# Vapor−Liquid Equilibrium for Tetrahydrothiophene + *n*-Butane, + *trans*-2-Butene, + 2-Methylpropane, and + 2-Methylpropene

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Isothermal vapor−liquid equilibrium of binary systems of tetrahydrothiophene + *n*-butane, + *trans*-2-butene, + 2-methylpropane, and + 2-methylpropene was measured at (318 and 346) K or 347 K with a static total pressure apparatus. The measured data were reduced to phase equilibrium data with the Barker's method. Legendre, Wilson, NRTL, and UNIQUAC parameters were calculated. All binaries exhibited a positive deviation from the Raoult's Law. No azeotropes were observed.

## Introduction

Commercial liquefied petroleum gas (LPG) is obtained as a byproduct of the petroleum refining process. It consists of liquefied propane and butane. It is colorless, odorless, and heavier than air. When LPG is mixed with air it forms a flammable mixture from (1.8 to 10) % by volume.[1] To detect the presence of LPG at concentrations below one-fifth of the lower limit of flammability, it is marked with compounds that have a very low odor treshold, like tetrahydrothiophene (THT).[2] The vapor−liquid equilibrium (VLE) data for THT is required for estimating the concentration of THT in the gas phase. As THT is also present in the hydrocarbon streams of the petroleum refineries, the VLE data are required for modeling the behavior of the organic sulfur compounds in the oil refining processes, especially in the production of sulfur-free fuels.

## Experimental Section

***Materials.*** The suppliers and the purities of the materials used are presented in Table 1. THT was batch distilled at atmospheric pressure before use. The middle fraction was collected and analyzed with a GC, equipped with a flame ionization detector, which does not detect the presence of water. The purity of THT was better than 99.3 mass %. The middle fraction was dried over molecule sieves (Merck, 3A), and the water content was analyzed with Karl Fischer titration; it was no greater than 0.018 mass %. The degassing of THT was performed by vacuum rectification[3] with modifications.[4] Success of the purification was determined by comparing the measured vapor pressure and the refractive index with values obtained from the literature. Vapor pressures are shown in Table 2. Each reported pure component vapor pressure value was separately measured in separate VLE runs. The measured refractive index of THT was 1.5023 ± 0.0001, in comparison to a literature value of 1.50213.[5] Alkanes and alkenes were degassed in the syringe pump before use by opening the vacuum valve 10 times for a period of 10 s.

***Apparatus.*** The static total pressure apparatus employed in the experiment has been explained in detail by Uusi-Kyyny et al.[6] Temperatures were measured with Pt-100 probes connected to a temperature meter (Termolyzer S2541, Frontek). Probes had been calibrated at the Centre for Metrology and Accreditation, Finland. The pressure of the cell was measured with a Digiquartz 2300A-101-CE pressure transducer connected to a Digiquartz 740 intelligent display unit (Paroscientific). The range of the pressure measurement was from (0 to 2070) kPa with a temperature range from (219 to 380) K. The equilibrium cell had a total volume of 103.3 $cm^3$ with an uncertainty of 0.02 $cm^3$. The cell volume had been determined by injecting degassed water in the cell at 298.15 K. Injections of the compounds were made with syringe pumps (ISCO 260D and 100D).

***Procedure.*** After degassing, the first compound was injected into the cell, and the pure compound vapor pressure

**Table 1. Supplier and the Purity of the Material**

| compound | supplier | mass fraction purity/% |
|---|---|---|
| *n*-butane | Intergas | 99.95 |
| 2-methylpropane | Intergas | 99.95 |
| 2-methylpropene | Linde Gas | 99.91 |
| *trans*-2-butene | Linde Gas | 99.91 |
| tetrahydrothiophene | Aldrich | 99.3 (GC) |

**Table 2. Pure Compound Vapor Pressures[a]**

| | | *p*/kPa | | | |
|---|---|---|---|---|---|
| compound | *T*/K | this work | 5 | 16 | 17 |
| *n*-butane | 318.35 | 437.5 | 437.1 | 437.7 | 437.2 |
| | 346.97 | 881.7 | 883.7 | 885.3 | 883.4 |
| 2-methylpropane | 318.34 | 608.3 | 607.1 | 604.4 | 610.35 |
| | 346.96 | 1177.5 | 1179.4 | 1174.3 | 1180.2 |
| 2-methylpropene | 318.35 | 542.1 | 534.6 | 535.0 | 543.0 |
| | 346.14 | 1054.9 | 1041.3 | 1046.9 | 1058.9 |
| *trans*-2-butene | 318.34 | 423.5 | 424.1 | 419.6 | 423.9 |
| | 347.06 | 868.5 | 871.1 | 852.0 | 871.6 |
| tetrahydrothiophene | 318.34 | 7.3 | 6.7 | NA | 6.7 |
| | 318.35 | 6.7 | 6.7 | NA | 6.7 |
| | 318.35 | 6.9 | 6.7 | NA | 6.7 |
| | 318.35 | 6.9 | 6.7 | NA | 6.7 |
| | 346.14 | 21.4 | 21.3 | NA | 21.3 |
| | 346.97 | 22.2 | 22.0 | NA | 22.0 |
| | 346.97 | 22.5 | 22.0 | NA | 22.0 |
| | 347.07 | 22.2 | 22.0 | NA | 22.1 |

[a] Each value was measured in separate VLE runs.

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**Table 3. Pure Compound Physical Properties**[a]

| compound | tetrahydrothiophene | *n*-butane | 2-methylpropane | 2-methylpropene | *trans*-2-butene |
|---|---|---|---|---|---|
| CAS | 110-01-0 | 106-97-8 | 75-28-5 | 115-11-7 | 624-64-6 |
| $T_C$/K | 631.95 | 425.12 | 407.8 | 417.9 | 428.6 |
| $p_C$/MPa | 5.16 | 3.80 | 3.60 | 4.00 | 4.10 |
| $\omega$ | 0.199551 | 0.200164 | 0.183521 | 0.19484 | 0.217592 |
| $\nu_i$/cm$^3$·mol$^{-1}$ | 88.7032 | 101.394 | 105.35 | 95.3646 | 93.6136 |
| $R$ | 3.3342 | 3.1510 | 3.1503 | 2.9196 | 2.9189 |
| $Q$ | 2.4520 | 2.7760 | 2.7720 | 2.6840 | 2.5600 |

[a] Critical temperature, $T_C$, critical pressure, $p_C$, acentric factor, $\omega$, liquid molar volume at 298 K, $\nu_i$, relative van der Waals volume, $R$, relative van der Waals surface area, $Q$.[5] Normalization factors for volume and surface parameters are given in Abrams et al.[15]

**Table 4. VLE Data for *n*-Butane (1) + Tetrahydrothiophene (2)**[a]

| $T$/K | $n_1$/mol | $n_2$/mol | $z_1$ | $p_{exp}$/kPa | $p_{Leg}$/kPa | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 318.35 | 0.4242 ± 0.0016 | 0.0000 ± 0.0000 | 1.0000 ± 0.0000 | 437.5 | 437.5 | 1.0000 ± 0.0000 | 1.0000 ± 0.0000 | 1.00 ± 0.00 | 3.13 ± 0.05 |
| 318.35 | 0.4242 ± 0.0016 | 0.0022 ± 0.0000 | 0.9949 ± 0.0001 | 434.9 | 435.1 | 0.9948 ± 0.0001 | 0.9997 ± 0.0000 | 1.00 ± 0.00 | 3.08 ± 0.05 |
| 318.35 | 0.4242 ± 0.0016 | 0.0102 ± 0.0001 | 0.9765 ± 0.0003 | 426.5 | 426.6 | 0.9759 ± 0.0003 | 0.9986 ± 0.0001 | 1.00 ± 0.00 | 2.93 ± 0.04 |
| 318.35 | 0.4242 ± 0.0016 | 0.0229 ± 0.0001 | 0.9487 ± 0.0005 | 414.6 | 414.7 | 0.9476 ± 0.0005 | 0.9971 ± 0.0002 | 1.00 ± 0.00 | 2.72 ± 0.03 |
| 318.35 | 0.4242 ± 0.0016 | 0.0460 ± 0.0002 | 0.9022 ± 0.0007 | 396.7 | 396.7 | 0.9003 ± 0.0007 | 0.9949 ± 0.0003 | 1.01 ± 0.00 | 2.43 ± 0.02 |
| 318.35 | 0.4242 ± 0.0016 | 0.0731 ± 0.0002 | 0.8529 ± 0.0008 | 379.7 | 379.6 | 0.8506 ± 0.0008 | 0.9929 ± 0.0005 | 1.03 ± 0.00 | 2.18 ± 0.01 |
| 318.35 | 0.4242 ± 0.0016 | 0.1054 ± 0.0002 | 0.8010 ± 0.0010 | 363.5 | 363.4 | 0.7983 ± 0.0010 | 0.9911 ± 0.0005 | 1.05 ± 0.00 | 1.96 ± 0.00 |
| 318.35 | 0.4242 ± 0.0016 | 0.1397 ± 0.0003 | 0.7523 ± 0.0011 | 349.4 | 349.4 | 0.7494 ± 0.0011 | 0.9896 ± 0.0006 | 1.08 ± 0.00 | 1.79 ± 0.00 |
| 318.35 | 0.4242 ± 0.0016 | 0.1790 ± 0.0003 | 0.7033 ± 0.0011 | 336.0 | 336.0 | 0.7005 ± 0.0011 | 0.9881 ± 0.0007 | 1.11 ± 0.00 | 1.65 ± 0.00 |
| 318.34 | 0.4242 ± 0.0016 | 0.2270 ± 0.0003 | 0.6514 ± 0.0012 | 322.3 | 322.2 | 0.6488 ± 0.0012 | 0.9866 ± 0.0008 | 1.16 ± 0.00 | 1.53 ± 0.00 |
| 318.34 | 0.4242 ± 0.0016 | 0.2809 ± 0.0004 | 0.6016 ± 0.0012 | 309.1 | 309.1 | 0.5993 ± 0.0012 | 0.9852 ± 0.0009 | 1.20 ± 0.00 | 1.43 ± 0.00 |
| 318.35 | 0.4242 ± 0.0016 | 0.3455 ± 0.0004 | 0.5511 ± 0.0012 | 295.7 | 295.6 | 0.5492 ± 0.0012 | 0.9837 ± 0.0010 | 1.26 ± 0.00 | 1.35 ± 0.00 |
| 318.35 | 0.4242 ± 0.0016 | 0.4224 ± 0.0004 | 0.5010 ± 0.0011 | 281.9 | 281.7 | 0.4997 ± 0.0012 | 0.9822 ± 0.0011 | 1.32 ± 0.00 | 1.28 ± 0.00 |
| 318.35 | 0.4253 ± 0.0015 | 0.4233 ± 0.0005 | 0.5012 ± 0.0012 | 281.6 | 281.7 | 0.4999 ± 0.0012 | 0.9822 ± 0.0011 | 1.32 ± 0.00 | 1.28 ± 0.00 |
| 318.35 | 0.3487 ± 0.0013 | 0.4233 ± 0.0005 | 0.4517 ± 0.0012 | 266.5 | 266.7 | 0.4496 ± 0.0012 | 0.9804 ± 0.0012 | 1.39 ± 0.00 | 1.22 ± 0.00 |
| 318.35 | 0.2853 ± 0.0011 | 0.4233 ± 0.0005 | 0.4026 ± 0.0012 | 250.3 | 250.4 | 0.3997 ± 0.0012 | 0.9783 ± 0.0013 | 1.47 ± 0.00 | 1.17 ± 0.00 |
| 318.34 | 0.2292 ± 0.0009 | 0.4233 ± 0.0005 | 0.3513 ± 0.0012 | 231.6 | 231.6 | 0.3476 ± 0.0012 | 0.9757 ± 0.0015 | 1.57 ± 0.01 | 1.12 ± 0.00 |
| 318.35 | 0.1840 ± 0.0008 | 0.4233 ± 0.0005 | 0.3029 ± 0.0011 | 211.8 | 211.8 | 0.2986 ± 0.0011 | 0.9726 ± 0.0016 | 1.68 ± 0.01 | 1.09 ± 0.00 |
| 318.34 | 0.1442 ± 0.0006 | 0.4233 ± 0.0005 | 0.2541 ± 0.0010 | 189.3 | 189.3 | 0.2494 ± 0.0011 | 0.9684 ± 0.0019 | 1.80 ± 0.01 | 1.06 ± 0.00 |
| 318.34 | 0.1099 ± 0.0005 | 0.4233 ± 0.0005 | 0.2062 ± 0.0010 | 164.1 | 164.1 | 0.2012 ± 0.0010 | 0.9624 ± 0.0022 | 1.93 ± 0.01 | 1.04 ± 0.00 |
| 318.34 | 0.0791 ± 0.0004 | 0.4233 ± 0.0005 | 0.1574 ± 0.0008 | 134.8 | 134.8 | 0.1526 ± 0.0008 | 0.9529 ± 0.0026 | 2.09 ± 0.01 | 1.02 ± 0.00 |
| 318.34 | 0.0526 ± 0.0003 | 0.4233 ± 0.0005 | 0.1105 ± 0.0007 | 102.6 | 102.6 | 0.1064 ± 0.0007 | 0.9365 ± 0.0035 | 2.26 ± 0.02 | 1.01 ± 0.00 |
| 318.34 | 0.0269 ± 0.0002 | 0.4233 ± 0.0005 | 0.0597 ± 0.0005 | 62.3 | 62.3 | 0.0569 ± 0.0005 | 0.8925 ± 0.0058 | 2.47 ± 0.03 | 1.00 ± 0.00 |
| 318.35 | 0.0155 ± 0.0002 | 0.4233 ± 0.0005 | 0.0353 ± 0.0004 | 40.8 | 40.8 | 0.0335 ± 0.0004 | 0.8339 ± 0.0081 | 2.58 ± 0.03 | 1.00 ± 0.00 |
| 318.35 | 0.0077 ± 0.0001 | 0.4233 ± 0.0005 | 0.0180 ± 0.0003 | 24.6 | 24.6 | 0.0170 ± 0.0003 | 0.7218 ± 0.0128 | 2.67 ± 0.04 | 1.00 ± 0.00 |
| 318.35 | 0.0000 ± 0.0000 | 0.4233 ± 0.0005 | 0.0000 ± 0.0000 | 6.9 | 6.9 | 0.0000 ± 0.0000 | 0.0000 ± 0.0000 | 2.76 ± 0.04 | 1.00 ± 0.00 |
| 346.97 | 0.4213 ± 0.0015 | 0.0000 ± 0.0000 | 1.0000 ± 0.0000 | 881.7 | 881.7 | 1.0000 ± 0.0000 | 1.0000 ± 0.0000 | 1.00 ± 0.00 | 2.88 ± 0.04 |
| 346.97 | 0.4213 ± 0.0015 | 0.0040 ± 0.0000 | 0.9906 ± 0.0001 | 871.8 | 872.0 | 0.9898 ± 0.0001 | 0.9990 ± 0.0000 | 1.00 ± 0.00 | 2.81 ± 0.04 |
| 346.97 | 0.4213 ± 0.0015 | 0.0468 ± 0.0002 | 0.8999 ± 0.0007 | 791.8 | 791.6 | 0.8929 ± 0.0007 | 0.9910 ± 0.0003 | 1.01 ± 0.00 | 2.25 ± 0.01 |
| 346.97 | 0.4213 ± 0.0015 | 0.0741 ± 0.0002 | 0.8504 ± 0.0008 | 755.0 | 754.8 | 0.8410 ± 0.0009 | 0.9876 ± 0.0003 | 1.03 ± 0.00 | 2.03 ± 0.01 |
| 346.97 | 0.4213 ± 0.0015 | 0.1055 ± 0.0002 | 0.7997 ± 0.0010 | 720.9 | 720.8 | 0.7886 ± 0.0010 | 0.9845 ± 0.0004 | 1.05 ± 0.00 | 1.84 ± 0.00 |
| 346.97 | 0.4213 ± 0.0015 | 0.1412 ± 0.0003 | 0.7490 ± 0.0011 | 689.2 | 689.2 | 0.7366 ± 0.0011 | 0.9817 ± 0.0004 | 1.08 ± 0.00 | 1.69 ± 0.00 |
| 346.96 | 0.4213 ± 0.0015 | 0.1812 ± 0.0003 | 0.6992 ± 0.0011 | 659.6 | 659.7 | 0.6861 ± 0.0012 | 0.9791 ± 0.0004 | 1.11 ± 0.00 | 1.57 ± 0.00 |
| 346.96 | 0.4213 ± 0.0015 | 0.2272 ± 0.0003 | 0.6497 ± 0.0012 | 631.3 | 631.4 | 0.6362 ± 0.0013 | 0.9765 ± 0.0005 | 1.15 ± 0.00 | 1.47 ± 0.00 |
| 346.97 | 0.4213 ± 0.0015 | 0.2814 ± 0.0004 | 0.5996 ± 0.0012 | 602.9 | 602.9 | 0.5861 ± 0.0013 | 0.9740 ± 0.0005 | 1.20 ± 0.00 | 1.38 ± 0.00 |
| 346.97 | 0.4213 ± 0.0015 | 0.3462 ± 0.0004 | 0.5489 ± 0.0012 | 574.0 | 573.8 | 0.5359 ± 0.0013 | 0.9713 ± 0.0006 | 1.25 ± 0.00 | 1.31 ± 0.00 |
| 346.96 | 0.4213 ± 0.0015 | 0.4224 ± 0.0006 | 0.4994 ± 0.0013 | 544.6 | 544.4 | 0.4870 ± 0.0013 | 0.9685 ± 0.0006 | 1.31 ± 0.00 | 1.25 ± 0.00 |
| 346.96 | 0.4213 ± 0.0015 | 0.4224 ± 0.0006 | 0.4994 ± 0.0013 | 544.6 | 544.4 | 0.4870 ± 0.0013 | 0.9685 ± 0.0006 | 1.31 ± 0.00 | 1.25 ± 0.00 |
| 346.96 | 0.4213 ± 0.0015 | 0.4224 ± 0.0004 | 0.4994 ± 0.0011 | 544.6 | 544.4 | 0.4870 ± 0.0012 | 0.9685 ± 0.0006 | 1.31 ± 0.00 | 1.25 ± 0.00 |
| 346.97 | 0.4230 ± 0.0015 | 0.4233 ± 0.0005 | 0.4998 ± 0.0012 | 544.2 | 544.7 | 0.4875 ± 0.0013 | 0.9685 ± 0.0006 | 1.31 ± 0.00 | 1.25 ± 0.00 |
| 346.97 | 0.3466 ± 0.0013 | 0.4233 ± 0.0005 | 0.4502 ± 0.0012 | 511.8 | 512.2 | 0.4363 ± 0.0013 | 0.9652 ± 0.0007 | 1.38 ± 0.00 | 1.20 ± 0.00 |
| 346.97 | 0.2830 ± 0.0011 | 0.4233 ± 0.0005 | 0.4007 ± 0.0012 | 477.2 | 477.4 | 0.3854 ± 0.0012 | 0.9614 ± 0.0008 | 1.46 ± 0.00 | 1.15 ± 0.00 |
| 346.97 | 0.2285 ± 0.0009 | 0.4233 ± 0.0005 | 0.3505 ± 0.0012 | 439.3 | 439.2 | 0.3342 ± 0.0012 | 0.9567 ± 0.0009 | 1.55 ± 0.00 | 1.11 ± 0.00 |
| 346.98 | 0.1814 ± 0.0007 | 0.4233 ± 0.0005 | 0.2999 ± 0.0011 | 397.0 | 396.8 | 0.2830 ± 0.0011 | 0.9506 ± 0.0010 | 1.65 ± 0.01 | 1.08 ± 0.00 |
| 346.97 | 0.1419 ± 0.0006 | 0.4233 ± 0.0005 | 0.2511 ± 0.0010 | 351.6 | 351.4 | 0.2342 ± 0.0011 | 0.9428 ± 0.0011 | 1.77 ± 0.01 | 1.05 ± 0.00 |
| 346.97 | 0.1081 ± 0.0005 | 0.4233 ± 0.0005 | 0.2034 ± 0.0009 | 302.3 | 302.3 | 0.1873 ± 0.0010 | 0.9319 ± 0.0013 | 1.90 ± 0.01 | 1.03 ± 0.00 |
| 346.97 | 0.0771 ± 0.0004 | 0.4233 ± 0.0005 | 0.1541 ± 0.0008 | 245.6 | 245.7 | 0.1399 ± 0.0008 | 0.9144 ± 0.0015 | 2.05 ± 0.01 | 1.02 ± 0.00 |
| 346.97 | 0.0490 ± 0.0003 | 0.4233 ± 0.0005 | 0.1038 ± 0.0007 | 180.8 | 180.9 | 0.0926 ± 0.0007 | 0.8814 ± 0.0020 | 2.22 ± 0.02 | 1.01 ± 0.00 |
| 346.97 | 0.0259 ± 0.0002 | 0.4233 ± 0.0005 | 0.0577 ± 0.0005 | 114.8 | 114.8 | 0.0506 ± 0.0005 | 0.8100 ± 0.0030 | 2.40 ± 0.03 | 1.00 ± 0.00 |
| 346.97 | 0.0169 ± 0.0002 | 0.4233 ± 0.0005 | 0.0383 ± 0.0004 | 85.0 | 85.0 | 0.0333 ± 0.0004 | 0.7418 ± 0.0038 | 2.48 ± 0.03 | 1.00 ± 0.00 |
| 346.97 | 0.0072 ± 0.0001 | 0.4233 ± 0.0005 | 0.0168 ± 0.0003 | 50.4 | 50.3 | 0.0145 ± 0.0003 | 0.5610 ± 0.0057 | 2.57 ± 0.04 | 1.00 ± 0.00 |
| 346.97 | 0.0000 ± 0.0000 | 0.4233 ± 0.0005 | 0.0000 ± 0.0000 | 22.2 | 22.2 | 0.0000 ± 0.0000 | 0.0000 ± 0.0000 | 2.65 ± 0.04 | 1.00 ± 0.00 |

[a] Experimental temperature, $T$; amount of compound in the equilibrium cell, $n_i$; total mole fraction, $z_1$; experimental pressure, $p_{exp}$; pressure calculated with Legendre model, $p_{Leg}$; liquid and vapor phase equilibrium mole fractions, $x_1$ and $y_1$; activity coefficients calculated with Legendre model, $\gamma_i$.

was measured and compared to the value obtained from the literature. If the error was within an acceptable limit, the second compound was added into the cell, and after the pressure had reached equilibrium, in about 30 min, the total pressure was measured. The addition of the second compound was repeated until an approximately equimolar composition

**Table 5. VLE Data for 2-Methylpropane (1) + Tetrahydrothiophene (2)[a]**

| $T$/K | $n_1$/mol | $n_2$/mol | $z_1$ | $p_{exp}$/kPa | $p_{Leg}$/kPa | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 318.34 | 0.4427 ± 0.0015 | 0.0000 ± 0.0000 | 1.0000 ± 0.0000 | 608.3 | 608.3 | 1.0000 ± 0.0000 | 1.0000 ± 0.0000 | 1.00 ± 0.00 | 3.64 ± 0.02 |
| 318.35 | 0.4427 ± 0.0015 | 0.0045 ± 0.0001 | 0.9898 ± 0.0002 | 601.1 | 601.2 | 0.9895 ± 0.0002 | 0.9994 ± 0.0000 | 1.00 ± 0.00 | 3.52 ± 0.02 |
| 318.34 | 0.4427 ± 0.0015 | 0.0136 ± 0.0002 | 0.9701 ± 0.0005 | 588.2 | 588.4 | 0.9693 ± 0.0005 | 0.9983 ± 0.0001 | 1.00 ± 0.00 | 3.30 ± 0.02 |
| 318.34 | 0.4427 ± 0.0015 | 0.0195 ± 0.0001 | 0.9577 ± 0.0004 | 580.5 | 580.7 | 0.9565 ± 0.0004 | 0.9977 ± 0.0001 | 1.00 ± 0.00 | 3.17 ± 0.02 |
| 318.34 | 0.4427 ± 0.0015 | 0.0481 ± 0.0002 | 0.9019 ± 0.0006 | 549.8 | 549.9 | 0.8996 ± 0.0007 | 0.9953 ± 0.0003 | 1.02 ± 0.00 | 2.70 ± 0.01 |
| 318.35 | 0.4427 ± 0.0015 | 0.0786 ± 0.0002 | 0.8493 ± 0.0008 | 525.1 | 525.1 | 0.8462 ± 0.0008 | 0.9936 ± 0.0004 | 1.04 ± 0.00 | 2.35 ± 0.01 |
| 318.35 | 0.4427 ± 0.0015 | 0.1106 ± 0.0002 | 0.8001 ± 0.0009 | 504.6 | 504.6 | 0.7967 ± 0.0009 | 0.9922 ± 0.0005 | 1.06 ± 0.00 | 2.10 ± 0.01 |
| 318.35 | 0.4427 ± 0.0015 | 0.1477 ± 0.0003 | 0.7498 ± 0.0010 | 485.5 | 485.5 | 0.7462 ± 0.0010 | 0.9909 ± 0.0005 | 1.09 ± 0.00 | 1.90 ± 0.00 |
| 318.35 | 0.4427 ± 0.0015 | 0.1904 ± 0.0003 | 0.6992 ± 0.0011 | 467.5 | 467.5 | 0.6958 ± 0.0011 | 0.9898 ± 0.0006 | 1.13 ± 0.00 | 1.73 ± 0.00 |
| 318.35 | 0.4427 ± 0.0015 | 0.2382 ± 0.0003 | 0.6502 ± 0.0011 | 450.7 | 450.7 | 0.6470 ± 0.0011 | 0.9887 ± 0.0006 | 1.18 ± 0.00 | 1.60 ± 0.00 |
| 318.35 | 0.4427 ± 0.0015 | 0.2949 ± 0.0004 | 0.6002 ± 0.0011 | 433.8 | 433.7 | 0.5975 ± 0.0012 | 0.9877 ± 0.0007 | 1.23 ± 0.00 | 1.48 ± 0.00 |
| 318.35 | 0.4427 ± 0.0015 | 0.3628 ± 0.0004 | 0.5496 ± 0.0012 | 416.3 | 416.2 | 0.5475 ± 0.0012 | 0.9866 ± 0.0007 | 1.30 ± 0.00 | 1.39 ± 0.00 |
| 318.35 | 0.4427 ± 0.0015 | 0.4419 ± 0.0004 | 0.5004 ± 0.0011 | 398.6 | 398.4 | 0.4991 ± 0.0011 | 0.9855 ± 0.0008 | 1.37 ± 0.00 | 1.31 ± 0.00 |
| 318.34 | 0.4431 ± 0.0015 | 0.4442 ± 0.0005 | 0.4993 ± 0.0011 | 397.9 | 398.0 | 0.4980 ± 0.0011 | 0.9855 ± 0.0008 | 1.37 ± 0.00 | 1.31 ± 0.00 |
| 318.34 | 0.3639 ± 0.0013 | 0.4442 ± 0.0005 | 0.4503 ± 0.0011 | 378.1 | 378.2 | 0.4479 ± 0.0012 | 0.9843 ± 0.0009 | 1.45 ± 0.00 | 1.24 ± 0.00 |
| 318.34 | 0.2956 ± 0.0010 | 0.4442 ± 0.0005 | 0.3996 ± 0.0011 | 355.5 | 355.6 | 0.3960 ± 0.0012 | 0.9827 ± 0.0010 | 1.55 ± 0.01 | 1.18 ± 0.00 |
| 318.35 | 0.2396 ± 0.0009 | 0.4442 ± 0.0005 | 0.3504 ± 0.0011 | 331.2 | 331.1 | 0.3458 ± 0.0011 | 0.9809 ± 0.0011 | 1.66 ± 0.01 | 1.14 ± 0.00 |
| 318.34 | 0.1907 ± 0.0007 | 0.4442 ± 0.0005 | 0.3004 ± 0.0011 | 302.8 | 302.7 | 0.2948 ± 0.0011 | 0.9786 ± 0.0012 | 1.79 ± 0.01 | 1.10 ± 0.00 |
| 318.34 | 0.1490 ± 0.0006 | 0.4442 ± 0.0005 | 0.2512 ± 0.0010 | 270.6 | 270.6 | 0.2449 ± 0.0010 | 0.9755 ± 0.0014 | 1.93 ± 0.01 | 1.07 ± 0.00 |
| 318.34 | 0.1126 ± 0.0005 | 0.4442 ± 0.0005 | 0.2023 ± 0.0009 | 233.6 | 233.6 | 0.1956 ± 0.0009 | 0.9709 ± 0.0016 | 2.10 ± 0.01 | 1.04 ± 0.00 |
| 318.34 | 0.0795 ± 0.0004 | 0.4442 ± 0.0005 | 0.1517 ± 0.0008 | 189.1 | 189.2 | 0.1453 ± 0.0008 | 0.9633 ± 0.0020 | 2.29 ± 0.01 | 1.02 ± 0.00 |
| 318.35 | 0.0511 ± 0.0003 | 0.4442 ± 0.0005 | 0.1032 ± 0.0006 | 139.5 | 139.5 | 0.0978 ± 0.0006 | 0.9494 ± 0.0026 | 2.51 ± 0.02 | 1.01 ± 0.00 |
| 318.35 | 0.0256 ± 0.0002 | 0.4442 ± 0.0005 | 0.0545 ± 0.0004 | 82.0 | 81.9 | 0.0510 ± 0.0004 | 0.9123 ± 0.0046 | 2.75 ± 0.03 | 1.00 ± 0.00 |
| 318.35 | 0.0158 ± 0.0002 | 0.4442 ± 0.0005 | 0.0344 ± 0.0004 | 55.7 | 55.7 | 0.0320 ± 0.0004 | 0.8701 ± 0.0063 | 2.86 ± 0.04 | 1.00 ± 0.00 |
| 318.35 | 0.0077 ± 0.0001 | 0.4442 ± 0.0005 | 0.0170 ± 0.0003 | 31.7 | 31.7 | 0.0157 ± 0.0003 | 0.7709 ± 0.0104 | 2.96 ± 0.04 | 1.00 ± 0.00 |
| 318.34 | 0.0000 ± 0.0000 | 0.4442 ± 0.0005 | 0.0000 ± 0.0000 | 7.3 | 7.3 | 0.0000 ± 0.0000 | 0.0000 ± 0.0000 | 3.06 ± 0.05 | 1.00 ± 0.00 |
| 346.96 | 0.4133 ± 0.0014 | 0.0000 ± 0.0000 | 1.0000 ± 0.0000 | 1177.5 | 1177.5 | 1.0000 ± 0.0000 | 1.0000 ± 0.0000 | 1.00 ± 0.00 | 3.37 ± 0.02 |
| 346.99 | 0.4133 ± 0.0014 | 0.0034 ± 0.0001 | 0.9918 ± 0.0002 | 1166.1 | 1165.9 | 0.9913 ± 0.0002 | 0.9991 ± 0.0000 | 1.00 ± 0.00 | 3.28 ± 0.02 |
| 346.97 | 0.4133 ± 0.0014 | 0.0123 ± 0.0002 | 0.9711 ± 0.0004 | 1136.5 | 1136.0 | 0.9693 ± 0.0005 | 0.9971 ± 0.0001 | 1.00 ± 0.00 | 3.06 ± 0.02 |
| 346.97 | 0.4133 ± 0.0014 | 0.0195 ± 0.0001 | 0.9550 ± 0.0004 | 1114.8 | 1114.6 | 0.9524 ± 0.0004 | 0.9956 ± 0.0001 | 1.00 ± 0.00 | 2.92 ± 0.02 |
| 346.97 | 0.4133 ± 0.0014 | 0.0440 ± 0.0002 | 0.9037 ± 0.0006 | 1054.6 | 1054.1 | 0.8989 ± 0.0007 | 0.9917 ± 0.0002 | 1.02 ± 0.00 | 2.52 ± 0.01 |
| 346.97 | 0.4133 ± 0.0014 | 0.0732 ± 0.0002 | 0.8496 ± 0.0008 | 1000.1 | 999.7 | 0.8434 ± 0.0009 | 0.9884 ± 0.0003 | 1.04 ± 0.00 | 2.21 ± 0.01 |
| 346.97 | 0.4133 ± 0.0014 | 0.1039 ± 0.0002 | 0.7991 ± 0.0009 | 955.2 | 955.1 | 0.7922 ± 0.0010 | 0.9859 ± 0.0003 | 1.06 ± 0.00 | 1.98 ± 0.01 |
| 346.97 | 0.4133 ± 0.0014 | 0.1389 ± 0.0003 | 0.7484 ± 0.0010 | 914.1 | 914.2 | 0.7414 ± 0.0011 | 0.9836 ± 0.0004 | 1.09 ± 0.00 | 1.80 ± 0.00 |
| 346.96 | 0.4133 ± 0.0014 | 0.1791 ± 0.0003 | 0.6977 ± 0.0011 | 875.5 | 875.6 | 0.6909 ± 0.0012 | 0.9816 ± 0.0004 | 1.13 ± 0.00 | 1.65 ± 0.00 |
| 346.97 | 0.4133 ± 0.0014 | 0.2245 ± 0.0003 | 0.6480 ± 0.0011 | 839.7 | 839.7 | 0.6419 ± 0.0012 | 0.9797 ± 0.0004 | 1.17 ± 0.00 | 1.53 ± 0.00 |
| 346.97 | 0.4133 ± 0.0014 | 0.2788 ± 0.0004 | 0.5972 ± 0.0012 | 803.3 | 803.1 | 0.5920 ± 0.0012 | 0.9777 ± 0.0005 | 1.22 ± 0.00 | 1.43 ± 0.00 |
| 346.98 | 0.4133 ± 0.0014 | 0.3428 ± 0.0004 | 0.5466 ± 0.0012 | 767.1 | 766.4 | 0.5427 ± 0.0012 | 0.9757 ± 0.0005 | 1.28 ± 0.00 | 1.35 ± 0.00 |
| 346.99 | 0.4133 ± 0.0014 | 0.4184 ± 0.0004 | 0.4970 ± 0.0011 | 730.2 | 729.2 | 0.4944 ± 0.0011 | 0.9737 ± 0.0005 | 1.34 ± 0.00 | 1.28 ± 0.00 |
| 346.97 | 0.4180 ± 0.0014 | 0.4203 ± 0.0005 | 0.4986 ± 0.0012 | 728.6 | 729.9 | 0.4963 ± 0.0012 | 0.9738 ± 0.0005 | 1.34 ± 0.00 | 1.28 ± 0.00 |
| 346.97 | 0.3426 ± 0.0012 | 0.4203 ± 0.0005 | 0.4491 ± 0.0012 | 686.8 | 687.6 | 0.4446 ± 0.0012 | 0.9713 ± 0.0006 | 1.42 ± 0.00 | 1.22 ± 0.00 |
| 346.97 | 0.2798 ± 0.0010 | 0.4203 ± 0.0005 | 0.3996 ± 0.0012 | 641.5 | 641.8 | 0.3931 ± 0.0012 | 0.9685 ± 0.0006 | 1.51 ± 0.00 | 1.17 ± 0.00 |
| 346.97 | 0.2256 ± 0.0008 | 0.4203 ± 0.0005 | 0.3493 ± 0.0011 | 590.7 | 590.7 | 0.3409 ± 0.0012 | 0.9649 ± 0.0007 | 1.61 ± 0.01 | 1.12 ± 0.00 |
| 346.96 | 0.1800 ± 0.0007 | 0.4203 ± 0.0005 | 0.2998 ± 0.0011 | 535.0 | 534.8 | 0.2899 ± 0.0011 | 0.9605 ± 0.0008 | 1.73 ± 0.01 | 1.09 ± 0.00 |
| 346.96 | 0.1408 ± 0.0006 | 0.4203 ± 0.0005 | 0.2509 ± 0.0010 | 473.3 | 473.0 | 0.2399 ± 0.0010 | 0.9546 ± 0.0009 | 1.86 ± 0.01 | 1.06 ± 0.00 |
| 346.97 | 0.1066 ± 0.0005 | 0.4203 ± 0.0005 | 0.2023 ± 0.0009 | 404.7 | 404.4 | 0.1909 ± 0.0009 | 0.9461 ± 0.0010 | 2.01 ± 0.01 | 1.04 ± 0.00 |
| 346.97 | 0.0756 ± 0.0004 | 0.4203 ± 0.0005 | 0.1524 ± 0.0008 | 325.5 | 325.4 | 0.1417 ± 0.0008 | 0.9322 ± 0.0012 | 2.18 ± 0.01 | 1.02 ± 0.00 |
| 346.98 | 0.0510 ± 0.0003 | 0.4203 ± 0.0005 | 0.1082 ± 0.0007 | 247.4 | 247.4 | 0.0991 ± 0.0007 | 0.9100 ± 0.0015 | 2.35 ± 0.02 | 1.01 ± 0.00 |
| 346.96 | 0.0252 ± 0.0002 | 0.4203 ± 0.0005 | 0.0565 ± 0.0004 | 145.7 | 145.9 | 0.0508 ± 0.0004 | 0.8464 ± 0.0025 | 2.57 ± 0.03 | 1.00 ± 0.00 |
| 346.97 | 0.0175 ± 0.0002 | 0.4203 ± 0.0005 | 0.0399 ± 0.0005 | 110.8 | 111.2 | 0.0357 ± 0.0005 | 0.7980 ± 0.0031 | 2.64 ± 0.03 | 1.00 ± 0.00 |
| 346.97 | 0.0055 ± 0.0001 | 0.4203 ± 0.0005 | 0.0130 ± 0.0002 | 52.3 | 52.1 | 0.0115 ± 0.0002 | 0.5679 ± 0.0052 | 2.77 ± 0.04 | 1.00 ± 0.00 |
| 346.97 | 0.0000 ± 0.0000 | 0.4203 ± 0.0005 | 0.0000 ± 0.0000 | 22.5 | 22.5 | 0.0000 ± 0.0000 | 0.0000 ± 0.0000 | 2.84 ± 0.04 | 1.00 ± 0.00 |

[a] Experimental temperature, $T$; amount of compound in the equilibrium cell, $n_i$; total mole fraction, $z_1$; experimental pressure, $p_{exp}$; pressure calculated with Legendre model, $p_{Leg}$; liquid and vapor phase equilibrium mole fractions, $x_1$ and $y_1$; activity coefficients calculated with Legendre model, $\gamma_i$.

was reached. At this point, the cell was drained and emptied with a vacuum. Then the injection of the compounds was repeated in a reversed order to obtain the other half of the data set. The quality of the data was evaluated based on how well the vapor pressure of each half coincided at the equimolar composition and how well the measured pure component vapor pressure agreed with the values reported in the literature.

***Data Reduction.*** The data measured in the experiment consisted of the total pressure, temperature, and the total composition inside the cell at equilibrium. To obtain the compositions of the vapor and liquid phases, the data were reduced by the Legendre polynomials as the liquid activity model[7] and the cubic Soave−Redlich−Kwong[8] equation of state; the binary interaction parameters were set to 0. The data reduction was performed according to the Barker method.[9] The amount of parameters for Legendre polynomials was increased until the absolute deviation was below the uncertainty in the measured cell pressure. The details of this data reduction have been reported by Uusi-Kyyny et al.[6] The data were reduced with the in-house software, VLEFIT.[10] The compound properties used in the data reduction are shown in Table 3.

***Error Analysis.*** Maximum uncertainty in the liquid density correlation was estimated as the maximum absolute error between the data sets used to obtain the correlation and the

**Table 6. VLE Data for 2-Methylpropene (1) + Tetrahydrothiophene (2)[a]**

| $T$/K | $n_1$/mol | $n_2$/mol | $z_1$ | $p_{exp}$/kPa | $p_{Leg}$/kPa | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 318.35 | 0.4611 ± 0.0010 | 0.0000 ± 0.0000 | 1.0000 ± 0.0000 | 542.1 | 542.1 | 1.0000 ± 0.0000 | 1.0000 ± 0.0000 | 1.00 ± 0.00 | 2.44 ± 0.02 |
| 318.35 | 0.4611 ± 0.0010 | 0.0047 ± 0.0001 | 0.9900 ± 0.0002 | 535.6 | 535.9 | 0.9897 ± 0.0002 | 0.9996 ± 0.0000 | 1.00 ± 0.00 | 2.39 ± 0.01 |
| 318.35 | 0.4611 ± 0.0010 | 0.0143 ± 0.0001 | 0.9699 ± 0.0004 | 523.9 | 524.1 | 0.9691 ± 0.0004 | 0.9988 ± 0.0001 | 1.00 ± 0.00 | 2.28 ± 0.01 |
| 318.34 | 0.4611 ± 0.0010 | 0.0243 ± 0.0001 | 0.9499 ± 0.0003 | 512.7 | 512.9 | 0.9487 ± 0.0004 | 0.9981 ± 0.0001 | 1.00 ± 0.00 | 2.19 ± 0.01 |
| 318.34 | 0.4611 ± 0.0010 | 0.0514 ± 0.0002 | 0.8996 ± 0.0005 | 486.9 | 487.0 | 0.8975 ± 0.0005 | 0.9965 ± 0.0002 | 1.01 ± 0.00 | 1.98 ± 0.01 |
| 318.35 | 0.4611 ± 0.0010 | 0.0819 ± 0.0002 | 0.8492 ± 0.0006 | 463.6 | 463.6 | 0.8465 ± 0.0006 | 0.9950 ± 0.0003 | 1.03 ± 0.00 | 1.80 ± 0.01 |
| 318.35 | 0.4611 ± 0.0010 | 0.1159 ± 0.0003 | 0.7991 ± 0.0007 | 442.1 | 442.2 | 0.7961 ± 0.0007 | 0.9937 ± 0.0004 | 1.04 ± 0.00 | 1.66 ± 0.01 |
| 318.35 | 0.4611 ± 0.0010 | 0.1539 ± 0.0003 | 0.7498 ± 0.0007 | 422.2 | 422.4 | 0.7467 ± 0.0008 | 0.9925 ± 0.0005 | 1.07 ± 0.00 | 1.54 ± 0.00 |
| 318.35 | 0.4611 ± 0.0010 | 0.1988 ± 0.0003 | 0.6987 ± 0.0008 | 402.2 | 402.6 | 0.6957 ± 0.0008 | 0.9913 ± 0.0006 | 1.10 ± 0.00 | 1.44 ± 0.00 |
| 318.34 | 0.4611 ± 0.0010 | 0.2489 ± 0.0004 | 0.6494 ± 0.0008 | 383.3 | 383.8 | 0.6467 ± 0.0008 | 0.9901 ± 0.0006 | 1.13 ± 0.00 | 1.35 ± 0.00 |
| 318.34 | 0.4611 ± 0.0010 | 0.3088 ± 0.0004 | 0.5989 ± 0.0008 | 364.1 | 364.4 | 0.5967 ± 0.0008 | 0.9888 ± 0.0007 | 1.16 ± 0.00 | 1.28 ± 0.00 |
| 318.34 | 0.4611 ± 0.0010 | 0.3794 ± 0.0004 | 0.5486 ± 0.0008 | 344.9 | 344.6 | 0.5469 ± 0.0008 | 0.9874 ± 0.0008 | 1.21 ± 0.00 | 1.23 ± 0.00 |
| 318.35 | 0.4611 ± 0.0010 | 0.4625 ± 0.0004 | 0.4992 ± 0.0008 | 326.1 | 324.3 | 0.4981 ± 0.0008 | 0.9858 ± 0.0009 | 1.25 ± 0.00 | 1.18 ± 0.00 |
| 318.35 | 0.4617 ± 0.0008 | 0.4608 ± 0.0005 | 0.5005 ± 0.0007 | 325.5 | 324.7 | 0.4994 ± 0.0007 | 0.9859 ± 0.0008 | 1.25 ± 0.00 | 1.18 ± 0.00 |
| 318.34 | 0.3790 ± 0.0008 | 0.4608 ± 0.0005 | 0.4513 ± 0.0008 | 302.2 | 302.5 | 0.4494 ± 0.0008 | 0.9841 ± 0.0010 | 1.30 ± 0.00 | 1.14 ± 0.00 |
| 318.35 | 0.3098 ± 0.0007 | 0.4608 ± 0.0005 | 0.4021 ± 0.0008 | 278.3 | 278.9 | 0.3994 ± 0.0008 | 0.9819 ± 0.0011 | 1.35 ± 0.00 | 1.11 ± 0.00 |
| 318.35 | 0.2504 ± 0.0006 | 0.4608 ± 0.0005 | 0.3521 ± 0.0008 | 252.6 | 253.2 | 0.3488 ± 0.0008 | 0.9792 ± 0.0013 | 1.41 ± 0.00 | 1.08 ± 0.00 |
| 318.35 | 0.2000 ± 0.0005 | 0.4608 ± 0.0005 | 0.3027 ± 0.0008 | 225.6 | 225.9 | 0.2988 ± 0.0008 | 0.9757 ± 0.0015 | 1.47 ± 0.00 | 1.06 ± 0.00 |
| 318.35 | 0.1554 ± 0.0004 | 0.4608 ± 0.0005 | 0.2522 ± 0.0007 | 196.0 | 196.0 | 0.2480 ± 0.0007 | 0.9709 ± 0.0018 | 1.54 ± 0.00 | 1.04 ± 0.00 |
| 318.35 | 0.1177 ± 0.0004 | 0.4608 ± 0.0005 | 0.2035 ± 0.0007 | 165.1 | 164.9 | 0.1992 ± 0.0007 | 0.9642 ± 0.0021 | 1.61 ± 0.01 | 1.03 ± 0.00 |
| 318.34 | 0.0835 ± 0.0003 | 0.4608 ± 0.0005 | 0.1534 ± 0.0006 | 130.7 | 130.6 | 0.1494 ± 0.0006 | 0.9532 ± 0.0027 | 1.70 ± 0.01 | 1.01 ± 0.00 |
| 318.34 | 0.0543 ± 0.0002 | 0.4608 ± 0.0005 | 0.1053 ± 0.0005 | 95.2 | 95.1 | 0.1020 ± 0.0005 | 0.9337 ± 0.0037 | 1.79 ± 0.01 | 1.01 ± 0.00 |
| 318.34 | 0.0271 ± 0.0002 | 0.4608 ± 0.0005 | 0.0555 ± 0.0004 | 55.2 | 55.3 | 0.0534 ± 0.0004 | 0.8825 ± 0.0064 | 1.90 ± 0.02 | 1.00 ± 0.00 |
| 318.34 | 0.0172 ± 0.0002 | 0.4608 ± 0.0005 | 0.0360 ± 0.0004 | 38.8 | 38.8 | 0.0346 ± 0.0004 | 0.8307 ± 0.0085 | 1.94 ± 0.02 | 1.00 ± 0.00 |
| 318.35 | 0.0070 ± 0.0001 | 0.4608 ± 0.0005 | 0.0149 ± 0.0002 | 20.2 | 20.2 | 0.0142 ± 0.0002 | 0.6710 ± 0.0141 | 2.00 ± 0.03 | 1.00 ± 0.00 |
| 318.35 | 0.0000 ± 0.0000 | 0.4608 ± 0.0005 | 0.0000 ± 0.0000 | 6.7 | 6.7 | 0.0000 ± 0.0000 | 0.0000 ± 0.0000 | 2.04 ± 0.03 | 1.00 ± 0.00 |
| 346.14 | 0.4453 ± 0.0004 | 0.0000 ± 0.0000 | 1.0000 ± 0.0000 | 1054.9 | 1054.9 | 1.0000 ± 0.0000 | 1.0000 ± 0.0000 | 1.00 ± 0.00 | 2.37 ± 0.02 |
| 346.14 | 0.4453 ± 0.0004 | 0.0047 ± 0.0001 | 0.9897 ± 0.0002 | 1041.1 | 1041.2 | 0.9891 ± 0.0002 | 0.9992 ± 0.0000 | 1.00 ± 0.00 | 2.31 ± 0.02 |
| 346.14 | 0.4453 ± 0.0004 | 0.0139 ± 0.0001 | 0.9698 ± 0.0003 | 1015.8 | 1016.2 | 0.9683 ± 0.0003 | 0.9978 ± 0.0001 | 1.00 ± 0.00 | 2.21 ± 0.01 |
| 346.14 | 0.4453 ± 0.0004 | 0.0236 ± 0.0001 | 0.9496 ± 0.0003 | 992.1 | 992.3 | 0.9472 ± 0.0003 | 0.9964 ± 0.0001 | 1.00 ± 0.00 | 2.11 ± 0.01 |
| 346.15 | 0.4453 ± 0.0004 | 0.0496 ± 0.0002 | 0.8997 ± 0.0004 | 938.2 | 938.3 | 0.8956 ± 0.0004 | 0.9934 ± 0.0002 | 1.01 ± 0.00 | 1.91 ± 0.01 |
| 346.15 | 0.4453 ± 0.0004 | 0.0786 ± 0.0002 | 0.8500 ± 0.0004 | 889.7 | 890.1 | 0.8449 ± 0.0004 | 0.9908 ± 0.0002 | 1.03 ± 0.00 | 1.75 ± 0.00 |
| 346.14 | 0.4453 ± 0.0004 | 0.1119 ± 0.0002 | 0.7992 ± 0.0004 | 844.4 | 845.1 | 0.7936 ± 0.0005 | 0.9883 ± 0.0002 | 1.04 ± 0.00 | 1.62 ± 0.00 |
| 346.14 | 0.4453 ± 0.0004 | 0.1490 ± 0.0002 | 0.7493 ± 0.0004 | 802.9 | 803.6 | 0.7436 ± 0.0005 | 0.9860 ± 0.0003 | 1.07 ± 0.00 | 1.51 ± 0.00 |
| 346.15 | 0.4453 ± 0.0004 | 0.1910 ± 0.0002 | 0.6998 ± 0.0004 | 763.5 | 764.2 | 0.6944 ± 0.0005 | 0.9838 ± 0.0003 | 1.09 ± 0.00 | 1.42 ± 0.00 |
| 346.15 | 0.4453 ± 0.0004 | 0.2407 ± 0.0002 | 0.6492 ± 0.0004 | 724.1 | 724.7 | 0.6444 ± 0.0004 | 0.9815 ± 0.0004 | 1.12 ± 0.00 | 1.34 ± 0.00 |
| 346.14 | 0.4453 ± 0.0004 | 0.2978 ± 0.0003 | 0.5993 ± 0.0004 | 685.5 | 686.0 | 0.5953 ± 0.0004 | 0.9792 ± 0.0004 | 1.16 ± 0.00 | 1.28 ± 0.00 |
| 346.15 | 0.4453 ± 0.0004 | 0.3652 ± 0.0003 | 0.5494 ± 0.0004 | 646.9 | 646.8 | 0.5465 ± 0.0004 | 0.9767 ± 0.0005 | 1.19 ± 0.00 | 1.22 ± 0.00 |
| 346.15 | 0.4453 ± 0.0004 | 0.4472 ± 0.0002 | 0.4989 ± 0.0003 | 607.1 | 606.1 | 0.4972 ± 0.0003 | 0.9738 ± 0.0005 | 1.24 ± 0.00 | 1.18 ± 0.00 |
| 346.14 | 0.4448 ± 0.0003 | 0.4452 ± 0.0003 | 0.4998 ± 0.0003 | 607.9 | 606.8 | 0.4980 ± 0.0003 | 0.9739 ± 0.0005 | 1.24 ± 0.00 | 1.18 ± 0.00 |
| 346.14 | 0.3651 ± 0.0003 | 0.4452 ± 0.0003 | 0.4506 ± 0.0004 | 563.3 | 563.0 | 0.4474 ± 0.0004 | 0.9706 ± 0.0006 | 1.28 ± 0.00 | 1.14 ± 0.00 |
| 346.14 | 0.2977 ± 0.0003 | 0.4452 ± 0.0003 | 0.4008 ± 0.0004 | 516.3 | 516.5 | 0.3961 ± 0.0004 | 0.9666 ± 0.0007 | 1.34 ± 0.00 | 1.10 ± 0.00 |
| 346.14 | 0.2411 ± 0.0003 | 0.4452 ± 0.0003 | 0.3513 ± 0.0004 | 467.5 | 467.7 | 0.3455 ± 0.0004 | 0.9618 ± 0.0008 | 1.39 ± 0.00 | 1.08 ± 0.00 |
| 346.15 | 0.1934 ± 0.0003 | 0.4452 ± 0.0003 | 0.3028 ± 0.0004 | 417.1 | 417.1 | 0.2961 ± 0.0004 | 0.9558 ± 0.0009 | 1.46 ± 0.00 | 1.06 ± 0.00 |
| 346.15 | 0.1513 ± 0.0002 | 0.4452 ± 0.0003 | 0.2536 ± 0.0004 | 362.4 | 362.4 | 0.2463 ± 0.0004 | 0.9475 ± 0.0010 | 1.52 ± 0.00 | 1.04 ± 0.00 |
| 346.14 | 0.1138 ± 0.0002 | 0.4452 ± 0.0003 | 0.2036 ± 0.0004 | 303.2 | 303.3 | 0.1962 ± 0.0004 | 0.9355 ± 0.0012 | 1.60 ± 0.00 | 1.02 ± 0.00 |
| 346.14 | 0.0813 ± 0.0002 | 0.4452 ± 0.0003 | 0.1545 ± 0.0004 | 241.3 | 241.5 | 0.1476 ± 0.0004 | 0.9170 ± 0.0014 | 1.68 ± 0.01 | 1.01 ± 0.00 |
| 346.14 | 0.0518 ± 0.0002 | 0.4452 ± 0.0003 | 0.1041 ± 0.0004 | 174.1 | 174.3 | 0.0985 ± 0.0004 | 0.8822 ± 0.0020 | 1.77 ± 0.01 | 1.01 ± 0.00 |
| 346.14 | 0.0270 ± 0.0001 | 0.4452 ± 0.0003 | 0.0572 ± 0.0003 | 107.8 | 107.7 | 0.0536 ± 0.0003 | 0.8054 ± 0.0032 | 1.86 ± 0.01 | 1.00 ± 0.00 |
| 346.14 | 0.0177 ± 0.0001 | 0.4452 ± 0.0003 | 0.0382 ± 0.0003 | 79.7 | 79.7 | 0.0356 ± 0.0003 | 0.7350 ± 0.0039 | 1.90 ± 0.02 | 1.00 ± 0.00 |
| 346.15 | 0.0072 ± 0.0001 | 0.4452 ± 0.0003 | 0.0159 ± 0.0002 | 45.9 | 45.9 | 0.0147 ± 0.0002 | 0.5365 ± 0.0058 | 1.94 ± 0.02 | 1.00 ± 0.00 |
| 346.14 | 0.0000 ± 0.0000 | 0.4452 ± 0.0003 | 0.0000 ± 0.0000 | 21.4 | 21.4 | 0.0000 ± 0.0000 | 0.0000 ± 0.0000 | 1.98 ± 0.02 | 1.00 ± 0.00 |

[a] *E*xperimental temperature, $T$; amount of compound in the equilibrium cell, $n_i$; total mole fraction, $z_1$; experimental pressure, $p_{exp}$; pressure calculated with Legendre model, $p_{Leg}$; liquid and vapor phase equilibrium mole fractions, $x_1$ and $y_1$; activity coefficients calculated with Legendre model, $\gamma_i$.

corresponding calculated value at temperatures from (270 to 310) K.[5] The maximum error in density was 0.30 % for *n*-butane, 0.28 % for 2-methylpropane, 0.15 % for 2-methylpropene, 0.76 % for *trans*-2-butene, and 0.06 % for tetrahydrothiophene. Uncertainty in the injection volume was ± 0.02 cm$^3$, obtained from calibration experiments with distilled water. Uncertainty in the temperature of the pump was ± 0.1 K, and uncertainty in the pressure of the pump was ± 20 kPa, which affected the uncertainty in the density and the uncertainty in the compressibility of the liquid inside the pump. Maximum theoretical error of the overall molar composition was calculated by the method presented by Hynynen et al.[11] Uncertainty in the cell temperature measurements was estimated to be ± 0.02 K. Uncertainty in the cell pressure measurement was ± 0.4 kPa. Uncertainty in the reduced data depended on the uncertainty in the measured values of the temperature, the pressure, and the overall molar composition. Maximum uncertainty of the reduced data was obtained by alternating the measurement uncertainties between their minimum and maximum values, one at a time, and calculating the average deviation of the results.[11,12]

## Results and Discussion

The measured pure component vapor pressures agreed well with the pressures calculated with literature correlations, as shown in Table 2. The total pressure of each measured system coincided well at the equimolar composition. The experi-

**Table 7. VLE Data for *trans*-2-Butene (1) + Tetrahydrothiophene (2)[a]**

| $T$/K | $n_1$/mol | $n_2$/mol | $z_1$ | $p_{exp}$/kPa | $p_{Leg}$/kPa | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 318.34 | 0.4681 ± 0.0039 | 0.0000 ± 0.0000 | 1.0000 ± 0.0000 | 423.5 | 423.5 | 1.0000 ± 0.0000 | 1.0000 ± 0.0000 | 1.00 ± 0.00 | 2.42 ± 0.06 |
| 318.35 | 0.4681 ± 0.0039 | 0.0047 ± 0.0001 | 0.9902 ± 0.0002 | 418.9 | 419.0 | 0.9899 ± 0.0003 | 0.9995 ± 0.0000 | 1.00 ± 0.00 | 2.36 ± 0.05 |
| 318.35 | 0.4681 ± 0.0039 | 0.0144 ± 0.0001 | 0.9701 ± 0.0005 | 410.2 | 410.2 | 0.9695 ± 0.0006 | 0.9986 ± 0.0001 | 1.00 ± 0.00 | 2.26 ± 0.04 |
| 318.35 | 0.4681 ± 0.0039 | 0.0246 ± 0.0001 | 0.9500 ± 0.0006 | 401.7 | 401.7 | 0.9491 ± 0.0007 | 0.9977 ± 0.0002 | 1.00 ± 0.00 | 2.16 ± 0.03 |
| 318.34 | 0.4681 ± 0.0039 | 0.0527 ± 0.0002 | 0.8988 ± 0.0011 | 381.8 | 381.9 | 0.8973 ± 0.0011 | 0.9957 ± 0.0003 | 1.01 ± 0.00 | 1.95 ± 0.02 |
| 318.34 | 0.4681 ± 0.0039 | 0.0832 ± 0.0002 | 0.8491 ± 0.0014 | 364.2 | 364.3 | 0.8470 ± 0.0015 | 0.9939 ± 0.0004 | 1.02 ± 0.00 | 1.78 ± 0.01 |
| 318.34 | 0.4681 ± 0.0039 | 0.1172 ± 0.0002 | 0.7998 ± 0.0017 | 347.8 | 348.0 | 0.7976 ± 0.0017 | 0.9922 ± 0.0005 | 1.04 ± 0.00 | 1.65 ± 0.01 |
| 318.35 | 0.4681 ± 0.0039 | 0.1571 ± 0.0003 | 0.7487 ± 0.0019 | 331.8 | 332.0 | 0.7464 ± 0.0020 | 0.9906 ± 0.0006 | 1.07 ± 0.00 | 1.53 ± 0.00 |
| 318.35 | 0.4681 ± 0.0039 | 0.2020 ± 0.0003 | 0.6986 ± 0.0021 | 316.5 | 316.7 | 0.6964 ± 0.0021 | 0.9890 ± 0.0007 | 1.09 ± 0.00 | 1.44 ± 0.00 |
| 318.35 | 0.4681 ± 0.0039 | 0.2536 ± 0.0004 | 0.6486 ± 0.0022 | 301.4 | 301.7 | 0.6466 ± 0.0023 | 0.9874 ± 0.0008 | 1.12 ± 0.00 | 1.36 ± 0.00 |
| 318.34 | 0.4681 ± 0.0039 | 0.3137 ± 0.0004 | 0.5988 ± 0.0023 | 286.3 | 286.6 | 0.5971 ± 0.0023 | 0.9857 ± 0.0009 | 1.16 ± 0.01 | 1.29 ± 0.00 |
| 318.34 | 0.4681 ± 0.0039 | 0.3837 ± 0.0004 | 0.5495 ± 0.0023 | 271.2 | 271.3 | 0.5482 ± 0.0024 | 0.9840 ± 0.0010 | 1.20 ± 0.01 | 1.23 ± 0.00 |
| 318.34 | 0.4681 ± 0.0039 | 0.4689 ± 0.0004 | 0.4996 ± 0.0023 | 255.3 | 255.3 | 0.4988 ± 0.0023 | 0.9820 ± 0.0011 | 1.24 ± 0.01 | 1.19 ± 0.00 |
| 318.35 | 0.4710 ± 0.0037 | 0.4701 ± 0.0005 | 0.5005 ± 0.0023 | 256.1 | 255.7 | 0.4997 ± 0.0023 | 0.9820 ± 0.0011 | 1.24 ± 0.01 | 1.19 ± 0.00 |
| 318.35 | 0.3856 ± 0.0032 | 0.4701 ± 0.0005 | 0.4506 ± 0.0023 | 238.8 | 238.5 | 0.4493 ± 0.0024 | 0.9796 ± 0.0013 | 1.29 ± 0.01 | 1.15 ± 0.00 |
| 318.35 | 0.3145 ± 0.0026 | 0.4701 ± 0.0005 | 0.4009 ± 0.0023 | 220.4 | 220.3 | 0.3989 ± 0.0023 | 0.9769 ± 0.0014 | 1.34 ± 0.01 | 1.11 ± 0.00 |
| 318.35 | 0.2547 ± 0.0022 | 0.4701 ± 0.0005 | 0.3514 ± 0.0022 | 201.1 | 200.9 | 0.3489 ± 0.0022 | 0.9735 ± 0.0016 | 1.40 ± 0.01 | 1.08 ± 0.00 |
| 318.35 | 0.2029 ± 0.0018 | 0.4701 ± 0.0005 | 0.3015 ± 0.0021 | 180.0 | 179.9 | 0.2986 ± 0.0021 | 0.9691 ± 0.0019 | 1.47 ± 0.01 | 1.06 ± 0.00 |
| 318.34 | 0.1584 ± 0.0014 | 0.4701 ± 0.0005 | 0.2520 ± 0.0019 | 157.4 | 157.4 | 0.2488 ± 0.0019 | 0.9633 ± 0.0022 | 1.54 ± 0.01 | 1.04 ± 0.00 |
| 318.34 | 0.1184 ± 0.0011 | 0.4701 ± 0.0005 | 0.2012 ± 0.0017 | 132.2 | 132.4 | 0.1979 ± 0.0017 | 0.9546 ± 0.0026 | 1.62 ± 0.01 | 1.03 ± 0.00 |
| 318.34 | 0.0845 ± 0.0008 | 0.4701 ± 0.0005 | 0.1523 ± 0.0014 | 105.9 | 106.0 | 0.1492 ± 0.0014 | 0.9412 ± 0.0033 | 1.71 ± 0.02 | 1.01 ± 0.00 |
| 318.35 | 0.0540 ± 0.0006 | 0.4701 ± 0.0005 | 0.1030 ± 0.0011 | 76.9 | 77.0 | 0.1004 ± 0.0011 | 0.9162 ± 0.0045 | 1.81 ± 0.02 | 1.01 ± 0.00 |
| 318.35 | 0.0274 ± 0.0003 | 0.4701 ± 0.0005 | 0.0551 ± 0.0007 | 46.2 | 46.1 | 0.0535 ± 0.0007 | 0.8556 ± 0.0074 | 1.92 ± 0.03 | 1.00 ± 0.00 |
| 318.35 | 0.0170 ± 0.0003 | 0.4701 ± 0.0005 | 0.0349 ± 0.0006 | 32.2 | 32.2 | 0.0337 ± 0.0006 | 0.7903 ± 0.0099 | 1.97 ± 0.03 | 1.00 ± 0.00 |
| 318.35 | 0.0073 ± 0.0002 | 0.4701 ± 0.0005 | 0.0153 ± 0.0003 | 18.2 | 18.2 | 0.0147 ± 0.0003 | 0.6244 ± 0.0149 | 2.01 ± 0.04 | 1.00 ± 0.00 |
| 318.35 | 0.0000 ± 0.0000 | 0.4701 ± 0.0005 | 0.0000 ± 0.0000 | 6.9 | 6.9 | 0.0000 ± 0.0000 | 0.0000 ± 0.0000 | 2.05 ± 0.04 | 1.00 ± 0.00 |
| 347.06 | 0.4536 ± 0.0038 | 0.0000 ± 0.0000 | 1.0000 ± 0.0000 | 868.5 | 868.5 | 1.0000 ± 0.0000 | 1.0000 ± 0.0000 | 1.00 ± 0.00 | 2.26 ± 0.05 |
| 347.06 | 0.4536 ± 0.0038 | 0.0049 ± 0.0001 | 0.9893 ± 0.0003 | 857.6 | 857.7 | 0.9889 ± 0.0003 | 0.9991 ± 0.0001 | 1.00 ± 0.00 | 2.21 ± 0.04 |
| 347.06 | 0.4536 ± 0.0038 | 0.0143 ± 0.0001 | 0.9694 ± 0.0006 | 838.1 | 838.2 | 0.9682 ± 0.0006 | 0.9975 ± 0.0001 | 1.00 ± 0.00 | 2.12 ± 0.04 |
| 347.06 | 0.4536 ± 0.0038 | 0.0241 ± 0.0001 | 0.9496 ± 0.0006 | 819.3 | 819.7 | 0.9477 ± 0.0007 | 0.9960 ± 0.0002 | 1.00 ± 0.00 | 2.04 ± 0.03 |
| 347.06 | 0.4536 ± 0.0038 | 0.0507 ± 0.0002 | 0.8995 ± 0.0011 | 776.5 | 776.8 | 0.8964 ± 0.0012 | 0.9926 ± 0.0003 | 1.01 ± 0.00 | 1.86 ± 0.02 |
| 347.06 | 0.4536 ± 0.0038 | 0.0805 ± 0.0002 | 0.8492 ± 0.0014 | 737.3 | 737.5 | 0.8453 ± 0.0015 | 0.9894 ± 0.0004 | 1.02 ± 0.00 | 1.72 ± 0.01 |
| 347.06 | 0.4536 ± 0.0038 | 0.1137 ± 0.0002 | 0.7996 ± 0.0017 | 701.3 | 701.7 | 0.7952 ± 0.0018 | 0.9865 ± 0.0004 | 1.04 ± 0.00 | 1.60 ± 0.01 |
| 347.05 | 0.4536 ± 0.0038 | 0.1516 ± 0.0003 | 0.7495 ± 0.0019 | 667.1 | 667.5 | 0.7450 ± 0.0020 | 0.9837 ± 0.0005 | 1.06 ± 0.00 | 1.50 ± 0.00 |
| 347.05 | 0.4536 ± 0.0038 | 0.1947 ± 0.0003 | 0.6997 ± 0.0021 | 634.5 | 634.8 | 0.6955 ± 0.0022 | 0.9810 ± 0.0005 | 1.08 ± 0.00 | 1.41 ± 0.00 |
| 347.05 | 0.4536 ± 0.0038 | 0.2447 ± 0.0004 | 0.6496 ± 0.0022 | 602.3 | 602.6 | 0.6459 ± 0.0023 | 0.9782 ± 0.0005 | 1.11 ± 0.00 | 1.34 ± 0.00 |
| 347.06 | 0.4536 ± 0.0038 | 0.3022 ± 0.0004 | 0.6001 ± 0.0023 | 571.0 | 571.0 | 0.5970 ± 0.0024 | 0.9753 ± 0.0006 | 1.15 ± 0.01 | 1.28 ± 0.00 |
| 347.06 | 0.4536 ± 0.0038 | 0.3710 ± 0.0004 | 0.5501 ± 0.0024 | 538.8 | 538.7 | 0.5478 ± 0.0024 | 0.9722 ± 0.0006 | 1.18 ± 0.01 | 1.22 ± 0.00 |
| 347.06 | 0.4536 ± 0.0038 | 0.4517 ± 0.0004 | 0.5010 ± 0.0023 | 506.6 | 506.3 | 0.4996 ± 0.0024 | 0.9689 ± 0.0007 | 1.22 ± 0.01 | 1.18 ± 0.00 |
| 347.06 | 0.4538 ± 0.0037 | 0.4521 ± 0.0005 | 0.5009 ± 0.0023 | 506.4 | 506.2 | 0.4996 ± 0.0024 | 0.9688 ± 0.0007 | 1.22 ± 0.01 | 1.18 ± 0.00 |
| 347.06 | 0.3711 ± 0.0031 | 0.4521 ± 0.0005 | 0.4508 ± 0.0024 | 470.2 | 470.2 | 0.4483 ± 0.0024 | 0.9648 ± 0.0008 | 1.27 ± 0.01 | 1.14 ± 0.00 |
| 347.06 | 0.3027 ± 0.0025 | 0.4521 ± 0.0005 | 0.4010 ± 0.0023 | 432.8 | 432.7 | 0.3974 ± 0.0024 | 0.9600 ± 0.0009 | 1.32 ± 0.01 | 1.11 ± 0.00 |
| 347.06 | 0.2454 ± 0.0021 | 0.4521 ± 0.0005 | 0.3518 ± 0.0022 | 393.6 | 393.5 | 0.3472 ± 0.0023 | 0.9542 ± 0.0010 | 1.38 ± 0.01 | 1.08 ± 0.00 |
| 347.07 | 0.1959 ± 0.0017 | 0.4521 ± 0.0005 | 0.3023 ± 0.0021 | 351.7 | 351.6 | 0.2969 ± 0.0021 | 0.9469 ± 0.0011 | 1.44 ± 0.01 | 1.06 ± 0.00 |
| 347.07 | 0.1528 ± 0.0014 | 0.4521 ± 0.0005 | 0.2526 ± 0.0019 | 306.7 | 306.5 | 0.2467 ± 0.0019 | 0.9369 ± 0.0013 | 1.51 ± 0.01 | 1.04 ± 0.00 |
| 347.07 | 0.1156 ± 0.0011 | 0.4521 ± 0.0005 | 0.2037 ± 0.0017 | 259.1 | 259.1 | 0.1977 ± 0.0017 | 0.9231 ± 0.0015 | 1.58 ± 0.01 | 1.02 ± 0.00 |
| 347.07 | 0.0820 ± 0.0008 | 0.4521 ± 0.0005 | 0.1536 ± 0.0014 | 206.9 | 207.1 | 0.1480 ± 0.0014 | 0.9008 ± 0.0018 | 1.67 ± 0.02 | 1.01 ± 0.00 |
| 347.07 | 0.0524 ± 0.0005 | 0.4521 ± 0.0005 | 0.1039 ± 0.0011 | 151.4 | 151.6 | 0.0993 ± 0.0011 | 0.8608 ± 0.0022 | 1.76 ± 0.02 | 1.01 ± 0.00 |
| 347.07 | 0.0263 ± 0.0003 | 0.4521 ± 0.0005 | 0.0549 ± 0.0007 | 92.8 | 92.9 | 0.0520 ± 0.0007 | 0.7671 ± 0.0034 | 1.85 ± 0.03 | 1.00 ± 0.00 |
| 347.07 | 0.0160 ± 0.0003 | 0.4521 ± 0.0005 | 0.0342 ± 0.0006 | 67.0 | 66.9 | 0.0323 ± 0.0006 | 0.6733 ± 0.0044 | 1.90 ± 0.03 | 1.00 ± 0.00 |
| 347.07 | 0.0058 ± 0.0001 | 0.4521 ± 0.0005 | 0.0126 ± 0.0003 | 39.0 | 38.9 | 0.0119 ± 0.0003 | 0.4328 ± 0.0059 | 1.94 ± 0.04 | 1.00 ± 0.00 |
| 347.07 | 0.0000 ± 0.0000 | 0.4521 ± 0.0005 | 0.0000 ± 0.0000 | 22.2 | 22.2 | 0.0000 ± 0.0000 | 0.0000 ± 0.0000 | 1.97 ± 0.04 | 1.00 ± 0.00 |

[a] *E*xperimental temperature, $T$; amount of compound in the equilibrium cell, $n_i$; total mole fraction, $z_1$; experimental pressure, $p_{exp}$; pressure calculated with Legendre model, $p_{Leg}$; liquid and vapor phase equilibrium mole fractions, $x_1$ and $y_1$; activity coefficients calculated with Legendre model, $\gamma_i$.

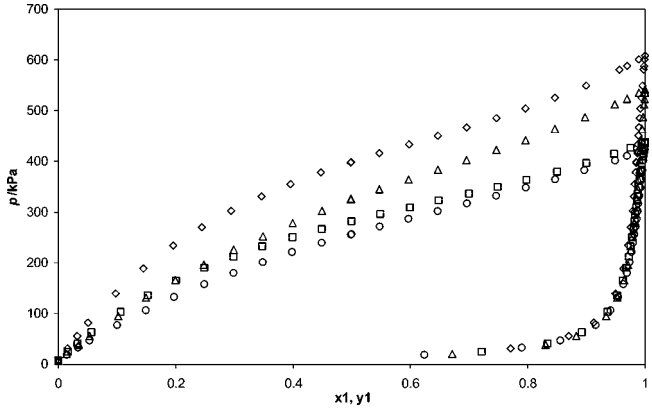


**Figure 1.** Experimental pressure and liquid and vapor phase equilibrium composition in mole fractions at 318 K of □, tetrahydrothiophene (2) + *n*-butane; ◇, + 2-methylpropane; △, + 2-methylpropene; ○, + *trans*-2-butene.

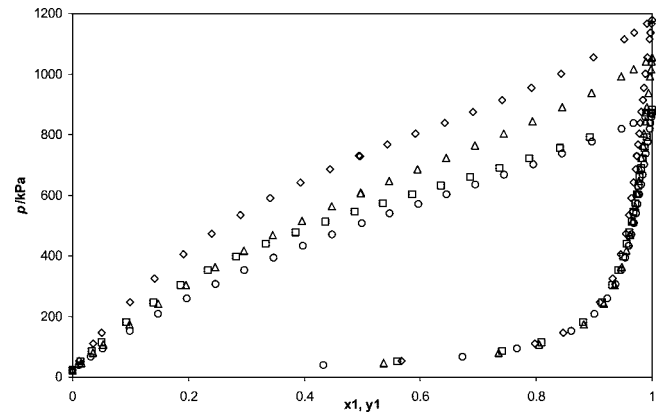


**Figure 2.** Experimental pressure and liquid and vapor phase equilibrium composition in mole fractions at (346 or 347) K of □, tetrahydrothiophene (2) + *n*-butane; ◇, + 2-methylpropane; △, + 2-methylpropene; ○, + *trans*-2-butene.

**Table 8. Liquid Activity Coefficient Model Parameters**[a]

| tetrahydrothiophene (2) | + *n*-butane | | + 2-methylpropane | | + 2-methylpropene | | + *trans*-2-butene | |
|---|---|---|---|---|---|---|---|---|
| *T*/K | 318.35 | 346.97 | 318.35 | 346.97 | 318.35 | 346.14 | 318.35 | 347.06 |
| Legendre, $a_{1,0}$ | 1.05703 | 0.99410 | 1.17828 | 1.09980 | 0.78438 | 0.75706 | 0.78213 | 0.73621 |
| Legendre, $a_{2,0}$ | 0.06312 | 0.04201 | 0.08325 | 0.08187 | 0.09756 | 0.09033 | 0.08134 | 0.06836 |
| Legendre, $a_{3,0}$ | 0.02049 | 0.02180 | 0.02752 | 0.02881 | 0.01714 | 0.01584 | 0.01908 | 0.01168 |
| Legendre, $a_{4,0}$ | - | - | 0.00348 | 0.00400 | −0.00686 | - | - | - |
| $\Delta p$/kPa | 0.0 | 0.0 | 0.0 | −0.1 | 0.0 | 0.1 | 0.0 | 0.1 |
| $\lvert\Delta p\rvert$/kPa | 0.1 | 0.1 | 0.1 | 0.3 | 0.3 | 0.3 | 0.1 | 0.2 |
| Wilson, $\lambda_{12}$/K | 114.44 | | 111.59 | | 32.81 | | 54.26 | |
| Wilson, $\lambda_{21}$/K | 283.57 | | 342.86 | | 265.40 | | 233.79 | |
| $\Delta p$/kPa | −0.1 | | −0.1 | | −0.3 | | −0.2 | |
| $\lvert\Delta p\rvert$/kPa | 0.3 | | 0.6 | | 1.1 | | 0.4 | |
| NRTL, $\lambda_{12}$/K | 233.64 | | 273.24 | | 247.71 | | 219.41 | |
| NRTL, $\lambda_{21}$/K | 150.13 | | 161.15 | | 43.38 | | 61.30 | |
| NRTL $\alpha_{12}=\alpha_{21}$ | 0.4 | | 0.4 | | 0.4 | | 0.4 | |
| $\Delta p$/kPa | −0.3 | | −0.6 | | −0.4 | | −0.3 | |
| $\lvert\Delta p\rvert$/kPa | 0.6 | | 0.9 | | 1.2 | | 0.6 | |
| UNIQUAC, $\lambda_{12}$ | 134.50 | | 155.11 | | 176.39 | | 128.84 | |
| UNIQUAC, $\lambda_{21}$ | −18.54 | | −20.30 | | −89.13 | | −40.11 | |
| $\Delta p$/kPa | −0.3 | | −0.8 | | −0.1 | | −0.2 | |
| $\lvert\Delta p\rvert$/kPa | 0.9 | | 1.8 | | 0.6 | | 0.4 | |

[a] $\Delta p$/kPa is the average pressure residual. $\lvert\Delta p\rvert$/kPa is the absolute average pressure residual. Each set of Legendre parameters represents a measured binary system at one temperature. Each set of Wilson, NRTL, and UNIQUAC model parameters represents a measured binary system at both temperatures.

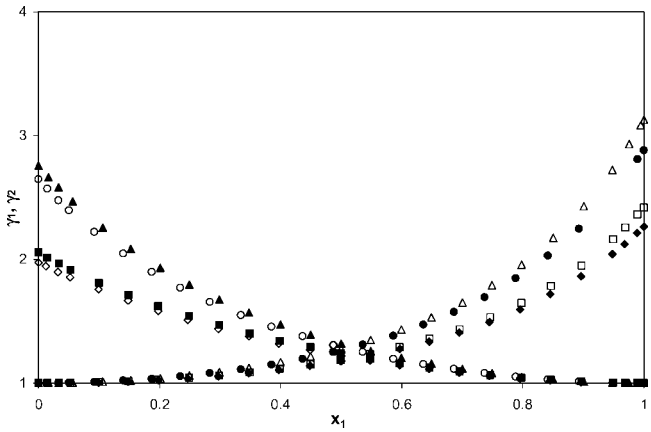


**Figure 3.** Liquid activity coefficients. ▲, *n*-Butane (1) + △, THT system at 318.35 K; ○, *n*-butane (1), + ●, THT system at 346.97 K; ■, *trans*-2-butene (1), + □, THT system at 318.35 K; ◇, *trans*-2-butene (1), + ◆, THT system at 347.06 K.

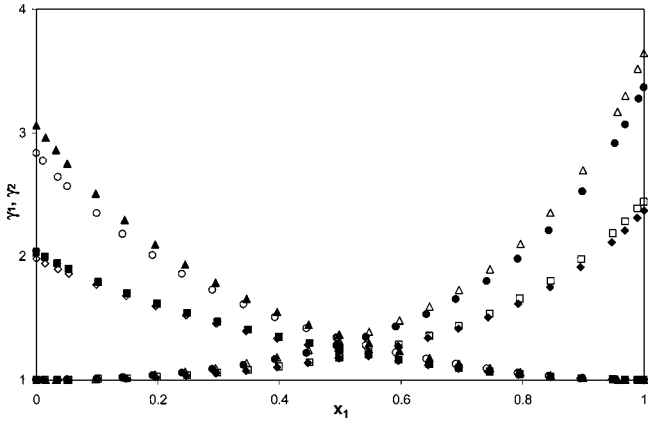


**Figure 4.** Liquid activity coefficients. ▲, 2-Methylpropane (1), + △, THT system at 318.35 K; ○, 2-methylpropane (1), + ●, THT system at 346.97 K; ■, 2-methylpropene (1), + □, THT system at 318.35 K; ◇, 2-methylpropene (1), + ◆, THT system at 346.14 K.

mental data were regressed separately for each experiment to obtain gas and liquid phase concentrations. The regression was done with Barker's method[9] using Legendre polynomials[7] as the liquid activity model and the cubic SRK equation of state.[8] The amount of parameters for the Legendre polynomials was increased until the pressure absolute deviation was below the uncertainty of the cell pressure measurement. No more than four parameters were needed. The measured data, equilibrium phase compositions, and compound activity coefficients are shown in Tables 4 to 7. Equilibrium phase compositions are presented in Figures 1 and 2. All measured binaries showed a positive deviation from the Raoult's law. No azeotropes were observed. The systems showed weak temperature dependency, as shown in the liquid activity coefficient graph in Figures 3 and 4. As the measured pure component vapor pressures were acceptable, both sides of measured binaries coincided, and the Legendre polynomials could describe the data with good accuracy. The data were considered to be of good quality.

Parameters for the local composition models were regressed for each system based on the data collected at two different temperatures. The calculated pressure agreed well with the experimental pressure. For the local composition models, the best accuracy was obtained in most cases with the Wilson model,[13] except for the system of THT + 2-methylpropane, where the UNIQUAC[15] model was better. The best accuracy in all cases was obtained with the Legendre polynomials, which used more parameters and described the system at only one temperature. The parameters for Legendre, Wilson, NRTL,[14] and UNIQUAC are shown in Table 8. With all four models, the absolute deviation from the experimental pressure was no higher than 1.8 kPa, and for Legendre polynomials, the absolute deviation was no higher than 0.3 kPa.

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