1628 *J. Chem. Eng. Data* **2004,** *49,* 1628−1634

# Vapor−Liquid Equilibrium for 1-Propanol + 1-Butene, + *cis*-2-Butene, + 2-Methyl-propene, + *trans*-2-Butene, + *n*-Butane, and + 2-Methyl-propane

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Isothermal VLE for six binary systems 1-propanol + 1-butene, + *cis*-2-butene, + 2-methyl-propene, + *trans*-2-butene, + *n*-butane, and + 2-methyl-propane was measured from (318.6 to 331.9) K with a static total pressure apparatus. The Barker method was used to calculate the concentrations of vapor and liquid phases from measured pressure and the total amounts of components injected into the measurement cell. Error analysis was conducted for measured *pTz* data. Binary interaction parameters were optimized for the Legendre polynomial, Wilson, and UNIQUAC activity coefficient models. Interaction parameters for the relatively new UNIQUAC association model were also fit. Good agreement was found between literature VLE data and values measured in this work. The performance of the UNIQUAC association model was found to be better than that of the traditional UNIQUAC model for all measured mixtures.

## Introduction

Accurate VLE data are required for the modeling of thermal separation processes in the chemical industry. In the last few decades, oxygenates such as tertiary ethers and alcohols have grown in their importance as fuel additives that enhance the octane number, improve the combustion process, and reduce emissions. Components measured in this work are relevant to production processes for tertiary ethers.

Of the six systems studied, the *n*-butane + 1-propanol VLE was measured previously[1] with a high-pressure capillary glass tube apparatus using a synthetic method in the temperature range of (323 to 523) K and the pressure range of (0.162 to 5.271) Mpa. The solubility of *n*-butane in 1-propanol has been measured[2] at atmospheric pressure and for temperatures ranging from (283.15 to 313.15) K. The 2-methyl-propane + 1-propanol VLE was found in the literature[3] in the temperature range of (318.4 to 363.6) K and at pressures from (0.418 to 1.657) MPa. Excess enthalpies for the *n*-butane + 1-propanol mixture have been measured[4] at 298.15 K and 2.985 MPa and have also been measured[5,6] at temperatures of (298.15, 323.15, and 348.15) K and at pressures of 5, 10, and 15 MPa.

## Experimental Section

***Materials.*** 1-Propanol (99.8 mass %) was provided by Riedel-de Haën, and 1-butene (99.6 mass %), *cis*-2-butene (99.4 mass %), 2-methyl-propene (99.8 mass %), and *trans*-2-butene (99.4 mass %) were provided by Messer Finland Oy. 2-Methyl-propane (99.95 mass %) and *n*-butane (99.95 mass %) were provided by AGA Oy. 1-Propanol was dried over molecular sieves (Merck3A) before the degassing procedure. All materials were used without further purification. The degassing of 1-propanol was conducted with a distillation method similar to the one described by Fischer and Gmehling.[7] Other components were degassed in the syringe pump by opening the vacuum line valve 10 times for a period of 10 s.

The success of the degassing procedure of all components was checked through comparing the measured vapor pressures with the values calculated from literature correlations. Pure-component physical properties as well as measured and calculated vapor pressures are presented in Tables 1 and 2, respectively.

***Apparatus and Procedures.*** The apparatus used in this work is an automated version of the equipment presented in previous work[8] for static total pressure measurements. For communication between the PC and the devices, RS232 ports were used. The temperature of the water bath, syringe pumps, and equilibrium cell was measured with Pt-100 temperature probes connected to the Systemteknik S2541 temperature meter. The temperature of the equilibrium cell was measured with a probe located in contact with a cell wall. The temperature meter and the probes were calibrated at the 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 system was estimated to be ±0.03 K.

The pressure was measured with a Digiquartz 2100A-101-CE pressure transducer (0 to 689 kPa) equipped with a Digiquartz 740 intelligent display unit. The calibration of the pressure measurement system was conducted at the Finnish National Standards Laboratory. The uncertainty of the display unit was ±0.069 kPa, and the total uncertainty in the pressure measurement system was estimated to be ±0.169 kPa because of limitations in the automation software used.

The components were injected with syringe pumps (Isco 260 D and Isco 100 DM). The temperatures and the pressures of the barrels of the 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 controlled with built-in strain gauge

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10.1021/je049959i CCC: $27.50

**Table 1. Pure-Component Physical Properties—Critical Temperature $T_C$, Critical Pressure $P_C$, Acentric Factor $\omega$, and Liquid Molar Volume $v$**

| component | $T_C$/K | $p_C$/MPa | $\omega$ | $v^a/(\mathrm{cm^3 \cdot mol^{-1}})$ |
|---|---|---|---|---|
| 1-propanol[10] | 536.71 ± 5.4 | 5.1696 ± 0.155 | 0.6279 | 74.939 ± 0.15 |
| 1-butene[10] | 419.59 ± 4 | 4.0196 ± 0.12 | 0.1867 | 89.621± 0.9 |
| *cis*-2-butene[10] | 435.58 ± 4 | 4.2058 ± 0.04 | 0.203 | 87.45 ±1.7 |
| 2-methylpropene[10] | 417.9 ± 4 | 3.999 ± 0.04 | 0.1893 | 89.424 ± 0.18 |
| *trans*-2-butene[10] | 428.63 ± 4 | 4.1024 ± 0.04 | 0.2182 | 89.415 ± 0.89 |
| *n*-butane[10] | 425.18 ± 4 | 3.7967 ± 0.19 | 0.1993 | 96.553 ± 0.96 |
| 2-methylpropane[10] | 408.14 ± 4 | 3.648 ± 0.04 | 0.177 | 97.704 ± 0.195 |

[a] At normal boiling point.

**Table 2. Measured Vapor Pressures and Values Calculated from Literature Correlations**

| | | vapor pressure/kPa | | | |
|---|---|---|---|---|---|
| component | $T$/K | this work | Reid et al.[20] | Yaws et al.[21] | Perry et al.[22] |
| 1-propanol | 318.58 | 9.47 | 9.52 | 9.54 | 9.41 |
| | 323.07 | 12.07 | 12.14 | 12.16 | 12.06 |
| | 323.26 | 12.27 | 12.26 | 12.28 | 12.14 |
| | 330.16 | 17.57 | 17.55 | 17.55 | 17.39 |
| | 331.91 | 19.07 | 19.16 | 19.16 | 18.99 |
| | 332.05 | 19.17 | 19.29 | 19.29 | 19.12 |
| 1-butene | 323.27 | 596.14 | 598.03 | 606.28 | 596.17 |
| *cis*-2-butene | 331.92 | 561.34 | 560.43 | 557.72 | 562.74 |
| 2-methylpropene | 323.07 | 607.94 | 604.76 | 614.18 | 606.95 |
| 2-methylpropane | 318.59 | 610.84 | 607.50 | 614.34 | 612.27 |
| *n*-butane | 330.16 | 592.44 | 594.49 | 593.70 | 593.60 |
| *trans*-2-butene | 332.05 | 606.54 | | 607.25 | 607.14 |

**Table 3. VLE Data for the 1-Butene (1) + 1-Propanol (2) System at 323.3 K[a]**

| $n_1$ | $n_2$ | $z_1$ | $T$/K | $p_{exp}$/kPa | $p_{leg}$/kPa | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.5802 ± 0.0062 | 0.0 | 1.0 | 323.27 ± 0.02 | 596.14 ± 0.17 | 596.14 | 1.0 | 1.0 | 1.00 | 13.13 |
| 0.5802 ± 0.0062 | 0.007 ± 0.0003 | 0.9881 ± 0.0007 | 323.27 ± 0.02 | 591.04 ± 0.17 | 590.83 | 0.9879 | 0.9964 | 1.00 | 11.27 |
| 0.5802 ± 0.0062 | 0.0188 ± 0.0005 | 0.9686 ± 0.0011 | 323.26 ± 0.02 | 584.44 ± 0.17 | 583.32 | 0.9680 | 0.9924 | 1.01 | 8.97 |
| 0.5802 ± 0.0062 | 0.0316 ± 0.0006 | 0.9483 ± 0.0014 | 323.27 ± 0.02 | 579.24 ± 0.17 | 576.99 | 0.9474 | 0.9898 | 1.02 | 7.27 |
| 0.5802 ± 0.0062 | 0.0651 ± 0.0009 | 0.8991 ± 0.0022 | 323.27 ± 0.02 | 569.44 ± 0.17 | 566.14 | 0.8975 | 0.9867 | 1.05 | 4.80 |
| 0.5802 ± 0.0062 | 0.1026 ± 0.0013 | 0.8497 ± 0.003 | 323.27 ± 0.02 | 560.84 ± 0.17 | 558.85 | 0.8475 | 0.9854 | 1.10 | 3.52 |
| 0.5802 ± 0.0062 | 0.145 ± 0.0017 | 0.8001 ± 0.0036 | 323.27 ± 0.02 | 552.54 ± 0.17 | 552.53 | 0.7974 | 0.9845 | 1.16 | 2.78 |
| 0.5802 ± 0.0062 | 0.1932 ± 0.0022 | 0.7501 ± 0.0041 | 323.27 ± 0.02 | 544.24 ± 0.17 | 545.65 | 0.7473 | 0.9838 | 1.22 | 2.31 |
| 0.5802 ± 0.0062 | 0.2485 ± 0.0028 | 0.7001 ± 0.0046 | 323.27 ± 0.02 | 535.55 ± 0.17 | 537.5 | 0.6973 | 0.9830 | 1.29 | 2.00 |
| 0.5802 ± 0.0062 | 0.3116 ± 0.0034 | 0.6506 ± 0.0049 | 323.28 ± 0.02 | 526.55 ± 0.17 | 528.05 | 0.6481 | 0.9822 | 1.37 | 1.78 |
| 0.5802 ± 0.0062 | 0.3854 ± 0.0042 | 0.6009 ± 0.0051 | 323.28 ± 0.02 | 516.35 ± 0.17 | 517.12 | 0.5987 | 0.9813 | 1.45 | 1.61 |
| 0.5802 ± 0.0062 | 0.4732 ± 0.0051 | 0.5508 ± 0.0053 | 323.28 ± 0.02 | 504.65 ± 0.17 | 504.65 | 0.5492 | 0.9803 | 1.55 | 1.48 |
| 0.5802 ± 0.0062 | 0.5777 ± 0.0061 | 0.5011 ± 0.0053 | 323.28 ± 0.02 | 491.05 ± 0.17 | 490.56 | 0.5002 | 0.9793 | 1.65 | 1.37 |
| 0.5718 ± 0.0061 | 0.5757 ± 0.0061 | 0.4983 ± 0.0053 | 323.28 ± 0.02 | 490.35 ± 0.17 | 489.7 | 0.4974 | 0.9792 | 1.66 | 1.37 |
| 0.468 ± 0.005 | 0.5757 ± 0.0061 | 0.4484 ± 0.0053 | 323.27 ± 0.02 | 472.85 ± 0.17 | 472.37 | 0.4463 | 0.9780 | 1.79 | 1.28 |
| 0.3822 ± 0.0041 | 0.5757 ± 0.0061 | 0.399 ± 0.0052 | 323.27 ± 0.02 | 451.65 ± 0.17 | 451.65 | 0.3956 | 0.9765 | 1.94 | 1.21 |
| 0.3086 ± 0.0034 | 0.5757 ± 0.0061 | 0.349 ± 0.0049 | 323.28 ± 0.02 | 425.15 ± 0.17 | 425.79 | 0.3443 | 0.9745 | 2.11 | 1.15 |
| 0.2458 ± 0.0027 | 0.5757 ± 0.0061 | 0.2992 ± 0.0046 | 323.27 ± 0.02 | 392.85 ± 0.17 | 393.68 | 0.2934 | 0.9719 | 2.30 | 1.10 |
| 0.1915 ± 0.0022 | 0.5757 ± 0.0061 | 0.2496 ± 0.0041 | 323.27 ± 0.02 | 353.36 ± 0.17 | 354.03 | 0.2430 | 0.9681 | 2.51 | 1.07 |
| 0.1456 ± 0.0017 | 0.5757 ± 0.0061 | 0.2019 ± 0.0036 | 323.27 ± 0.02 | 307.66 ± 0.17 | 307.66 | 0.1948 | 0.9625 | 2.73 | 1.04 |
| 0.1036 ± 0.0013 | 0.5757 ± 0.0061 | 0.1526 ± 0.003 | 323.27 ± 0.02 | 251.46 ± 0.17 | 250.84 | 0.1457 | 0.9531 | 2.99 | 1.02 |
| 0.0666 ± 0.0009 | 0.5757 ± 0.0061 | 0.1037 ± 0.0023 | 323.27 ± 0.02 | 185.66 ± 0.17 | 185.3 | 0.0978 | 0.9355 | 3.28 | 1.01 |
| 0.0329 ± 0.0006 | 0.5757 ± 0.0061 | 0.054 ± 0.0014 | 323.27 ± 0.02 | 108.77 ± 0.17 | 108.79 | 0.0503 | 0.8886 | 3.62 | 1.00 |
| 0.0207 ± 0.0004 | 0.5757 ± 0.0061 | 0.0346 ± 0.0011 | 323.26 ± 0.02 | 75.67 ± 0.17 | 75.97 | 0.0321 | 0.8397 | 3.77 | 1.00 |
| 0.0082 ± 0.0003 | 0.5757 ± 0.0061 | 0.0141 ± 0.0007 | 323.26 ± 0.02 | 38.87 ± 0.17 | 39.06 | 0.0130 | 0.6867 | 3.95 | 1.00 |
| 0.0 | 0.5757 ± 0.0061 | 0.0 | 323.26 ± 0.02 | 12.27 ± 0.17 | 12.27 | 0.0 | 0.0 | 4.09 | 1.00 |

[a] $n_1$ and $n_2$ moles of components were injected into the equilibrium cell, $z_1$ is the total composition, $x_1$ and $y_1$ are the calculated concentrations in the liquid and vapor phases, respectively, $p_{leg}$ is the pressure calculated from the Legendre polynomial fit, and $\gamma_i$ represents the calculated liquid-phase activity coefficients.

pressure meters in the pumps. The injection volumes of the pumps were calibrated gravimetrically prior to the measurements with distilled water.

The equilibrium cell was immersed in a 70-dm$^3$ water bath. The temperature stability of the bath was ±0.02 K as discussed previously by Uusi-Kyyny et al.[8] The total volume of the equilibrium cell was 113.10 cm$^3$. The content of the cell was agitated with a magnetic stirrer. The valves welded to the lid of the equilibrium cell were operated with Vexta stepping motors equipped with gearboxes. The interface cards connected the stepping motors to the PC. Isco 260 D and Isco 100 DM syringe pumps injected the components into the equilibrium cell, and the pump volumes were read from Isco control units.

The data transfer between water bath, temperature and pressure meters, stepping motors and syringe pumps, and the PC was operated via a Smartio C168H/8 port card at a PCI bus. The actual run was planned in a spreadsheet program that was typed into the Wonderware InTouch program.

Isotherms were measured in two parts starting from pure components and ending with a nearly equimolar mixture. Injected volumes were optimized so that the equilibrium cell became almost entirely filled at the end

**Table 4. VLE Data for the *cis*-2-Butene (1) + 1-Propanol (2) System at 331.9 K**[a]

| $n_1$ | $n_2$ | $z_1$ | $T$/K | $p_{\mathrm{exp}}$/kPa | $p_{\mathrm{leg}}$/kPa | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.5962 ± 0.0182 | 0.0 | 1.0 | 331.92 ± 0.02 | 561.34 ± 0.17 | 561.34 | 1.0 | 1.0 | 1.00 | 11.12 |
| 0.5962 ± 0.0182 | 0.007 ± 0.0003 | 0.9884 ± 0.0009 | 331.92 ± 0.02 | 557.34 ± 0.17 | 557.31 | 0.9883 | 0.9952 | 1.00 | 9.72 |
| 0.5962 ± 0.0182 | 0.019 ± 0.0005 | 0.9692 ± 0.0016 | 331.92 ± 0.02 | 551.54 ± 0.17 | 551.13 | 0.9688 | 0.9896 | 1.01 | 7.93 |
| 0.5962 ± 0.0182 | 0.0319 ± 0.0006 | 0.9492 ± 0.0023 | 331.92 ± 0.02 | 546.64 ± 0.17 | 545.55 | 0.9485 | 0.9857 | 1.01 | 6.56 |
| 0.5962 ± 0.0182 | 0.0674 ± 0.001 | 0.8985 ± 0.004 | 331.92 ± 0.02 | 536.65 ± 0.17 | 534.63 | 0.8971 | 0.9804 | 1.05 | 4.42 |
| 0.5962 ± 0.0182 | 0.1058 ± 0.0013 | 0.8492 ± 0.0054 | 331.92 ± 0.02 | 528.15 ± 0.17 | 526.83 | 0.8473 | 0.9779 | 1.09 | 3.31 |
| 0.5962 ± 0.0182 | 0.1493 ± 0.0018 | 0.7997 ± 0.0067 | 331.92 ± 0.02 | 519.85 ± 0.17 | 519.84 | 0.7975 | 0.9763 | 1.14 | 2.66 |
| 0.5962 ± 0.0182 | 0.1986 ± 0.0023 | 0.7501 ± 0.0077 | 331.92 ± 0.02 | 511.45 ± 0.17 | 512.47 | 0.7477 | 0.9749 | 1.20 | 2.23 |
| 0.5962 ± 0.0182 | 0.2549 ± 0.0029 | 0.7005 ± 0.0086 | 331.92 ± 0.02 | 502.65 ± 0.17 | 504.10 | 0.6982 | 0.9735 | 1.27 | 1.95 |
| 0.5962 ± 0.0182 | 0.321 ± 0.0035 | 0.65 ± 0.0093 | 331.92 ± 0.02 | 493.15 ± 0.17 | 494.31 | 0.6479 | 0.9720 | 1.34 | 1.73 |
| 0.5962 ± 0.0182 | 0.397 ± 0.0043 | 0.6003 ± 0.0098 | 331.92 ± 0.02 | 482.65 ± 0.17 | 483.30 | 0.5985 | 0.9704 | 1.42 | 1.58 |
| 0.5962 ± 0.0182 | 0.4868 ± 0.0052 | 0.5505 ± 0.0101 | 331.92 ± 0.02 | 470.85 ± 0.17 | 470.85 | 0.5492 | 0.9687 | 1.51 | 1.45 |
| 0.5962 ± 0.0182 | 0.5943 ± 0.0063 | 0.5008 ± 0.0102 | 331.92 ± 0.02 | 457.15 ± 0.17 | 456.72 | 0.5002 | 0.9669 | 1.61 | 1.35 |
| 0.5993 ± 0.0183 | 0.6026 ± 0.0064 | 0.4986 ± 0.0102 | 331.92 ± 0.02 | 456.45 ± 0.17 | 456.06 | 0.4981 | 0.9668 | 1.62 | 1.35 |
| 0.4903 ± 0.015 | 0.6026 ± 0.0064 | 0.4486 ± 0.0101 | 331.92 ± 0.02 | 439.25 ± 0.17 | 438.91 | 0.4471 | 0.9646 | 1.74 | 1.26 |
| 0.3994 ± 0.0123 | 0.6026 ± 0.0064 | 0.3986 ± 0.0099 | 331.92 ± 0.02 | 418.45 ± 0.17 | 418.45 | 0.3960 | 0.9619 | 1.87 | 1.20 |
| 0.323 ± 0.01 | 0.6026 ± 0.0064 | 0.3489 ± 0.0094 | 331.92 ± 0.02 | 393.55 ± 0.17 | 393.89 | 0.3453 | 0.9585 | 2.03 | 1.14 |
| 0.2571 ± 0.008 | 0.6026 ± 0.0064 | 0.2991 ± 0.0087 | 331.92 ± 0.02 | 363.25 ± 0.17 | 363.76 | 0.2945 | 0.9540 | 2.20 | 1.10 |
| 0.2017 ± 0.0063 | 0.6026 ± 0.0064 | 0.2508 ± 0.0079 | 331.92 ± 0.02 | 327.86 ± 0.17 | 328.31 | 0.2456 | 0.9478 | 2.38 | 1.07 |
| 0.1519 ± 0.0048 | 0.6026 ± 0.0064 | 0.2013 ± 0.0068 | 331.92 ± 0.02 | 284.76 ± 0.17 | 284.76 | 0.1957 | 0.9383 | 2.59 | 1.04 |
| 0.1079 ± 0.0035 | 0.6026 ± 0.0064 | 0.1519 ± 0.0055 | 331.92 ± 0.02 | 233.46 ± 0.17 | 233.30 | 0.1465 | 0.9230 | 2.83 | 1.02 |
| 0.069 ± 0.0023 | 0.6026 ± 0.0064 | 0.1027 ± 0.0041 | 331.92 ± 0.02 | 173.97 ± 0.17 | 173.85 | 0.0981 | 0.8944 | 3.09 | 1.01 |
| 0.0337 ± 0.0012 | 0.6026 ± 0.0064 | 0.0529 ± 0.0024 | 331.92 ± 0.02 | 104.17 ± 0.17 | 104.52 | 0.0500 | 0.8209 | 3.40 | 1.00 |
| 0.0208 ± 0.0009 | 0.6026 ± 0.0064 | 0.0333 ± 0.0017 | 331.92 ± 0.02 | 74.17 ± 0.17 | 74.44 | 0.0313 | 0.7467 | 3.54 | 1.00 |
| 0.0086 ± 0.0005 | 0.6026 ± 0.0064 | 0.0141 ± 0.0009 | 331.92 ± 0.02 | 43.27 ± 0.17 | 43.27 | 0.0132 | 0.5613 | 3.69 | 1.00 |
| 0.0 | 0.6026 ± 0.0064 | 0.0 | 331.92 ± 0.02 | 19.07 ± 0.17 | 19.07 | 0.0 | 0.0 | 3.81 | 1.00 |

[a] $n_1$ and $n_2$ moles of components were injected into the equilibrium cell, $z_1$ is the total composition, $x_1$ and $y_1$ are the calculated concentrations in the liquid and vapor phases, respectively, $p_{\mathrm{leg}}$ is the pressure calculated from the Legendre polynomial fit, and $\gamma_i$ represents the calculated liquid-phase activity coefficients.

**Table 5. VLE Data for the 2-Methyl-propene (1) + 1-Propanol (2) System at 323.1 K**[a]

| $n_1$ | $n_2$ | $z_1$ | $T$/K | $p_{\mathrm{exp}}$/kPa | $p_{\mathrm{leg}}$/kPa | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.5807 ± 0.0178 | 0.0 | 1.0 | 323.07 ± 0.02 | 607.94 ± 0.17 | 607.94 | 1.0 | 1.0 | 1.00 | 12.29 |
| 0.5807 ± 0.0178 | 0.0069 ± 0.0003 | 0.9883 ± 0.0009 | 323.07 ± 0.02 | 602.24 ± 0.17 | 602.31 | 0.9881 | 0.9968 | 1.00 | 10.66 |
| 0.5807 ± 0.0178 | 0.0187 ± 0.0005 | 0.9688 ± 0.0016 | 323.07 ± 0.02 | 595.14 ± 0.17 | 594.26 | 0.9682 | 0.9930 | 1.01 | 8.57 |
| 0.5807 ± 0.0178 | 0.0313 ± 0.0006 | 0.9488 ± 0.0023 | 323.07 ± 0.02 | 589.54 ± 0.17 | 587.50 | 0.9479 | 0.9905 | 1.01 | 7.03 |
| 0.5807 ± 0.0178 | 0.0656 ± 0.0009 | 0.8985 ± 0.004 | 323.07 ± 0.02 | 578.74 ± 0.17 | 575.34 | 0.8967 | 0.9873 | 1.05 | 4.67 |
| 0.5807 ± 0.0178 | 0.103 ± 0.0013 | 0.8493 ± 0.0054 | 323.08 ± 0.02 | 569.64 ± 0.17 | 567.26 | 0.8470 | 0.9860 | 1.10 | 3.46 |
| 0.5807 ± 0.0178 | 0.1452 ± 0.0017 | 0.7999 ± 0.0067 | 323.07 ± 0.02 | 560.94 ± 0.17 | 560.34 | 0.7972 | 0.9851 | 1.15 | 2.75 |
| 0.5807 ± 0.0178 | 0.1934 ± 0.0022 | 0.7502 ± 0.0077 | 323.08 ± 0.02 | 552.24 ± 0.17 | 553.04 | 0.7473 | 0.9843 | 1.21 | 2.30 |
| 0.5807 ± 0.0178 | 0.2485 ± 0.0028 | 0.7003 ± 0.0086 | 323.08 ± 0.02 | 543.25 ± 0.17 | 544.64 | 0.6975 | 0.9836 | 1.28 | 1.99 |
| 0.5807 ± 0.0178 | 0.3124 ± 0.0034 | 0.6502 ± 0.0093 | 323.08 ± 0.02 | 533.55 ± 0.17 | 534.80 | 0.6476 | 0.9828 | 1.36 | 1.77 |
| 0.5807 ± 0.0178 | 0.3862 ± 0.0042 | 0.6006 ± 0.0098 | 323.08 ± 0.02 | 522.95 ± 0.17 | 523.59 | 0.5984 | 0.9819 | 1.44 | 1.60 |
| 0.5807 ± 0.0178 | 0.4738 ± 0.0051 | 0.5507 ± 0.0101 | 323.09 ± 0.02 | 510.75 ± 0.17 | 510.75 | 0.5491 | 0.9810 | 1.54 | 1.47 |
| 0.5807 ± 0.0178 | 0.5791 ± 0.0061 | 0.5007 ± 0.0102 | 323.09 ± 0.02 | 496.45 ± 0.17 | 496.00 | 0.4999 | 0.9799 | 1.64 | 1.37 |
| 0.5714 ± 0.0175 | 0.5741 ± 0.0061 | 0.4988 ± 0.0102 | 323.09 ± 0.02 | 495.75 ± 0.17 | 495.34 | 0.4978 | 0.9799 | 1.65 | 1.36 |
| 0.4681 ± 0.0144 | 0.5741 ± 0.0061 | 0.4492 ± 0.0102 | 323.09 ± 0.02 | 477.75 ± 0.17 | 477.38 | 0.4470 | 0.9786 | 1.77 | 1.27 |
| 0.3813 ± 0.0118 | 0.5741 ± 0.0061 | 0.3991 ± 0.0099 | 323.09 ± 0.02 | 455.55 ± 0.17 | 455.55 | 0.3956 | 0.9771 | 1.92 | 1.20 |
| 0.3084 ± 0.0095 | 0.5741 ± 0.0061 | 0.3494 ± 0.0094 | 323.09 ± 0.02 | 428.55 ± 0.17 | 428.95 | 0.3447 | 0.9752 | 2.08 | 1.15 |
| 0.2472 ± 0.0077 | 0.5741 ± 0.0061 | 0.301 ± 0.0088 | 323.08 ± 0.02 | 396.25 ± 0.17 | 396.94 | 0.2951 | 0.9726 | 2.26 | 1.10 |
| 0.1928 ± 0.006 | 0.5741 ± 0.0061 | 0.2514 ± 0.0079 | 323.09 ± 0.02 | 356.36 ± 0.17 | 356.84 | 0.2447 | 0.9689 | 2.47 | 1.07 |
| 0.1452 ± 0.0046 | 0.5741 ± 0.0061 | 0.2019 ± 0.0068 | 323.09 ± 0.02 | 308.26 ± 0.17 | 308.26 | 0.1947 | 0.9632 | 2.69 | 1.04 |
| 0.1033 ± 0.0033 | 0.5741 ± 0.0061 | 0.1525 ± 0.0056 | 323.09 ± 0.02 | 251.26 ± 0.17 | 250.82 | 0.1456 | 0.9539 | 2.94 | 1.02 |
| 0.0663 ± 0.0022 | 0.5741 ± 0.0061 | 0.1036 ± 0.0041 | 323.09 ± 0.02 | 185.16 ± 0.17 | 184.76 | 0.0977 | 0.9364 | 3.22 | 1.01 |
| 0.0324 ± 0.0012 | 0.5741 ± 0.0061 | 0.0534 ± 0.0024 | 323.09 ± 0.02 | 107.07 ± 0.17 | 107.10 | 0.0497 | 0.8887 | 3.55 | 1.00 |
| 0.02 ± 0.0008 | 0.5741 ± 0.0061 | 0.0337 ± 0.0017 | 323.09 ± 0.02 | 73.57 ± 0.17 | 73.78 | 0.0312 | 0.8376 | 3.69 | 1.00 |
| 0.0084 ± 0.0005 | 0.5741 ± 0.0061 | 0.0144 ± 0.0009 | 323.08 ± 0.02 | 38.97 ± 0.17 | 39.06 | 0.0132 | 0.6919 | 3.85 | 1.00 |
| 0.0 | 0.5741 ± 0.0061 | 0.0 | 323.07 ± 0.02 | 12.07 ± 0.17 | 12.07 | 0.0 | 0.0 | 3.98 | 1.00 |

[a] $n_1$ and $n_2$ moles of components were injected into the equilibrium cell, $z_1$ is the total composition, $x_1$ and $y_1$ are the calculated concentrations in the liquid and vapor phases, respectively, $p_{\mathrm{leg}}$ is the pressure calculated from the Legendre polynomial fit, and $\gamma_i$ represents the calculated liquid-phase activity coefficients.

of the measurements. The syringe pumps were operated in constant-pressure mode (900 kPa) to ensure the accuracy of the volume measurements to prevent the contamination of degassed materials. The amount of injected component was computed from the displacement of the piston of the pump, measured temperature and pressure, and liquid density calculated from literature correlation. The pressure effect on liquid densities was estimated with Hankinson−Brobst−Thomson correlation.[9] The cell content was mixed with a magnetic mixer, and the equilibration time for one experimental point was found to be less than 20 min. The readings of the pump temperature, volume, and pressure as well as the temperature of the equilibrium cell were recorded automatically during all runs.

Pure-component vapor pressures and 24 equilibrium points were measured for all studied systems except for the 1-propanol + *trans*-2-butene mixture for which only 23 equilibrium points were measured. Component 1 was first introduced into the cell, and its vapor pressure was measured. The unchanged pressure after a second addition

**Table 6. VLE Data for the *trans*-2-Butene (1) + 1-Propanol (2) System at 332.05 K**[a]

| $n_1$ | $n_2$ | $z_1$ | $T$/K | $p_{\text{exp}}$/kPa | $p_{\text{leg}}$/kPa | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.0 | 0.5968 ± 0.0063 | 0.0 | 332.05 ± 0.02 | 19.17 ± 0.17 | 19.17 | 0.0 | 0.0 | 4.01 | 1.00 |
| 0.0248 ± 0.001 | 0.5968 ± 0.0063 | 0.0398 ± 0.0019 | 332.05 ± 0.02 | 92.17 ± 0.17 | 92.35 | 0.0372 | 0.7946 | 3.66 | 1.00 |
| 0.0353 ± 0.0013 | 0.5968 ± 0.0063 | 0.0559 ± 0.0025 | 332.05 ± 0.02 | 119.47 ± 0.17 | 119.49 | 0.0524 | 0.8420 | 3.54 | 1.00 |
| 0.0717 ± 0.0024 | 0.5968 ± 0.0063 | 0.1072 ± 0.0042 | 332.06 ± 0.02 | 198.96 ± 0.17 | 198.26 | 0.1018 | 0.9064 | 3.20 | 1.01 |
| 0.1081 ± 0.0035 | 0.5968 ± 0.0063 | 0.1534 ± 0.0056 | 332.05 ± 0.02 | 260.26 ± 0.17 | 259.69 | 0.1472 | 0.9297 | 2.93 | 1.02 |
| 0.1516 ± 0.0048 | 0.5968 ± 0.0063 | 0.2026 ± 0.0068 | 332.05 ± 0.02 | 315.96 ± 0.17 | 315.96 | 0.1963 | 0.9434 | 2.68 | 1.04 |
| 0.2016 ± 0.0063 | 0.5968 ± 0.0063 | 0.2525 ± 0.0079 | 332.06 ± 0.02 | 363.15 ± 0.17 | 363.66 | 0.2466 | 0.9519 | 2.45 | 1.07 |
| 0.2582 ± 0.008 | 0.5968 ± 0.0063 | 0.302 ± 0.0088 | 332.05 ± 0.02 | 401.75 ± 0.17 | 402.44 | 0.2970 | 0.9575 | 2.24 | 1.11 |
| 0.3236 ± 0.01 | 0.5968 ± 0.0063 | 0.3516 ± 0.0094 | 332.06 ± 0.02 | 433.35 ± 0.17 | 433.86 | 0.3476 | 0.9614 | 2.06 | 1.15 |
| 0.3994 ± 0.0123 | 0.5968 ± 0.0063 | 0.4009 ± 0.0099 | 332.06 ± 0.02 | 459.15 ± 0.17 | 459.15 | 0.3981 | 0.9643 | 1.90 | 1.21 |
| 0.4904 ± 0.015 | 0.5968 ± 0.0063 | 0.451 ± 0.0101 | 332.06 ± 0.02 | 480.55 ± 0.17 | 480.1 | 0.4495 | 0.9666 | 1.75 | 1.28 |
| 0.5989 ± 0.0183 | 0.5968 ± 0.0063 | 0.5009 ± 0.0102 | 332.06 ± 0.02 | 498.05 ± 0.17 | 497.44 | 0.5004 | 0.9685 | 1.63 | 1.37 |
| 0.5913 ± 0.0181 | 0.5904 ± 0.0063 | 0.5004 ± 0.0102 | 332.07 ± 0.02 | 497.55 ± 0.17 | 497.22 | 0.4998 | 0.9685 | 1.63 | 1.37 |
| 0.5913 ± 0.0181 | 0.483 ± 0.0052 | 0.5504 ± 0.0101 | 332.07 ± 0.02 | 511.65 ± 0.17 | 511.65 | 0.5491 | 0.9701 | 1.52 | 1.48 |
| 0.5913 ± 0.0181 | 0.3942 ± 0.0043 | 0.6 ± 0.0098 | 332.06 ± 0.02 | 523.65 ± 0.17 | 524.23 | 0.5981 | 0.9716 | 1.43 | 1.60 |
| 0.5913 ± 0.0181 | 0.3183 ± 0.0035 | 0.6501 ± 0.0093 | 332.07 ± 0.02 | 534.25 ± 0.17 | 535.51 | 0.6478 | 0.9730 | 1.35 | 1.77 |
| 0.5913 ± 0.0181 | 0.2533 ± 0.0029 | 0.7001 ± 0.0086 | 332.06 ± 0.02 | 543.94 ± 0.17 | 545.45 | 0.6976 | 0.9743 | 1.27 | 1.99 |
| 0.5913 ± 0.0181 | 0.1971 ± 0.0023 | 0.75 ± 0.0078 | 332.06 ± 0.02 | 553.04 ± 0.17 | 554.13 | 0.7474 | 0.9756 | 1.21 | 2.29 |
| 0.5913 ± 0.0181 | 0.1478 ± 0.0018 | 0.8 ± 0.0067 | 332.06 ± 0.02 | 561.84 ± 0.17 | 561.84 | 0.7976 | 0.9769 | 1.15 | 2.74 |
| 0.5913 ± 0.0181 | 0.1046 ± 0.0013 | 0.8497 ± 0.0054 | 332.06 ± 0.02 | 570.54 ± 0.17 | 569.19 | 0.8476 | 0.9784 | 1.09 | 3.43 |
| 0.5913 ± 0.0181 | 0.0662 ± 0.0009 | 0.8992 ± 0.004 | 332.05 ± 0.02 | 579.64 ± 0.17 | 577.56 | 0.8978 | 0.9808 | 1.05 | 4.60 |
| 0.5913 ± 0.0181 | 0.0319 ± 0.0006 | 0.9488 ± 0.0023 | 332.05 ± 0.02 | 590.34 ± 0.17 | 589.1 | 0.9480 | 0.9858 | 1.01 | 6.80 |
| 0.5913 ± 0.0181 | 0.0193 ± 0.0005 | 0.9685 ± 0.0016 | 332.05 ± 0.02 | 595.54 ± 0.17 | 595.08 | 0.9680 | 0.9895 | 1.01 | 8.20 |
| 0.5913 ± 0.0181 | 0.0067 ± 0.0003 | 0.9887 ± 0.0009 | 332.05 ± 0.02 | 602.24 ± 0.17 | 602.22 | 0.9886 | 0.9954 | 1.00 | 10.20 |
| 0.5913 ± 0.0181 | 0.0 | 1.0 | 332.05 ± 0.02 | 606.54 ± 0.17 | 606.54 | 1.0 | 1.0 | 1.00 | 11.64 |

[a] $n_1$ and $n_2$ moles of components were injected into the equilibrium cell, $z_1$ is the total composition, $x_1$ and $y_1$ are the calculated concentrations in the liquid and vapor phases, respectively, $p_{\text{leg}}$ is the pressure calculated from the Legendre polynomial fit, and $\gamma_i$ represents the calculated liquid-phase activity coefficients.

of the first component into the cell indicated the success of the degassing. The vapor pressure would rise because of incomplete degassing of the component as a result of dissolved gases in the equilibrium cell. After a vapor pressure measurement of component 1, a predetermined volume of component 2 was injected into the equilibrium cell. The additions of component 2 were continued until a mole fraction of approximately 0.5 was reached. The cell was emptied and evacuated, and measurements continued with the other side of the isotherm.

***Error Analysis.*** The uncertainty of the molar amounts of components injected into the equilibrium cell depends on many quantities such as the uncertainty of the measured temperature and pressure of the pump, measured injected volumes, and liquid density correlation. The uncertainty of the injection volumes $\Delta V_1 = \pm 0.02\ \text{cm}^3$ was obtained from the calibration experiments with distilled water. The estimated inaccuracies in the temperature and pressure measurements in the pumps were found to be $\Delta T = \pm 0.1$ K and $\Delta p = \pm 20$ kPa. Uncertainties of density correlations[10] were <1% for 1-propanol, 1-butene, *n*-butane, and 2-methyl-propane and <3.0% for *cis*-2-butene, 2-methyl-propene, and *trans*-2-butene. Theoretical maximum errors of injected molar amounts were calculated from total derivative equations presented by Laakkonen et al.[11]

***Data Reduction.*** The Barker method[12] was used to calculate the concentrations in the vapor and liquid phases from measured amounts of components injected into the cell. Use of the Barker method requires that there exists a phase equilibrium model that predicts the bubble-point pressure of the mixture with greater accuracy than the pressure is measured. The Legendre polynomial[13] was chosen here to calculate liquid-phase activity coefficients. The choice is based on the fact that the Legendre polynomial is very flexible compared to local composition models and its accuracy is thereby assumed to be superior to other models for data reduction purposes. The Soave−Redlich−Kwong equation of state[14] was used to model the nonidealities of the vapor phase. In the equation of state, binary interaction parameters were set to a value of zero. Pure-component properties presented in Table 1 were used in data reduction. A scheme developed by Uusi-Kyyny et al.[8] was used in this article for data reduction with the Barker method. Data reduction was done with VLEFIT software.[16]

***UNIQUAC Association Model.*** In the UNIQUAC association model,[17] IR-spectroscopic information of H-bonding is used to model the chemical interactions between associating molecules. Physical interactions are modeled similarly to the traditional UNIQUAC model,[18] and interaction parameters are determined from thermodynamic data. Activities for associating species[19] are calculated as a ratio of activities of the monomer in the mixture to that in pure solution according to the following equation:

$$a_i = \frac{a_{\text{Mo}}}{a_{\text{Mo}}^0} \tag{1}$$

Equilibrium concentrations of monomers, dimers, and oligomers are calculated from material balances with equilibrium constants[17] determined from IR measurements. In associated UNIQUAC, area and volume parameters for associated components are calculated from parameters of monomers:

$$r_{A_i} = i r_{A_1} \qquad q_{A_i} = i q_{A_1} \tag{2}$$

Binary interaction parameters between different associated species are all set equal to one another.

## Results and Discussion

The results of data reduction with the Barker method for the measured binary pairs together with error estimates are presented in Tables 3−8. Injected amounts of moles are presented using more significant digits than their maximum theoretical errors would indicate. This is justified by giving the possibility to recalculate the measured data. Because of the total derivative method used in

**Table 7. VLE Data for the *n*-Butane (1) + 1-Propanol (2) System at 330.2 K**[a]

| $n_1$ | $n_2$ | $z_1$ | $T$/K | $p_{exp}$/kPa | $p_{leg}$/kPa | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.5645 ± 0.006 | 0.0 | 1.0 | 330.16 ± 0.02 | 592.44 ± 0.17 | 592.44 | 1.0 | 1.0 | 1.00 | 15.93 |
| 0.5645 ± 0.006 | 0.007 ± 0.0003 | 0.9878 ± 0.0007 | 330.16 ± 0.02 | 589.64 ± 0.17 | 588.93 | 0.9876 | 0.9938 | 1.00 | 13.45 |
| 0.5645 ± 0.006 | 0.019 ± 0.0005 | 0.9675 ± 0.0011 | 330.16 ± 0.02 | 585.54 ± 0.17 | 583.36 | 0.9671 | 0.9872 | 1.01 | 10.43 |
| 0.5645 ± 0.006 | 0.0308 ± 0.0006 | 0.9483 ± 0.0014 | 330.17 ± 0.02 | 582.14 ± 0.17 | 578.76 | 0.9475 | 0.9834 | 1.02 | 8.42 |
| 0.5645 ± 0.006 | 0.0635 ± 0.0009 | 0.8989 ± 0.0023 | 330.16 ± 0.02 | 574.44 ± 0.17 | 570.30 | 0.8974 | 0.9790 | 1.05 | 5.38 |
| 0.5645 ± 0.006 | 0.101 ± 0.0013 | 0.8482 ± 0.003 | 330.17 ± 0.02 | 567.24 ± 0.17 | 564.86 | 0.8462 | 0.9774 | 1.11 | 3.83 |
| 0.5645 ± 0.006 | 0.1424 ± 0.0017 | 0.7985 ± 0.0036 | 330.17 ± 0.02 | 560.34 ± 0.17 | 560.34 | 0.7961 | 0.9765 | 1.17 | 2.99 |
| 0.5645 ± 0.006 | 0.1887 ± 0.0022 | 0.7495 ± 0.0041 | 330.18 ± 0.02 | 553.54 ± 0.17 | 555.23 | 0.7469 | 0.9757 | 1.24 | 2.47 |
| 0.5645 ± 0.006 | 0.2429 ± 0.0027 | 0.6992 ± 0.0046 | 330.18 ± 0.02 | 546.34 ± 0.17 | 548.64 | 0.6966 | 0.9748 | 1.31 | 2.12 |
| 0.5645 ± 0.006 | 0.305 ± 0.0034 | 0.6492 ± 0.0049 | 330.18 ± 0.02 | 538.85 ± 0.17 | 540.69 | 0.6469 | 0.9738 | 1.39 | 1.88 |
| 0.5645 ± 0.006 | 0.3769 ± 0.0041 | 0.5996 ± 0.0051 | 330.18 ± 0.02 | 530.45 ± 0.17 | 531.46 | 0.5977 | 0.9727 | 1.48 | 1.69 |
| 0.5645 ± 0.006 | 0.4627 ± 0.005 | 0.5495 ± 0.0053 | 330.18 ± 0.02 | 520.95 ± 0.17 | 520.94 | 0.5482 | 0.9715 | 1.59 | 1.55 |
| 0.5645 ± 0.006 | 0.5652 ± 0.006 | 0.4997 ± 0.0053 | 330.18 ± 0.02 | 509.65 ± 0.17 | 509.06 | 0.4990 | 0.9703 | 1.71 | 1.43 |
| 0.5581 ± 0.0059 | 0.562 ± 0.006 | 0.4983 ± 0.0053 | 330.18 ± 0.02 | 509.35 ± 0.17 | 508.68 | 0.4975 | 0.9703 | 1.71 | 1.42 |
| 0.4568 ± 0.0049 | 0.562 ± 0.006 | 0.4484 ± 0.0053 | 330.19 ± 0.02 | 494.65 ± 0.17 | 494.09 | 0.4463 | 0.9688 | 1.86 | 1.32 |
| 0.3724 ± 0.004 | 0.562 ± 0.006 | 0.3985 ± 0.0051 | 330.18 ± 0.02 | 476.25 ± 0.17 | 476.25 | 0.3951 | 0.9671 | 2.03 | 1.24 |
| 0.301 ± 0.0033 | 0.562 ± 0.006 | 0.3488 ± 0.0049 | 330.18 ± 0.02 | 453.05 ± 0.17 | 453.66 | 0.3439 | 0.9649 | 2.23 | 1.18 |
| 0.2407 ± 0.0027 | 0.562 ± 0.006 | 0.2999 ± 0.0046 | 330.19 ± 0.02 | 423.85 ± 0.17 | 424.92 | 0.2937 | 0.9618 | 2.45 | 1.12 |
| 0.188 ± 0.0021 | 0.562 ± 0.006 | 0.2507 ± 0.0041 | 330.18 ± 0.02 | 386.95 ± 0.17 | 387.74 | 0.2434 | 0.9575 | 2.71 | 1.08 |
| 0.1414 ± 0.0017 | 0.562 ± 0.006 | 0.201 ± 0.0036 | 330.17 ± 0.02 | 340.06 ± 0.17 | 340.06 | 0.1931 | 0.9507 | 3.01 | 1.05 |
| 0.1005 ± 0.0012 | 0.562 ± 0.006 | 0.1518 ± 0.003 | 330.17 ± 0.02 | 282.16 ± 0.17 | 281.56 | 0.1440 | 0.9395 | 3.35 | 1.03 |
| 0.0648 ± 0.0009 | 0.562 ± 0.006 | 0.1034 ± 0.0022 | 330.17 ± 0.02 | 212.96 ± 0.17 | 212.16 | 0.0967 | 0.9186 | 3.74 | 1.01 |
| 0.0316 ± 0.0005 | 0.562 ± 0.006 | 0.0533 ± 0.0014 | 330.16 ± 0.02 | 126.77 ± 0.17 | 126.77 | 0.0490 | 0.8624 | 4.23 | 1.00 |
| 0.0193 ± 0.0004 | 0.562 ± 0.006 | 0.03328 ± 0.00102 | 330.16 ± 0.02 | 87.87 ± 0.17 | 88.23 | 0.0304 | 0.8017 | 4.45 | 1.00 |
| 0.0078 ± 0.0003 | 0.562 ± 0.006 | 0.01362 ± 0.000635 | 330.16 ± 0.02 | 47.17 ± 0.17 | 47.56 | 0.0123 | 0.6311 | 4.70 | 1.00 |
| 0.0 | 0.562 ± 0.006 | 0.0 | 330.16 ± 0.02 | 17.57 ± 0.17 | 17.57 | 0.0 | 0.0 | 4.89 | 1.00 |

[a] $n_1$ and $n_2$ moles of components are injected into the equilibrium cell, $z_1$ is the total composition, $x_1$ and $y_1$ are the calculated concentrations in the liquid and vapor phases, respectively, $p_{leg}$ is the pressure calculated from the Legendre polynomial fit, and $\gamma_\iota$ represents the calculated liquid-phase activity coefficients.

**Table 8. VLE Data for the 2-Methyl-propane (1) + 1-Propanol (2) System at 318.6 K**[a]

| $n_1$ | $n_2$ | $z_1$ | $T$/K | $p_{exp}$/kPa | $p_{leg}$/kPa | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.5478 ± 0.0059 | 0.0 | 1.0 | 318.59 ± 0.02 | 610.84 ± 0.17 | 610.84 | 1.0 | 1.0 | 1.00 | 17.67 |
| 0.5478 ± 0.0059 | 0.0069 ± 0.0003 | 0.9876 ± 0.0007 | 318.59 ± 0.02 | 606.54 ± 0.17 | 605.39 | 0.9874 | 0.9963 | 1.00 | 14.82 |
| 0.5478 ± 0.0059 | 0.0176 ± 0.0004 | 0.9688 ± 0.0011 | 318.6 ± 0.02 | 602.24 ± 0.17 | 598.46 | 0.9682 | 0.9925 | 1.01 | 11.61 |
| 0.5478 ± 0.0059 | 0.0294 ± 0.0006 | 0.9491 ± 0.0014 | 318.6 ± 0.02 | 598.74 ± 0.17 | 592.73 | 0.9482 | 0.9902 | 1.02 | 9.25 |
| 0.5478 ± 0.0059 | 0.0609 ± 0.0009 | 0.9 ± 0.0023 | 318.6 ± 0.02 | 591.14 ± 0.17 | 583.50 | 0.8981 | 0.9877 | 1.06 | 5.82 |
| 0.5478 ± 0.0059 | 0.0974 ± 0.0013 | 0.8491 ± 0.003 | 318.6 ± 0.02 | 583.94 ± 0.17 | 578.48 | 0.8465 | 0.9870 | 1.11 | 4.08 |
| 0.5478 ± 0.0059 | 0.1367 ± 0.0017 | 0.8003 ± 0.0037 | 318.6 ± 0.02 | 577.44 ± 0.17 | 575.02 | 0.7973 | 0.9867 | 1.18 | 3.15 |
| 0.5478 ± 0.0059 | 0.1822 ± 0.0021 | 0.7504 ± 0.0042 | 318.6 ± 0.02 | 571.04 ± 0.17 | 571.05 | 0.7472 | 0.9864 | 1.25 | 2.58 |
| 0.5478 ± 0.0059 | 0.2346 ± 0.0027 | 0.7001 ± 0.0046 | 318.6 ± 0.02 | 564.54 ± 0.17 | 565.77 | 0.6970 | 0.9860 | 1.33 | 2.19 |
| 0.5478 ± 0.0059 | 0.2938 ± 0.0033 | 0.6509 ± 0.005 | 318.61 ± 0.02 | 557.74 ± 0.17 | 559.11 | 0.6479 | 0.9856 | 1.41 | 1.93 |
| 0.5478 ± 0.0059 | 0.3639 ± 0.004 | 0.6009 ± 0.0052 | 318.61 ± 0.02 | 550.14 ± 0.17 | 550.94 | 0.5983 | 0.9851 | 1.51 | 1.73 |
| 0.5478 ± 0.0059 | 0.4459 ± 0.0048 | 0.5513 ± 0.0053 | 318.6 ± 0.02 | 541.45 ± 0.17 | 541.44 | 0.5494 | 0.9845 | 1.62 | 1.57 |
| 0.5976 ± 0.0065 | 0.5085 ± 0.0054 | 0.5403 ± 0.0053 | 318.59 ± 0.02 | 539.65 ± 0.17 | 539.37 | 0.5395 | 0.9844 | 1.64 | 1.55 |
| 0.5478 ± 0.0059 | 0.5455 ± 0.0058 | 0.501 ± 0.0054 | 318.61 ± 0.02 | 530.75 ± 0.17 | 530.22 | 0.4999 | 0.9840 | 1.74 | 1.45 |
| 0.5054 ± 0.0055 | 0.5085 ± 0.0054 | 0.4985 ± 0.0054 | 318.59 ± 0.02 | 529.95 ± 0.17 | 529.36 | 0.4965 | 0.9839 | 1.75 | 1.44 |
| 0.4138 ± 0.0045 | 0.5085 ± 0.0054 | 0.4487 ± 0.0054 | 318.59 ± 0.02 | 515.55 ± 0.17 | 515.09 | 0.4450 | 0.9832 | 1.91 | 1.33 |
| 0.3377 ± 0.0037 | 0.5085 ± 0.0054 | 0.3991 ± 0.0052 | 318.59 ± 0.02 | 497.25 ± 0.17 | 497.25 | 0.3936 | 0.9824 | 2.09 | 1.25 |
| 0.2734 ± 0.0031 | 0.5085 ± 0.0054 | 0.3497 ± 0.005 | 318.59 ± 0.02 | 473.65 ± 0.17 | 474.22 | 0.3424 | 0.9813 | 2.31 | 1.18 |
| 0.2183 ± 0.0025 | 0.5085 ± 0.0054 | 0.3004 ± 0.0047 | 318.59 ± 0.02 | 443.05 ± 0.17 | 444.04 | 0.2914 | 0.9797 | 2.55 | 1.13 |
| 0.1714 ± 0.002 | 0.5085 ± 0.0054 | 0.2521 ± 0.0042 | 318.59 ± 0.02 | 405.05 ± 0.17 | 405.69 | 0.2420 | 0.9775 | 2.83 | 1.09 |
| 0.1316 ± 0.0016 | 0.5085 ± 0.0054 | 0.2055 ± 0.0037 | 318.59 ± 0.02 | 358.76 ± 0.17 | 358.75 | 0.1947 | 0.9742 | 3.14 | 1.05 |
| 0.0948 ± 0.0012 | 0.5085 ± 0.0054 | 0.1571 ± 0.0031 | 318.59 ± 0.02 | 299.06 ± 0.17 | 298.48 | 0.1466 | 0.9687 | 3.50 | 1.03 |
| 0.0619 ± 0.0008 | 0.5085 ± 0.0054 | 0.1086 ± 0.0024 | 318.58 ± 0.02 | 226.06 ± 0.17 | 225.38 | 0.0994 | 0.9582 | 3.92 | 1.01 |
| 0.0308 ± 0.0005 | 0.5085 ± 0.0054 | 0.0572 ± 0.0015 | 318.58 ± 0.02 | 132.87 ± 0.17 | 133.05 | 0.0512 | 0.9288 | 4.46 | 1.00 |
| 0.0216 ± 0.0004 | 0.5085 ± 0.0054 | 0.0407 ± 0.0012 | 318.58 ± 0.02 | 99.97 ± 0.17 | 99.97 | 0.0362 | 0.9052 | 4.66 | 1.00 |
| 0.0 | 0,5085 ± 0,0054 | 0.0 | 318.58 ± 0.02 | 9.47 ± 0.17 | 9.47 | 0.0 | 0.0 | 5.22 | 1.00 |

[a] $n_1$ and $n_2$ moles of components are injected into the equilibrium cell, $z_1$ is the total composition, $x_1$ and $y_1$ are the calculated concentrations in the liquid and vapor phases, respectively, $p_{leg}$ is the pressure calculated from the Legendre polynomial fit, and $\gamma_\iota$ represents the calculated liquid-phase activity coefficients.

calculating the error estimates, actual errors for injected molar amounts are typically smaller than the values presented in Tables 3−8. The pressure−composition diagrams and activity coefficients as a function of composition along with the data found in the literature are presented in Figures 1−5. Vapor-phase compositions of the *n*-butane + 1-propanol solution in Figure 1 for the data presented by Deák et al.[1] are calculated from liquid-phase compositions with the Legendre polynomial as the activity coefficient model. According to the results, all six binary pairs exhibit positive deviation from Raoult's law, but no azeotropic points were detected. Generally good agreement was found between the measured and literature VLEs for $C_4$-alkane + 1-propanol binaries. The activity coefficients determined in this work for 1-propanol in 2-methyl-propane solution are somewhat lower in the dilute alcohol region compared to the ones calculated from measured pressure−composition data presented by Zabaloy et al.[3]

Parameters of the Legendre polynomial, Wilson,[15] UNIQUAC, and UNIQUAC association activity coefficient

**Table 9. Parameters of the Activity Coefficient Model and Averages of Absolute Pressure Residuals**[a]

| (1) + | (2) | (3) | (4) | (5) | (6) | (7) |
|---|---|---|---|---|---|---|
| $T$/K | 323.3 | 331.9 | 323.1 | 332.05 | 330.2 | 318.6 |
| Legendre, $a_{1,0}$ | 1.739100 | 1.64857 | 1.70725 | 1.6966 | 1.8927 | 1.9709 |
| Legendre, $a_{2,0}$ | 0.498693 | 0.462516 | 0.480434 | 0.45875 | 0.49511 | 0.51465 |
| Legendre, $a_{3,0}$ | 0.222024 | 0.199687 | 0.200166 | 0.19865 | 0.25119 | 0.25939 |
| Legendre, $a_{4,0}$ | 0.084914 | 0.0728299 | 0.0733821 | 0.074874 | 0.095607 | 0.094755 |
| Legendre, $a_{5,0}$ | 0.030467 | 0.0255032 | 0.0239104 | 0.025969 | 0.033617 | 0.032107 |
| $\Delta p$/kPa | 0.76 | 0.48 | 0.67 | 0.57 | 1.00 | 1.36 |
| Wilson $\lambda_{12}$/K | 91.51 | 89.757 | 82.027 | 96.314 | 126.02 | 125.7 |
| Wilson $\lambda_{21}$/K | 793.20 | 754.54 | 802.27 | 783.26 | 885.38 | 952.48 |
| $\Delta p$/kPa | 1.14 | 0.72 | 2.15 | 2.33 | 1.35 | 2.95 |
| UNIQUAC $a_{1,2}$ | 343.04 | 349.40 | 383.12 | 366.95 | 364.60 | 369.12 |
| UNIQUAC $a_{2,1}$ | −44.53 | −54.54 | −69.10 | −54.67 | −43.23 | −42.37 |
| $\Delta p$/kPa | 6.04 | 4.89 | 7.61 | 7.75 | 8.46 | 10.31 |
| UNIQUACA $a_{1,2}$ | −25.73 | −34.37 | −0.44 | −23.21 | 10.65 | 27.61 |
| UNIQUACA $a_{2,1}$ | 101.56 | 105.35 | 69.253 | 101.13 | 74.005 | 61.714 |
| $\Delta p$/kPa | 4.25 | 3.62 | 3.32 | 3.13 | 2.06 | 0.55 |

[a] Legendre model parameters obtained with data reduction from measured values, Wilson, UNIQUAC and UNIQUAC association model parameters fit with regressed values, and averages of the absolute pressure residuals of 1-propanol (1), 1-butene (2), *cis*-2-butene (3), isobutene (4), *trans*-2-butene (5), *n*-butane (6), and isobutene (7).

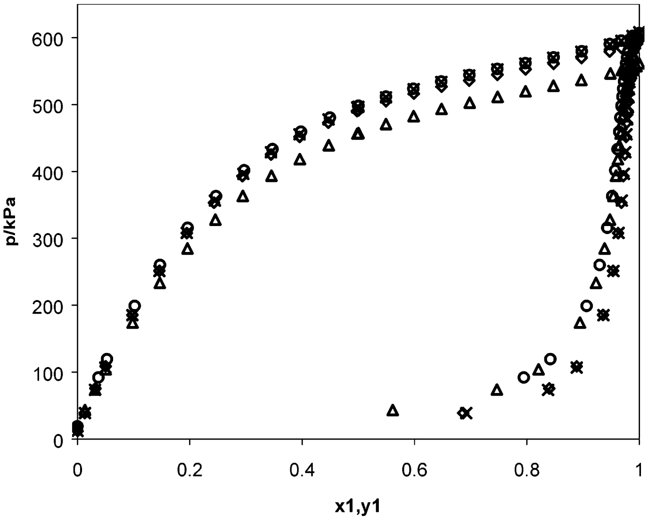

**Figure 1.** Pressure−composition diagram of the $C_4$-alkene (1) + 1-propanol (2) systems: ◇, 1-butene + (2) at 323.2 K; △, *cis*-2-butene + (2) at 331.9 K; ×, 2-methyl-2-propene + (2) at 323.1 K; ○, *trans*-2-butene + (2) at 332.05 K.

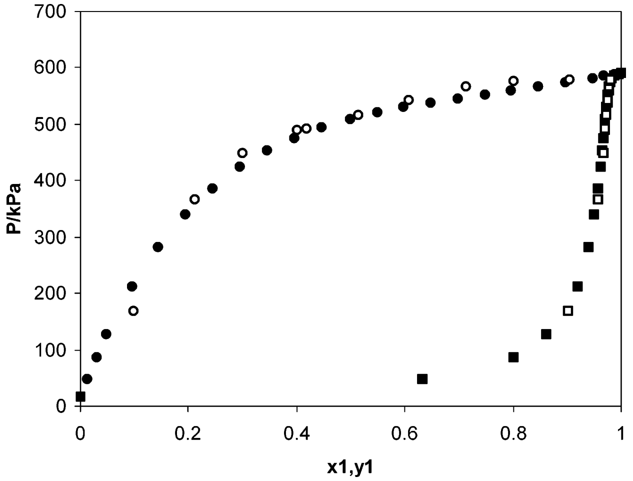

**Figure 2.** Pressure−composition diagram of the *n*-butane (1) + 1-propanol (2) system at 330.2 K: ●, liquid phase; ■, vapor phase, this work; ○, liquid phase; □, vapor phase, Deák et al.[1]

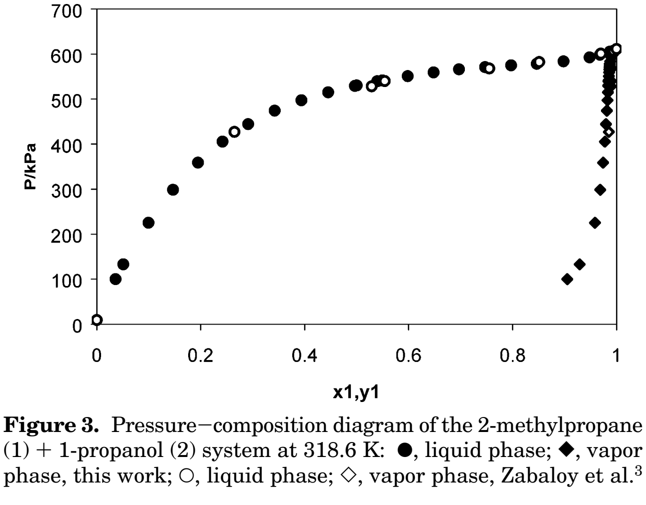

**Figure 3.** Pressure−composition diagram of the 2-methylpropane (1) + 1-propanol (2) system at 318.6 K: ●, liquid phase; ◆, vapor phase, this work; ○, liquid phase; ◇, vapor phase, Zabaloy et al.[3]

models together with the average of the absolute pressure residuals are presented in Table 9. Pressure residuals are in all cases much higher than the estimated uncertainty of the pressure measurements (0.069 kPa). The pressure residuals are also higher for 1-propanol + alkane systems than for 1-propanol + alkene systems. The UNIQUAC association model seems to give better results in all cases compared to traditional UNIQUAC. For the 1-propanol + isobutene mixture, the average pressure residual is even smaller than for Wilson, which in general is considered to be the most suitable model for these kinds of solutions. However, for 1-propanol + alkene mixtures, the UNIQUAC association model shows fairly poor accuracy.

According to the error analysis, the most significant error source is the uncertainty of the density correlation. It would therefore be well advised to measure the densities prior to the VLE measurements for all components at pump pressure and temperature.

## Conclusions

Six binary pairs were measured with a static pressure apparatus at temperatures from (318.6 to 331.9) K. Liquid- and vapor-phase compositions were calculated from measured $PTz$ data with the Barker method. All systems exhibited positive deviation from Raoult's law, but no azeotropic behavior was observed. Good agreement was found between the measured and the literature values for $C_4$-alkane + 1-propanol binaries. Error analysis was conducted on measured total compositions, and the most

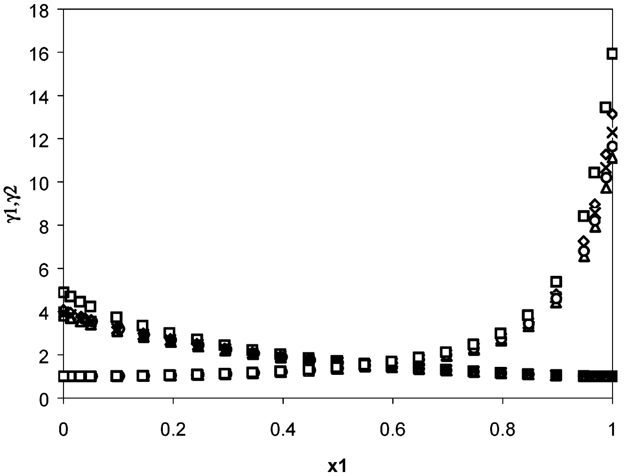

**Figure 4.** Activity coefficient−composition diagram of $C_4$ (1) + 1-propanol (2) systems: ◇, 1-butene + (2) at 323.2 K; △, *cis*-2-butene + (2) at 331.9 K; ×, 2-methylpropene + (2) at 323.1 K; ○, *trans*-2-butene + (2) at 332.05 K, □, *n*-butane + (2) at 330.2 K.

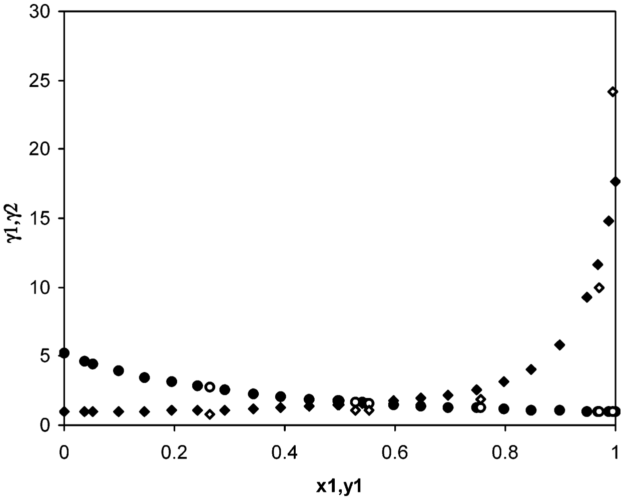

**Figure 5.** Activity coefficient−composition diagram of the 2-methylpropane (1) + 1-propanol (2) system at 318.6 K: ●, $\gamma_1$; ◆, $\gamma_2$ this work; ○, $\gamma_1$; ◇, $\gamma_2$ Zabaloy et al.[3]

significant source of error was found to be the uncertainty of the liquid density correlation. Parameters of Wilson, UNIQUAC, and UNIQUAC association activity coefficient models were optimized with the results from data reduction.

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Received for review January 15, 2004. Accepted August 26, 2004.

JE049959I