006	1.00 ± 0.01	2.30 ± 0.02
0.518 ± 0.0055	0.0583 ± 0.0009	0.8989 ± 0.0023	364.50	1466.80	1466.88 ± 0.05	0.8963 ± 0.0011	0.9409 ± 0.0009	1.01 ± 0.01	2.07 ± 0.01
0.518 ± 0.0055	0.0928 ± 0.0012	0.8481 ± 0.003	364.50	1425.00	1425.00 ± 0.08	0.8444 ± 0.0015	0.9181 ± 0.0011	1.03 ± 0.01	1.88 ± 0.01
0.518 ± 0.0055	0.1313 ± 0.0016	0.7978 ± 0.0037	364.50	1383.30	1383.27 ± 0.16	0.7934 ± 0.0019	0.8985 ± 0.0013	1.05 ± 0.01	1.73 ± 0.01
0.518 ± 0.0055	0.174 ± 0.002	0.7485 ± 0.0042	364.50	1342.30	1342.23 ± 0.23	0.7438 ± 0.0022	0.8812 ± 0.0014	1.07 ± 0.01	1.60 ± 0.01
0.518 ± 0.0055	0.2236 ± 0.0025	0.6985 ± 0.0046	364.50	1300.20	1300.10 ± 0.26	0.6937 ± 0.0025	0.8649 ± 0.0014	1.10 ± 0.01	1.49 ± 0.01
0.518 ± 0.0055	0.2805 ± 0.0031	0.6487 ± 0.005	364.50	1257.30	1257.29 ± 0.26	0.6443 ± 0.0026	0.8493 ± 0.0015	1.13 ± 0.01	1.40 ± 0.01
0.518 ± 0.0055	0.3464 ± 0.0038	0.5993 ± 0.0052	364.50	1213.10	1213.33 ± 0.22	0.5956 ± 0.0028	0.8339 ± 0.0015	1.17 ± 0.01	1.33 ± 0.01
0.518 ± 0.0055	0.4244 ± 0.0046	0.5496 ± 0.0053	364.50	1167.00	1167.26 ± 0.15	0.5469 ± 0.0028	0.8180 ± 0.0014	1.22 ± 0.01	1.26 ± 0.01
0.518 ± 0.0055	0.5187 ± 0.0055	0.4996 ± 0.0053	364.50	1118.40	1118.40 ± 0.09	0.4981 ± 0.0028	0.8011 ± 0.0014	1.26 ± 0.01	1.21 ± 0.01
0.5238 ± 0.0056	0.5266 ± 0.0056	0.4987 ± 0.0053	364.51	1116.90	1117.43 ± 0.12	0.4973 ± 0.0028	0.8008 ± 0.0014	1.27 ± 0.01	1.21 ± 0.01
0.4294 ± 0.0046	0.5266 ± 0.0056	0.4492 ± 0.0053	364.51	1062.40	1062.38 ± 0.07	0.4460 ± 0.0028	0.7813 ± 0.0014	1.32 ± 0.01	1.16 ± 0.01
0.3519 ± 0.0038	0.5266 ± 0.0056	0.4006 ± 0.0052	364.50	1003.90	1003.90 ± 0.07	0.3955 ± 0.0028	0.7596 ± 0.0014	1.38 ± 0.01	1.13 ± 0.01
0.2845 ± 0.0031	0.5266 ± 0.0056	0.3507 ± 0.005	364.50	939.00	939.04 ± 0.11	0.3439 ± 0.0027	0.7339 ± 0.0014	1.46 ± 0.01	1.09 ± 0.01
0.2272 ± 0.0025	0.5266 ± 0.0056	0.3014 ± 0.0046	364.50	869.40	869.33 ± 0.17	0.2931 ± 0.0025	0.7033 ± 0.0014	1.54 ± 0.01	1.07 ± 0.01
0.1782 ± 0.002	0.5266 ± 0.0056	0.2529 ± 0.0042	364.51	795.10	794.96 ± 0.19	0.2436 ± 0.0023	0.6663 ± 0.0014	1.62 ± 0.02	1.04 ± 0.01
0.1326 ± 0.0016	0.5266 ± 0.0056	0.2011 ± 0.0036	364.50	708.40	708.40 ± 0.08	0.1915 ± 0.0020	0.6152 ± 0.0013	1.73 ± 0.02	1.03 ± 0.01
0.0971 ± 0.0012	0.5266 ± 0.0056	0.1557 ± 0.0031	364.50	625.80	625.97 ± 0.09	0.1465 ± 0.0018	0.5548 ± 0.0011	1.82 ± 0.02	1.02 ± 0.01
0.0635 ± 0.0009	0.5266 ± 0.0056	0.1077 ± 0.0024	364.50	532.00	532.09 ± 0.27	0.1000 ± 0.0014	0.4650 ± 0.0008	1.94 ± 0.03	1.01 ± 0.01
0.0316 ± 0.0005	0.5266 ± 0.0056	0.0566 ± 0.0015	364.51	424.80	424.53 ± 0.16	0.0518 ± 0.0010	0.3156 ± 0.0005	2.06 ± 0.04	1.00 ± 0.01
0.0217 ± 0.0004	0.5266 ± 0.0056	0.0396 ± 0.0012	364.51	387.10	386.94 ± 0.44	0.0360 ± 0.0008	0.2444 ± 0.0013	2.11 ± 0.05	1.00 ± 0.01
0.0	0.5266 ± 0.0056	0.0	364.51	296.40	296.40 ± 0.01	0.0000 ± 0.0000	0.0000 ± 0.0000	2.21 ± 0.06	1.00 ± 0.00

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

Table 8. VLE Data for the *trans*-2-Butene (1) + 2-Propanone (2) System at 364.51 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
0.5247 ± 0.0057	0.0	1.0	364.50	1269.20	1269.20 ± 0.02	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	2.80 ± 0.01
0.5247 ± 0.0057	0.0059 ± 0.0003	0.9889 ± 0.0007	364.51	1266.10	1266.00 ± 0.09	0.9888 ± 0.0006	0.9908 ± 0.0005	1.00 ± 0.01	2.71 ± 0.01
0.5247 ± 0.0057	0.011 ± 0.0004	0.9795 ± 0.0009	364.51	1263.30	1263.04 ± 0.11	0.9793 ± 0.0006	0.9834 ± 0.0005	1.00 ± 0.01	2.65 ± 0.01
0.5247 ± 0.0057	0.0169 ± 0.0004	0.9688 ± 0.0011	364.51	1259.50	1259.30 ± 0.09	0.9684 ± 0.0005	0.9754 ± 0.0004	1.00 ± 0.01	2.57 ± 0.01
0.5247 ± 0.0057	0.0299 ± 0.0006	0.946 ± 0.0015	364.51	1250.60	1250.46 ± 0.10	0.9453 ± 0.0005	0.9596 ± 0.0004	1.00 ± 0.01	2.43 ± 0.01
0.5247 ± 0.0057	0.0601 ± 0.0009	0.8972 ± 0.0023	364.51	1228.20	1228.37 ± 0.08	0.8956 ± 0.0004	0.9304 ± 0.0002	1.01 ± 0.01	2.17 ± 0.01
0.5247 ± 0.0057	0.0944 ± 0.0012	0.8475 ± 0.0031	364.51	1202.90	1203.12 ± 0.13	0.8450 ± 0.0003	0.9055 ± 0.0001	1.03 ± 0.01	1.95 ± 0.01
0.5247 ± 0.0057	0.1327 ± 0.0016	0.7981 ± 0.0037	364.51	1176.20	1176.32 ± 0.16	0.7950 ± 0.0002	0.8842 ± 0.0002	1.05 ± 0.01	1.78 ± 0.01
0.5247 ± 0.0057	0.1761 ± 0.0021	0.7487 ± 0.0042	364.52	1148.20	1148.20 ± 0.17	0.7453 ± 0.0002	0.8650 ± 0.0002	1.08 ± 0.01	1.64 ± 0.01
0.5247 ± 0.0057	0.2265 ± 0.0026	0.6985 ± 0.0046	364.52	1118.60	1118.42 ± 0.15	0.6950 ± 0.0001	0.8471 ± 0.0003	1.11 ± 0.01	1.53 ± 0.01
0.5247 ± 0.0057	0.284 ± 0.0032	0.6488 ± 0.005	364.52	1087.80	1087.61 ± 0.16	0.6455 ± 0.0001	0.8301 ± 0.0003	1.14 ± 0.01	1.43 ± 0.01
0.5247 ± 0.0057	0.3516 ± 0.0038	0.5987 ± 0.0052	364.51	1054.90	1054.90 ± 0.12	0.5959 ± 0.0001	0.8133 ± 0.0003	1.18 ± 0.01	1.35 ± 0.01
0.5247 ± 0.0057	0.4303 ± 0.0046	0.5494 ± 0.0053	364.51	1020.70	1020.80 ± 0.10	0.5473 ± 0.0002	0.7965 ± 0.0003	1.23 ± 0.01	1.28 ± 0.01
0.5247 ± 0.0057	0.5259 ± 0.0056	0.4994 ± 0.0054	364.51	983.40	983.75 ± 0.05	0.4981 ± 0.0002	0.7786 ± 0.0003	1.28 ± 0.01	1.23 ± 0.01
0.5288 ± 0.0057	0.5327 ± 0.0057	0.4981 ± 0.0054	364.51	983.40	983.04 ± 0.06	0.4970 ± 0.0002	0.7781 ± 0.0003	1.28 ± 0.01	1.23 ± 0.01
0.4333 ± 0.0047	0.5327 ± 0.0057	0.4486 ± 0.0053	364.51	941.20	941.07 ± 0.05	0.4459 ± 0.0003	0.7579 ± 0.0004	1.35 ± 0.01	1.18 ± 0.01
0.3534 ± 0.0039	0.5327 ± 0.0057	0.3988 ± 0.0052	364.52	894.70	894.76 ± 0.05	0.3946 ± 0.0003	0.7350 ± 0.0004	1.41 ± 0.01	1.13 ± 0.01
0.2858 ± 0.0032	0.5327 ± 0.0057	0.3492 ± 0.005	364.51	843.80	843.78 ± 0.07	0.3435 ± 0.0004	0.7085 ± 0.0004	1.49 ± 0.01	1.10 ± 0.01
0.2278 ± 0.0026	0.5327 ± 0.0057	0.2996 ± 0.0046	364.51	787.30	787.30 ± 0.10	0.2926 ± 0.0004	0.6769 ± 0.0005	1.58 ± 0.01	1.07 ± 0.01
0.179 ± 0.0021	0.5327 ± 0.0057	0.2515 ± 0.0042	364.52	726.80	726.75 ± 0.13	0.2437 ± 0.0004	0.6393 ± 0.0005	1.67 ± 0.01	1.05 ± 0.01
0.1354 ± 0.0016	0.5327 ± 0.0057	0.2027 ± 0.0037	364.51	658.80	658.80 ± 0.16	0.1946 ± 0.0005	0.5905 ± 0.0006	1.77 ± 0.01	1.03 ± 0.01
0.0965 ± 0.0012	0.5327 ± 0.0057	0.1534 ± 0.003	364.51	583.20	583.15 ± 0.13	0.1456 ± 0.0005	0.5249 ± 0.0006	1.89 ± 0.01	1.02 ± 0.01
0.0623 ± 0.0009	0.5327 ± 0.0057	0.1047 ± 0.0023	364.51	501.00	501.01 ± 0.09	0.0982 ± 0.0005	0.4333 ± 0.0005	2.02 ± 0.01	1.01 ± 0.01
0.0312 ± 0.0005	0.5327 ± 0.0057	0.05526 ± 0.00148	364.51	409.50	409.50 ± 0.07	0.0511 ± 0.0005	0.2908 ± 0.0005	2.17 ± 0.02	1.00 ± 0.01
0.0199 ± 0.0004	0.5327 ± 0.0057	0.03608 ± 0.001123	364.51	372.00	371.75 ± 0.35	0.0332 ± 0.0005	0.2123 ± 0.0012	2.23 ± 0.02	1.00 ± 0.01
0.0	0.5327 ± 0.0057	0.0	364.51	297.10	297.10 ± 0.01	0.0000 ± 0.0000	0.0000 ± 0.0000	2.35 ± 0.03	1.00 ± 0.00

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

3 to 8. All investigated systems show positive deviation from Raoult's law. Error estimates are presented for measured pressure, temperature, and total compositions. Actual errors of calculated liquid, vapor mole fractions, and activity coefficients are typically smaller than theoretical maximum errors due to the high improbability of individual errors being at their upper or lower bounds simultaneously. Injected amount of moles are presented in Tables 3 to 8 using more significant digits than their error estimates would indicate. This is required if someone wants to recalculate the measurements. Experimental pressures for investigated systems are presented as a function of vapor- and liquid-phase compositions in Figure 1. An azeotropic point was found for the *n*-butane (1) + 2-propanone (2) mixture at $x_1 = 0.991$, $p = 1288.7$ kPa, and $T = 364.51$ K. Vapor-phase composition is presented as a function of liquid-phase composition for investigated systems in Figure 2.

Data regression results with Legendre polynomial, Wilson,[21] and UNIQUAC[22] activity coefficient models are presented in Table 9. The calculated average absolute pressure residuals are in all cases higher than the estimated uncertainty of the pressure

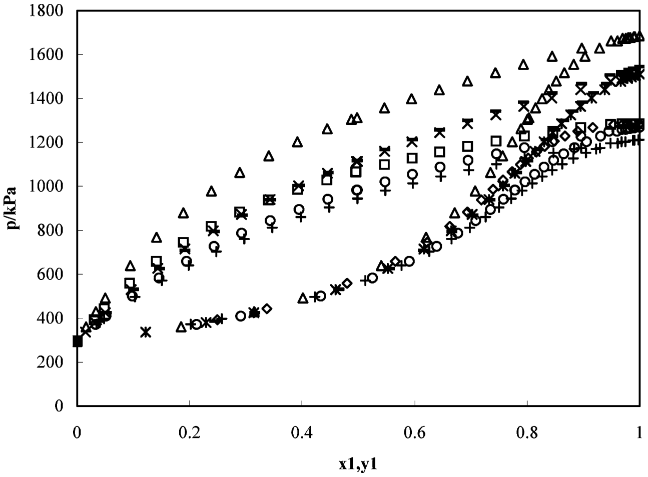

Figure 1. Pressure−composition diagram for C_4-hydrocarbon (1) + 2-propanone (2) systems: □, *n*-butene + (2) at 364.51 K; △, 2-methyl-2-propene + (2) at 364.1 K; ×, 1-butene + (2) at 364.52 K; +, *cis*-2-butene + (2) at 365.46 K; −, 2-methylpropene + (2) at 365.46 K; ○, *trans*-2-butene + (2) at 364.51 K.

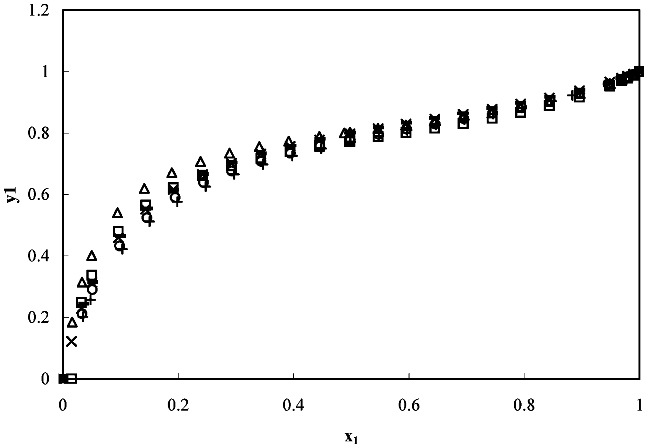

Figure 2. Composition diagram for C_4-hydrocarbon (1) + 2-propanone (2) systems: □, *n*-butene + (2) at 364.51 K; △, 2-methyl-2-propene + (2) at 364.1 K; ×, 1-butene + (2) at 364.52 K; +, *cis*-2-butene + (2) at 365.46 K; −, 2-methylpropene + (2) at 365.46 K; ○, *trans*-2-butene + (2) at 364.51 K.

measurements (0.069 kPa). The phase stability with the regressed UNIQUAC model parameters was checked by plotting the liquid-phase Gibbs energy of mixing at the measured temperature range against liquid-phase composition and by checking the convexity of the resulting curve.

The Wilson and UNIQUAC models seem to give fairly similar results regarding the absolute average pressure residuals of data regression. They also consistently over- and underestimate the total pressures for the same systems. According to the error analysis, the most significant source of uncertainty of the experimental data is the uncertainty of the liquid density correlation.

Results with Predictive Methods. Results obtained with UNIFAC and COSMO-RS methods are compared with Legendre polynomial data regression results in Table 10. In both COSMO and UNIFAC, all interactions between molecules are modeled as interactions between pairwise contacting molecular surfaces. However COSMO uses a far more accurate description for a single molecule, in which the binary surface interaction energies are calculated using screening charge densities determined from quantum mechanical calculations. Considering a single molecule as an entity enables COSMO-RS also to predict intramolecular interactions.

Despite the advantages of COSMO-RS over UNIFAC, the two predictive methods give fairly similar results in data reduction in terms of the average absolute pressure residuals. COSMO-RS consistently underestimates the total pressure while UNIFAC tends to give higher values as compared to the experimental pressure. The infinite dilution activity coefficients predicted with COSMO are respectively lower and with UNIFAC higher than the ones obtained with Legendre polynomial explaining the variations in total pressure. The average absolute pressure residuals are significantly lower with UNIFAC for 2-propanone + C_4-alkene systems. This is likely due to the fact that COSMO-RS is a relatively novel method, which despite being basically independent from experimental data has some lability in its fundamental parameters and requires further testing in order to enhance the reliability of the method. UNIFAC's better results are most likely due to the extensive amount of experimental data used to regress its parameters for these binaries. UNIFAC also seems to overestimate the infinite dilution activity coefficients of 2-propanone and C_4-hydrocarbons in every system except for systems 3 and 4 and for 2-methylpropene in System 2. As a result also the estimated total pressures are higher for every other mixture except for systems 3 and 6. In addition UNIFAC predicts the presence of an azeotropic point for *n*-butane + 2-propanone mixture ($x_1 = 0.919$, $p = 1312.2$ kPa, and $T = 364.51$ K) even though its

Table 9. Activity Coefficient Model Parameters (Legendre, Wilson, and UNIQUAC) and Averages of Pressure Residuals for 2-Propanone + *n*-Butane (system 1), + 2-Methylpropane (system 2), + 1-Butene (system 3), + *cis*-2-Butene (system 4), + 2-Methylpropene (system 5), + *trans*-2-Butene (system 6)

	system 1	system 2	system 3	system 4	system 5	system 6
T/K	364.51	364.1	364.52	365.46	365.46	364.51
Legendre, $a_{1,0}$	1.18	1.2049	0.90469	0.871	0.86019	0.91714
Legendre, $a_{2,0}$	0.032521	0.010753	0.072829	0.097218	0.076831	0.085446
Legendre, $a_{3,0}$	0.025946	0.016582	0.017315	0.017914	0.011819	0.023281
Legendre, $a_{4,0}$	−0.002390	−0.0073632	−0.00082632	0.00068041	−0.0012925	0.0017236
Legendre, $a_{5,0}$	−0.0001906	−0.0017862	−0.00029814	−0.0036924	−0.0029028	0.0015202
Δp/kPa	0.068	−0.026	0.063	−0.062	−0.042	0.035
$\lvert\Delta p\rvert$/kPa	0.194	0.213	0.108	0.163	0.109	0.114
Wilson $\lambda_{1,2}$/K	121.83	128.36	35.146	21.182	18.657	42.464
Wilson $\lambda_{2,1}$/K	392.4	398.53	347.41	351.05	345.98	353.24
Δp/kPa	−0.696	5.327	−1.474	−0.290	2.663	12.72
$\lvert\Delta p\rvert$/kPa	1.273	5.776	1.754	0.654	2.663	12.715
UNIQUAC $a_{1,2}$/K	183.33	175	172.74	201.29	193.94	185.86
UNIQUAC $a_{2,1}$/K	9.0205	18.499	−18.4	−44.72	−42.181	−24.396
Δp/kPa	−2.223	4.688	−1.963	−0.417	2.364	13.54
$\lvert\Delta p\rvert$/kPa	2.846	5.085	2.407	1.081	2.679	11.537

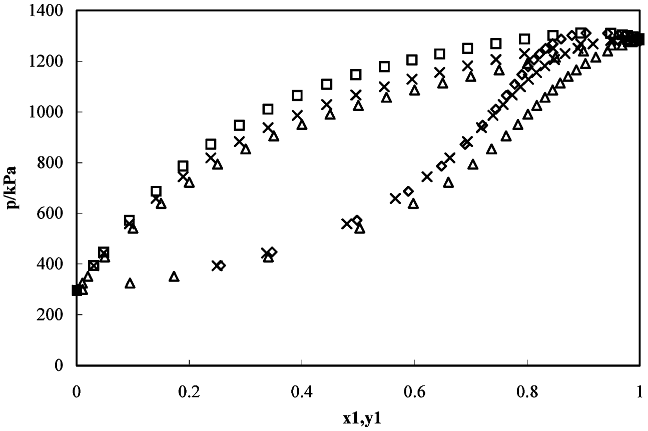

Figure 3. Pressure−composition diagrams for *n*-butane (1) + 2-propanone system at 364.51 K: ×, experimental values; □, UNIFAC results; △, COSMO-RS results.

Table 10. Comparison of VLE Data Obtained with Predictive Methods and Data Regressed with Legendre Polynomial: Average Pressure Residuals, Activity Coefficient at Infinite Dilution for *n*-Butane (1) + 2-Propanone (2) (system 1), 2-Methylpropane (1) + 2-Propanone (2) (system 2), 1-Butene (1) + 2-Propanone (2) (system 3), *cis*-2-Butene (2) + 2-Propanone (2) (system 4), Isobutene (1) + 2-Propanone (2) (system 5), and *trans*-2-Butene (1) + 2-Propanone (2) (system 6)

	system1	system2	system3	system4	system5	system6
T/K	364.51	364.1	364.52	365.46	365.46	364.51
Legendre	0.19					
Δp/kPa	0.068	−0.026	0.063	−0.062	−0.042	0.035
$\lvert\Delta p\rvert$/kPa	0.19	0.21	0.11	0.16	0.11	0.11
$\gamma_{\mathrm{inf},1}$	3.24	3.38	2.34	2.20	2.21	2.35
$\gamma_{\mathrm{inf},2}$	3.44	3.41	2.70	2.69	2.57	2.80
UNIFAC						
Δp/kPa	−45.39	−46.04	16.51	−9.47	−7.47	11.54
$\lvert\Delta p\rvert$/kPa	45.50	47.06	16.91	9.50	9.08	13.54
$\gamma_{\mathrm{inf},1}$	3.26	3.26	2.16	2.32	2.36	2.33
$\gamma_{\mathrm{inf},2}$	4.66	4.66	2.43	2.77	2.67	2.78
COSMO-RS						
Δp/kPa	31.44	30.63	48.79	45.50	48.30	40.72
$\lvert\Delta p\rvert$/kPa	31.45	30.63	48.79	45.50	48.30	40.72
$\gamma_{\mathrm{inf},1}$	2.43	2.36	1.56	1.58	1.50	1.71
$\gamma_{\mathrm{inf},2}$	3.04	2.98	1.80	1.83	1.71	2.01

location deviates significantly from the experimental azeotrope. COSMO-RS does not predict azeotrope for any of the investigated systems. Vapor pressures calculated with predictive methods for *n*-butane + 2-propanone mixture are presented together with experimental vapor pressures in Figure 3.

Conclusions

Isothermal VLE of five binary systems of 2-propanone + C_4-hydrocarbons were measured at 364.1 to 365.46 K with the static total pressure apparatus. The Barker method was used to reduce measured *PzT* data into pressure−composition data. All measured systems exhibit positive deviation from Raoult's law. An azetropic point was found for *n*-butane + 2-propanone mixture at $x_1 = 0.991$, $p = 1288.7$ kPa, and $T = 364.51$. Parameters of Wilson and UNIQUAC activity coefficient models were regressed with experimental VLE data. Comparing the average absolute pressure residuals calculated with optimized parameters the suitability of the models to extrapolate VLE data for investigated mixtures could be evaluated. Both models were found to give fairly good results and consistently reproduce the liquid-phase nonidealities. VLE data obtained with two predictive methods, UNIFAC and COSMO-RS, was compared with experimental results in terms of average pressure residuals and calculated activity coefficients at infinite dilution. UNIFAC was found to overestimate the total pressure for all investigated systems except for 2-propanone + 1-butene and + *trans*-butene mixtures. Pressures obtained with COSMO-RS were consistently lower than the experimental values, which are a result of underestimated activity coefficients for both 2-propanone and C_4-hydrocarbons. The azeotrope point for *n*-butane + 2-propanone system is predicted by UNIFAC, although its location deviates significantly from the experimental result. In terms of calculated average absolute pressure residuals, UNIFAC is more suitable for prediction of VLE data for alkene + 2-propanone mixtures than COSMO-RS whereas the latter was found to produce better results for alkane + 2-propanone systems.

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