# Liquid−Liquid Equilibria in Ternary Systems 2-Methylbutane + 2-Methyl-2-propanol + Water and Pentane + 2-Methyl-2-propanol + Water at 293.15 K[†]

**Zuzana Rečková,[‡] Karel Řehák,*[,‡] Petr Voňka,[‡] and Juha-Pekka Pokki[§]**

Department of Physical Chemistry, Institute of Chemical Technology, Prague, 166 28 Praha 6, Czech Republic, and Department of Biotechnology and Chemical Technology, Helsinki University of Technology, P.O. Box 6100, 02015 HUT, Finland

The liquid−liquid equilibria in ternary systems 2-methylbutane + 2-methyl-2-propanol + water and pentane + 2-methyl-2-propanol + water were experimentally determined at 293.15 K by direct analytical methods and a titration method. The ternary data along with other thermodynamic data of binary subsystems previously published were utilized for a thermodynamic description of the systems. The original UNIQUAC model was combined with a ternary term. Binary parameters of the model were considered to be temperature dependent, and they were calculated employing the maximum likelihood method. Ternary parameters were evaluated using a nonderivative numerical procedure.

## Introduction

An extensive production of 2-methoxy-2-methylpropane (i.e., MTBE) resulted in serious environmental problems. Consequently, there is a growing interest to find a way to economically utilize the MTBE manufacturing facilities for production of some other fuel components. One possible option is the production of isooctane as a high-quality fuel component. Isooctane can be prepared by hydrogenation of 2,4,4-trimethylpentene which is obtained from the dimerization of 2-methylpropene. Any further oligomerization reaction, however, must be inhibited. This can be achieved by the addition of a polar component. One option is to use 2-methyl-2-propanol, which is formed from the reaction of 2-methylpropene with water.[1] The amount of 2-methyl-2-propanol (i.e., *tert*-butanol) in the reactor must be small, otherwise the dimerization reaction can be hindered.

The solubility of water in 2-methylpropene is very small and can cause liquid−liquid phase splitting in the dimerization reactor.[2] In the determination of the kinetics of the dimerization of 2-methylpropene, 2-methylbutane has been used as a solvent. The mutual solubility of the components in the system 2-methylbutane + water is even smaller than that in the system 2-methylpropene + water. For the operation and successful modeling of chemical reactors, the formation of two liquid phases is not favorable.

For the above reasons, the liquid−liquid equilibrium (LLE) in the two ternary systems containing $C_5$ hydrocarbons, 2-methyl-2-propanol, and water was studied in this work. Specifically, our attention was focused on the systems 2-methylbutane + 2-methyl-2-propanol + water and pentane + 2-methyl-2-propanol + water.

## Experimental Section

***Chemicals.*** 2-Methylbutane was supplied by Aldrich, and pentane and 2-methyl-2-propanol were supplied by Fluka. All chemicals were used without any additional treatment. Their purities were determined by gas chromatography and their water contents by a Karl Fischer titration. They were found to be 99.80 %, $w(H_2O) = 9 \cdot 10^{-5}$ for pentane, 99.70 %, $w(H_2O) = 1 \cdot 10^{-4}$ for 2-methylbutane, and 99.75 %, $w(H_2O) = 3 \cdot 10^{-4}$ for 2-methyl-2-propanol. Water was deionized with a Millipore Milli-QRG Water Purification System to achieve its resistivity of 18 MΩ·cm. Other chemicals used were *n*-heptane (BDH AnalaR, GC purity 99.75 %) as the GC internal standard, methanol (Merck, GC purity greater than 99.8 %) as solvent for GC analyses, and Karl Fischer titration reagents (Merck, J. T. Baker Hydrapoint Composite 2).

***Procedure.*** The liquid−liquid equilibrium measurements were carried out by means of direct analytical determinations of components in the liquid phases and by a titration method. In the former method, a heterogeneous liquid mixture containing all three components was prepared in an equilibrium cell with a volume of 100 $cm^3$. The temperature of the cell was kept at (293.15 ± 0.01) K by means of a Lauda thermostat Ecoline RE 206. The mixture was agitated with a moderate speed for at least 20 h by a magnetic stirrer. This period was found to be necessary especially for the measurements of tie-lines with low contents of 2-methyl-2-propanol. After stirring, the heterogeneous mixture was allowed to stand for 4 h and then sampled for analyses. To ensure correct phase separation, the sampling was repeated after the next 4 h. No significant change in composition was observed. Samples of both liquid phases were then withdrawn for analytical determinations of two components. The third component was determined by a mass balance. Analyses of 2-methyl-2-propanol in both phases and 2-methylbutane or pentane in the aqueous phase were performed using an HP 6890 gas chromatograph. The GC analyses were carried out in split 50:1 mode on a capillary column HP-1 Methyl Siloxane (60 m × 250 $\mu$m × 1 $\mu$m) connected to an FID detector (temperature 280 °C, flow of $H_2$ 33 $mL \cdot min^{-1}$, flow of air 33 $mL \cdot min^{-1}$, flow of He as a makeup gas 20 $mL \cdot min^{-1}$). The

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* To whom correspondence should be addressed. E-mail: karel.rehak@vscht.cz. Tel.: +420 220 444 039. Fax: +420 220 444 333.

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[‡] Institute of Chemical Technology, Prague.

[§] Helsinki University of Technology.

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**Table 1. Experimental Data on Liquid−Liquid Equilibrium in the System 2-Methylbutane (1) + 2-Methyl-2-propanol (2) + Water (3) at 293.15 K**[a]

| $x'_1$ | $x'_2$ | $x'_3$ | $x''_1$ | $x''_2$ |
|---|---|---|---|---|
|  | 0.000 | $0.405 \cdot 10^{-3}$ | $0.110 \cdot 10^{-4}$ | 0.000 |
|  | $0.130 \cdot 10^{-1}$ | $0.928 \cdot 10^{-3}$ | $0.130 \cdot 10^{-4}$ | $0.165 \cdot 10^{-1}$ |
|  | $0.344 \cdot 10^{-1}$ | $0.373 \cdot 10^{-2}$ | $0.118 \cdot 10^{-4}$ | $0.287 \cdot 10^{-1}$ |
|  | $0.483 \cdot 10^{-1}$ | $0.625 \cdot 10^{-2}$ | $0.149 \cdot 10^{-4}$ | $0.298 \cdot 10^{-1}$ |
|  | $0.781 \cdot 10^{-1}$ | $0.185 \cdot 10^{-1}$ | $0.174 \cdot 10^{-4}$ | $0.346 \cdot 10^{-1}$ |
|  | 0.112 | $0.212 \cdot 10^{-1}$ | $0.168 \cdot 10^{-4}$ | $0.383 \cdot 10^{-1}$ |
|  | 0.161 | $0.328 \cdot 10^{-1}$ | $0.254 \cdot 10^{-4}$ | $0.419 \cdot 10^{-1}$ |
|  | 0.206 | $0.508 \cdot 10^{-1}$ | $0.276 \cdot 10^{-4}$ | $0.434 \cdot 10^{-1}$ |
|  | 0.236 | $0.528 \cdot 10^{-1}$ | $0.301 \cdot 10^{-4}$ | $0.486 \cdot 10^{-1}$ |
|  | 0.236 | $0.572 \cdot 10^{-1}$ | $0.291 \cdot 10^{-4}$ | $0.455 \cdot 10^{-1}$ |
|  | 0.289 | $0.670 \cdot 10^{-1}$ | $0.312 \cdot 10^{-4}$ | $0.490 \cdot 10^{-1}$ |
|  | 0.317 | $0.896 \cdot 10^{-1}$ | $0.451 \cdot 10^{-4}$ | $0.501 \cdot 10^{-1}$ |
|  | 0.348 | 0.111 | $0.570 \cdot 10^{-4}$ | $0.528 \cdot 10^{-1}$ |
|  | 0.381 | 0.155 | $0.753 \cdot 10^{-4}$ | $0.548 \cdot 10^{-1}$ |
|  | 0.403 | 0.181 | $0.797 \cdot 10^{-4}$ | $0.577 \cdot 10^{-1}$ |
|  | 0.415 | 0.224 | $0.119 \cdot 10^{-3}$ | $0.581 \cdot 10^{-1}$ |
|  | 0.433 | 0.270 | $0.159 \cdot 10^{-3}$ | $0.605 \cdot 10^{-1}$ |
|  | 0.432 | 0.295 | $0.164 \cdot 10^{-3}$ | $0.608 \cdot 10^{-1}$ |
|  | 0.431 | 0.349 | $0.222 \cdot 10^{-3}$ | $0.639 \cdot 10^{-1}$ |
|  | 0.432 | 0.351 | $0.237 \cdot 10^{-3}$ | $0.648 \cdot 10^{-1}$ |
|  | 0.415 | 0.433 | $0.376 \cdot 10^{-3}$ | $0.693 \cdot 10^{-1}$ |
|  | 0.384 | 0.514 | $0.591 \cdot 10^{-3}$ | $0.769 \cdot 10^{-1}$ |
|  | 0.300 | 0.656 | $0.183 \cdot 10^{-2}$ | $0.926 \cdot 10^{-1}$ |
|  | titration method data |  |  |  |
| 0.6115 | 0.3018 | 0.0867 |  |  |
| 0.5363 | 0.3418 | 0.1219 |  |  |
| 0.4186 | 0.3936 | 0.1878 |  |  |
| 0.3048 | 0.4247 | 0.2705 |  |  |
| 0.2975 | 0.4252 | 0.2773 |  |  |
| 0.2420 | 0.4267 | 0.3313 |  |  |
| 0.1892 | 0.4218 | 0.3890 |  |  |
| 0.1064 | 0.3794 | 0.5142 |  |  |
| 0.0747 | 0.3441 | 0.5812 |  |  |

[a] $x'_i$, mole fractions in organic phase; $x''_i$ mole fractions in aqueous phase.

**Table 2. Experimental Data on Liquid−Liquid Equilibrium in the System Pentane (1) + 2-Methyl-2-propanol (2) + Water (3) at 293.15 K**[a]

| $x'_1$ | $x'_2$ | $x'_3$ | $x''_1$ | $x''_2$ |
|---|---|---|---|---|
|  | 0.000 | $0.343 \cdot 10^{-3}$ | $0.100 \cdot 10^{-4}$ | 0.000 |
|  | $0.109 \cdot 10^{-1}$ | $0.684 \cdot 10^{-2}$ | $0.125 \cdot 10^{-4}$ | $0.197 \cdot 10^{-1}$ |
|  | $0.318 \cdot 10^{-1}$ | $0.125 \cdot 10^{-1}$ | $0.197 \cdot 10^{-4}$ | $0.288 \cdot 10^{-1}$ |
|  | $0.914 \cdot 10^{-1}$ | $0.208 \cdot 10^{-1}$ | $0.200 \cdot 10^{-4}$ | $0.386 \cdot 10^{-1}$ |
|  | 0.119 | $0.216 \cdot 10^{-1}$ | $0.213 \cdot 10^{-4}$ | $0.400 \cdot 10^{-1}$ |
|  | 0.177 | $0.337 \cdot 10^{-1}$ | $0.237 \cdot 10^{-4}$ | $0.448 \cdot 10^{-1}$ |
|  | 0.228 | $0.419 \cdot 10^{-1}$ | $0.289 \cdot 10^{-4}$ | $0.460 \cdot 10^{-1}$ |
|  | 0.233 | $0.420 \cdot 10^{-1}$ | $0.301 \cdot 10^{-4}$ | $0.486 \cdot 10^{-1}$ |
|  | 0.287 | $0.715 \cdot 10^{-1}$ | $0.390 \cdot 10^{-4}$ | $0.500 \cdot 10^{-1}$ |
|  | 0.351 | 0.118 | $0.603 \cdot 10^{-4}$ | $0.538 \cdot 10^{-1}$ |
|  | 0.398 | 0.188 | $0.897 \cdot 10^{-4}$ | $0.592 \cdot 10^{-1}$ |
|  | 0.420 | 0.254 | $0.137 \cdot 10^{-3}$ | $0.630 \cdot 10^{-1}$ |
|  | 0.430 | 0.319 | $0.199 \cdot 10^{-3}$ | $0.664 \cdot 10^{-1}$ |
|  | 0.432 | 0.361 | $0.270 \cdot 10^{-3}$ | $0.683 \cdot 10^{-1}$ |
|  | 0.417 | 0.430 | $0.394 \cdot 10^{-3}$ | $0.727 \cdot 10^{-1}$ |
|  | 0.349 | 0.577 | $0.105 \cdot 10^{-2}$ | $0.856 \cdot 10^{-1}$ |
|  | 0.299 | 0.654 | $0.192 \cdot 10^{-2}$ | $0.978 \cdot 10^{-1}$ |
|  | 0.237 | 0.741 | $0.562 \cdot 10^{-2}$ | 0.131 |
|  | titration method data |  |  |  |
| 0.4805 | 0.3704 | 0.1491 |  |  |
| 0.3549 | 0.4144 | 0.2307 |  |  |
| 0.2501 | 0.4277 | 0.3222 |  |  |
| 0.1520 | 0.4103 | 0.4377 |  |  |
| 0.0743 | 0.3467 | 0.5790 |  |  |

[a] $x'_i$, mole fractions in organic phase; $x''_i$ mole fractions in aqueous phase.

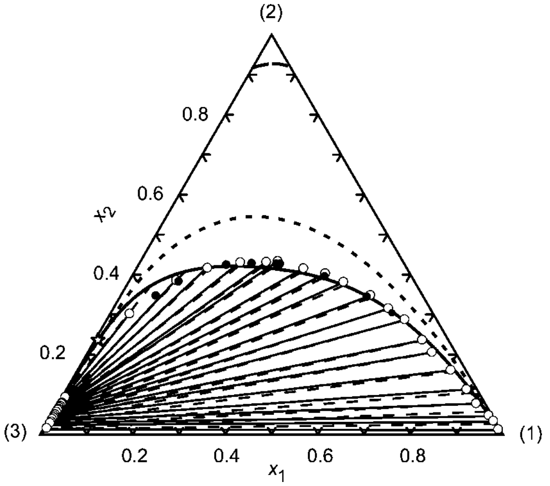

**Figure 1.** Liquid−liquid equilibrium data in the system 2-methybutane (1) + 2-methyl-2-propanol (2) + water (3) at 293.15 K. ○−○, experimental tie-lines; ●, titration method data; − •, calculated tie-lines; - - -, binodal LLE curve predicted by the UNIQUAC model without ternary parameters; −, binodal LLE curve calculated using the UNIQUAC model with optimized ternary parameters; − − •, calculated solid−liquid equilibrium curve; ☆, calculated critical point.

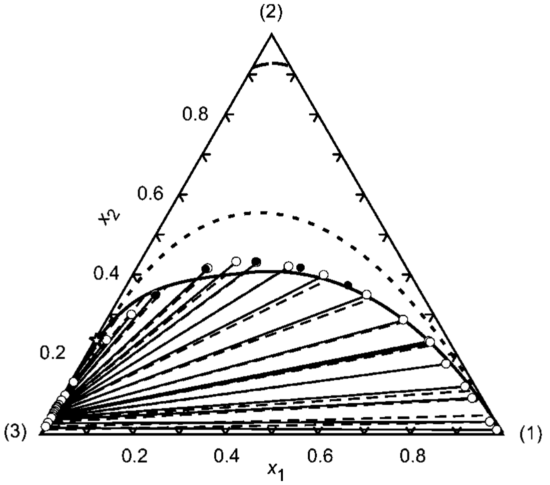

**Figure 2.** Liquid−liquid equilibrium data in the system pentane (1) + 2-methyl-2-propanol (2) + water (3) at 293.15 K. ○−○, experimental tie-lines; ●, titration method data; − •, calculated tie-lines; - - -, binodal LLE curve predicted by the UNIQUAC model without ternary parameters; −, binodal LLE curve calculated using the UNIQUAC model with optimized ternary parameters; − − •, calculated solid−liquid equilibrium curve; ☆, calculated critical point.

column was heated according to the temperature program 0 °C for 0.5 min, 1 K·min$^{-1}$ to 20 °C, and 20 K·min$^{-1}$ to 200 °C. Prior to analyses, calibration of the GC was carried out by means of calibration mixtures of known mole fraction of 2-methyl-2-propanol, 2-methylbutane (or pentane), and heptane used as an internal standard. For analyses of the equilibrium phases, samples from the cell were withdrawn using a sample-lock syringe and weighted. A known mass of the standard was then added to the samples for an internal normalization. The obtained mixtures were diluted by methanol. The additions of standard and methanol were optimized by the precalculation of absolute areas of chromatographic peaks to achieve values similar to that obtained during the calibration. After evaluation of the peak areas, compositions of desired substances were evaluated with the help of previously established calibration dependencies. The water content in the organic (hydrocarbon) phase was determined by means of a Karl Fischer titration. A reagent titer was obtained by the titration of a known amount of water determined by differential weighing. Equilibrium-phase samples were withdrawn from the cell and then directly titrated.

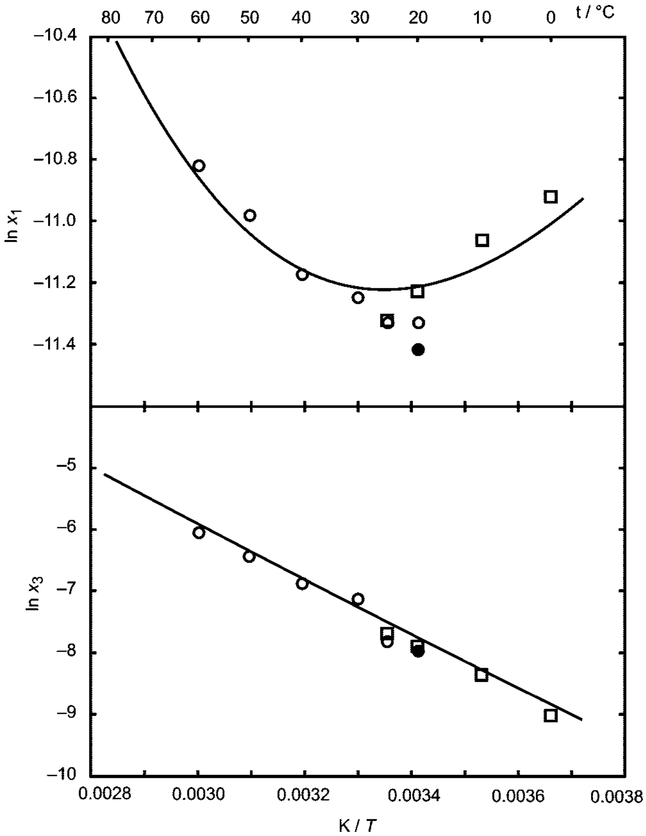

**Figure 3.** Solubility of 2-methylbutane (1) in water (3), and water (3) in 2-methylbutane (1) in coordinates ln $x_i$ vs $1/T$. Experimental data: ●, this work; ○, ref 3; □, ref 4; —, data modeled by the UNIQUAC equation.

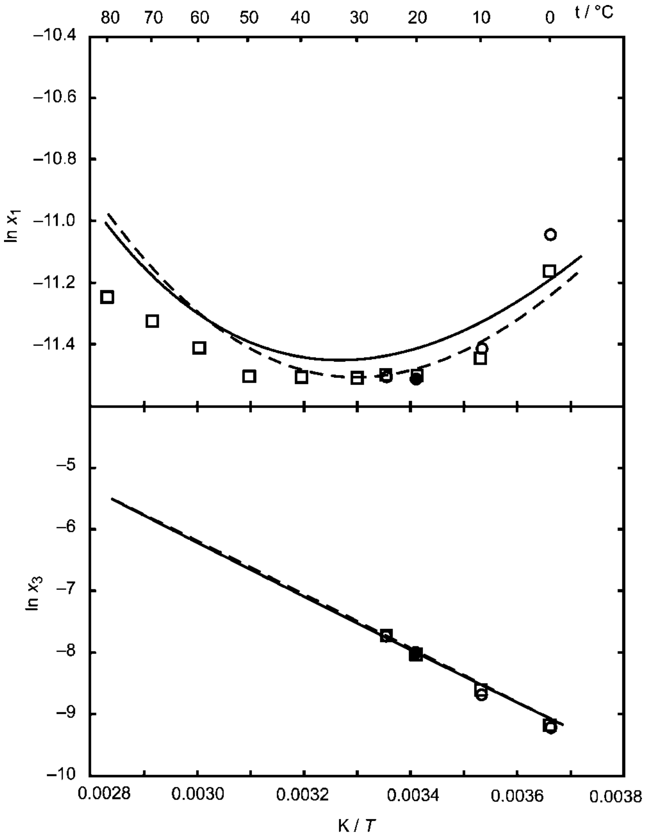

**Figure 4.** Solubility of pentane (1) in water and water (3) in pentane in coordinates ln $x_i$ vs $1/T$. Experimental data: ●, this work; ○, ref 3; □, ref 4; —, data modeled by the UNIQUAC equation; - -, data recommended by Tsonopoulos (ref 5).

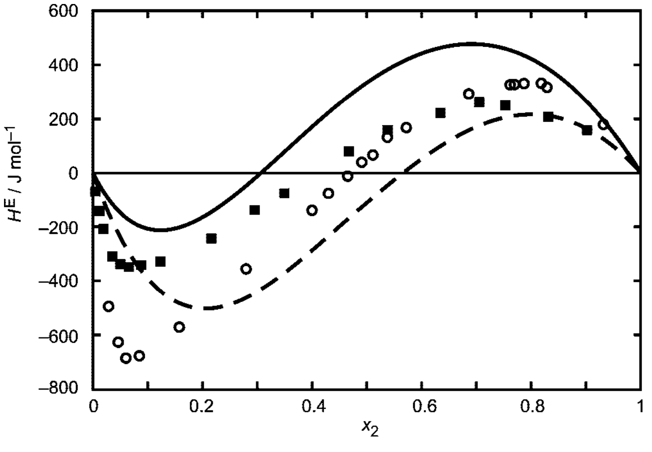

**Figure 5.** Excess enthalpy data for the system 2-methyl-2-propanol (2) + water (3). ○, experimental data at 298.15 K (ref 12); ■, experimental data at 323.15 K (ref 11); data modeled by the UNIQUAC equation: —, at 298.15 K; - -, at 323.15 K.

To check the reliability of the tie-line data obtained, binodal curve points pertaining to the organic phase were also determined by the titration method utilizing an optical determination of the cloud point. The ternary system components were weighed out into the thermostatted titration cell with a volume of 100 cm$^3$ so that the respective mixture remained homogeneous at 293.15 K. This homogeneous mixture, under permanent stirring, was titrated by pure water. An automatic Titronic Universal titrator from Schott operated with constant additions of 0.03 mL of water was used for this purpose. For the cloud point detection, an optical method, based on measuring of scattered-light intensity, was employed. A laser diode was used as the light source, and the intensity of scattered light was recorded using a photodiode, whose photocurrent was amplified by an operation amplifier and converted to a voltage. When the liquid phase was homogeneous (transparent), the laser beam was straight (i.e., light intensity was stabilized on a certain value). After the cloud-point (the second liquid phase), the laser beam was scattered by the heterogeneous mixture and the photodiode produced a higher signal. The added water volume and photodiode signal as a function of time were simultaneously recorded using a computer. The amount of water corresponding to one binodal curve point was evaluated from these data.

## Results and Discussion

Results of the LLE measurements are listed in Tables 1 and 2 and depicted in Figures 1 and 2. The tie-line data are reported by pairs of experimentally determined compositions, i.e., mole fractions of hydrocarbons C$_5$ (pentane or 2-methybutane) $x''_1$ and mole fraction of 2-methyl-2-propanol $x''_2$ in the aqueous phase (labeling $x''_i$) and mole fraction of 2-methyl-2-propanol $x'_2$ and mole fraction of water $x'_3$ in the hydrocarbon-rich phase (labeling $x'_i$). All experimental data pertaining to the aqueous phase were determined with estimated expanded uncertainties $\delta(x''_1) = 2 \cdot 10^{-7}$ and $\delta(x''_2) = 2 \cdot 10^{-4}$ (level of confidents 95 %). High volatilities of C$_5$ hydrocarbons make handling of the organic-phase samples and their analyses challenging. On this account, expanded uncertainties for $x'_2$ and $x'_3$ obtained in the composition region with high content of hydrocarbons (i.e., $x'_1 > 0.9$) were estimated to be $\delta(x'_2) = \delta(x'_3) = 0.002$. They are a bit higher than the value of $\delta(x'_2) = \delta(x'_3) = 0.0005$ corresponding to mole fractions from the central area of the triangular diagrams. In spite of this fact, the results on the LLE

**Table 3. Survey of Data Used for Evaluation of Binary Parameters and Obtained Root-Mean-Square Deviations $\delta_{Y_i}$ of Quantities $Y_i$ of Individual Data Sets**[a]

| | 2-Methylbutane + Water | | Pentane + Water |
|---|---|---|---|
| data | LLE | data | LLE |
| ref | 3, 4 | ref | 3, 4 |
| conditions | from (273 to 333) K | conditions | from (273 to 373) K |
| $N_p$ | 10 | $N_p$ | 29 |
| $\delta_x$ | $1.0 \cdot 10^{-6}$ | $\delta_x$ | $1.00 \cdot 10^{-6}$ |
| $\delta_z$ | $6.7 \cdot 10^{-5}$ | $\delta_z$ | $3.30 \cdot 10^{-5}$ |
| $\delta_T$/K | 0.00 | $\delta_T$/K | 0.01 |

| | 2-Methylbutane + 2-Methyl-2-propanol | | | Pentane + 2-Methyl-2-propanol | |
|---|---|---|---|---|---|
| data | VLE | VLE | data | VLE | VLE |
| ref | 7 | 7 | ref | 8 | 8 |
| $N_p$ | 18 | 14 | $N_p$ | 17 | 18 |
| conditions | 303 K | 373 K | conditions | 101.325 kPa | 79.97 kPa |
| $\delta_x$ | 0.0022 | 0.0016 | $\delta_x$ | 0.0053 | 0.0076 |
| $\delta_y$ | 0.0031 | 0.0015 | $\delta_y$ | 0.0078 | 0.0057 |
| $\delta_T$/K | 0.00 | 0.00 | $\delta_T$/K | 0.06 | 0.06 |
| $\delta_p$/kPa | 1.53 | 3.20 | $\delta_p$/kPa | 1.42 | 1.21 |

| | 2-Methyl-2-propanol + Water | | | | | | |
|---|---|---|---|---|---|---|---|
| data | VLE | VLE | VLE | VLE | $H^E$ | $\gamma_i^\infty$ | G22 |
| ref | 9 | 11 | 11 | 10 | 11−13 | 14−16 | 17 |
| $N_p$ | 14 | 7 | 10 | 19 | 70 | 3 | 3 |
| conditions | 298 K | 298 K | 323 K | 333 K | from (298 to 323) K | 293 K | from (293 to 323) K |
| $\delta_x$ | 0.0039 | 0.0045 | 0.0030 | 0.0090 | | | |
| $\delta_y$ | 0.0069 | 0.0030 | 0.0106 | 0.0088 | | | |
| $\delta_T$/K | 0.02 | 0.07 | 0.01 | 0.02 | | | |
| $\delta_p$/kPa | 0.18 | 0.10 | 0.66 | 0.15 | | | |
| $\delta_Y$ | | | | | $180\ \mathrm{J \cdot mol^{-1}}$ | 2.27 | 0.31 |

[a] Quantities $Y_i$ are mole fractions in liquid phases in equilibrium ($x$, $z$), mole fraction in vapor phase in equilibrium ($y$), temperature ($T$), pressure ($p$), excess enthalpy ($H^E$), and limiting activity coefficient ($\gamma\infty$). $\delta_{Y_i} = [\sum_{j=1}^{N_p} (Y_{i,\mathrm{exp}} - Y_{i,\mathrm{calc}})_j^2 / N_p\ ]^{0.5}$, where $N_p$ is the number of experimental data in data set.

obtained in binary systems 2-methylpentane (1) + water (3) and pentane (1) + water (3) correspond well to critically evaluated experimental data[3,4] (see Figures 3 and 4). Titration-method data and tie-line data were found to be also in good agreement.

***Correlation of Experimental Data.*** To obtain a reliable thermodynamic description of the ternary systems, the approach of stepped correlations was chosen. First, data of all the binary systems were collected and correlated separately for each subsystem by means of a model for the excess Gibbs energy ($Q_{\mathrm{bin}}$). Second, ternary parameters were introduced into the model ($Q_{\mathrm{ter}}$) and adjusted with the help of experimental tie-lines in ternary systems. This approach can be expressed as

$$Q = \frac{G^E}{RT} = Q_{\mathrm{bin}} + Q_{\mathrm{ter}} \tag{1}$$

For the thermodynamic description of binary subsystems, the original UNIQUAC equation[6] was employed. Parameters of the model were considered to be temperature dependent in the form

$$\tau_{ij} = \exp\left(-\frac{a_{ij}}{T}\right) = \exp\left(-\frac{a_{ij,0} + a_{ij,1}T + a_{ij,2}T^2}{T}\right) \tag{2}$$

$$\tau_{ji} = \exp\left(-\frac{a_{ji}}{T}\right) = \exp\left(-\frac{a_{ji,0} + a_{ji,1}T + a_{ji,2}T^2}{T}\right) \tag{3}$$

The quadratic temperature dependence of $a_{31}$ was utilized for description of systems pentane (1) + water (3) and 2-methylbutane (1) + water (3) only. For a description of the remaining systems, the linear temperature dependencies of parameters $a_{ij}$ were found to be sufficient. The survey of data utilized for evaluation of the binary system parameters along with resulting root-mean square deviations is given in Table 3. The listed data for each system were correlated simultaneously employing the maximum likelihood method (for data on LLE and VLE) and the method of weighted least-squares (for the other data).

The saturated vapor pressures of pure components were calculated by the Antoine equation with parameters listed in Table 4. Nonideality of the gaseous phase was described by means of fugacity coefficients. Their values were estimated by the virial equation of state with the second virial coefficients calculated according to the expression and data given in refs 18 and 19 (see Table 4). The parameters obtained by the simultaneous correlation of experimental data are given in Table 5.

As can be seen from Figure 4, the UNIQUAC model with the temperature-dependent parameters describes the LLE in the system pentane (1) + water (3) very closely to the recommended mutual solubilities[5] in the whole temperature range from (273 to 413) K. Analogous temperature dependence of the model parameters was utilized for correlation of the system 2-methylbutane (1) + water (3) (see Figure 3).

The binary system 2-methyl-2-propanol (2) + water (3) is homogeneous in the whole concentration range, but it exhibits very high deviations from ideal behavior. The system is very close to liquid phase splitting, which can be certified by a low positive value of the second derivative of the Gibbs energy of mixing with respect to composition $G22_{\min} = (\partial^2[G^M/(RT)]/(\partial x_2^2))_{\min}$. It can be questionable for many thermodynamic models to describe such behavior correctly. To handle this fact, the values of $G22_{\min}$ and the appropriate composition $x_{2,\min}$, evaluated from experimental data by Novák et al.[17] were included in the simultaneous correlation of thermodynamic data. The acquired description of the system is relatively good. As can be seen from Figure 5, the S-shape course of $H^E$ was achieved. From experimental data on $H^E$, the S-shape course of the excess heat capacity $C_p^{\,E}$ can be also detected. The only disadvantage in the description of this system is that the

**Table 4. Properties of Pure Components Used in Calculation**

| compound | $r^a$ | $q^a$ | temp range/K | $A^b$ | $B^b$ | $C^b$ |
|---|---|---|---|---|---|---|
| 2-methylbutane | 3.8246 | 3.3120 | 221.68 to 334.35 | 13.6770 | 2376.413 | −38.653 |
| | | | 334.35 to 373.15 | 13.7391 | 2395.54 | −38.559 |
| pentane | 3.8254 | 3.3160 | 228.70 to 330.72 | 13.85044 | 2492.643 | −39.254 |
| 2-methyl-2-propanol | 3.4528 | 3.1280 | 278.15 to 374.15 | 14.83979 | 2658.288 | −95.50 |
| water | 0.92 | 1.40 | 273.15 to 343.15 | 16.544811 | 3970.2477 | −40.20 |
| | | | 343.15 to 373.15 | 16.240349 | 3785.9731 | −47.39 |

| | $T_c$/K$^c$ | $(\bar{u}/k)$/K$^c$ | $V$/(cm$^3$·mol$^{-1}$)$^c$ | $R_1{}^c$ | $R_2{}^c$ | $R_3{}^c$ |
|---|---|---|---|---|---|---|
| 2-methylbutane | 460.39 | −935.9 | 113.4 | 0.667 | 1.110 | 4.928 |
| pentane | 469.6 | −945.9 | 110.4 | 0.680 | 1.152 | 4.511 |
| 2-methyl-2-propanol | 506.1 | $-178[1 + 2256/T]$ | 80.0 | 0.5 | 1.13 | 4.72 |
| water | 647.30 | $-89.17[1 + 6292/T]$ | 14.0 | 0.1 | 1.13 | 10.1 |

[a] Volume and surface area parametres of the UNIQUAC equation.[4] [b] Constants of the Antoine equation $\ln p/\text{kPa} = A - B/(T/\text{K} + C)$.[18,19] [c] Constants of the temperature dependence of the second virial coefficients.[18,19] $B = 2V\{R_1 - (1 - R_1)[\exp(\bar{u}/kT) - 1] - (R_2 - 1)[\exp(\bar{u}/kT) - 1] - (R_3 - R_2)[\exp(-0.21\bar{u}/kT) - 1]\}$.

**Table 5. Adjustable Parameters of the UNIQUAC Equation and the Ternary Term $Q_{\text{ter}}$**

| $ij$ | $a_{ij,0}$/K | $a_{ij,1}$ | $a_{ij,2}$/K$^{-1}$ | $d_1$ | $d_2$ | $d_3$ |
|---|---|---|---|---|---|---|
| | 2-Methylbutane (1) + 2-Methyl-2-propanol (2) + Water (3) | | | | | |
| 12 | 587.46 | −1.0084 | 0.0 | −5.76 | 3.99 | −6.85 |
| 21 | −179.169 | 0.32394 | 0.0 | | | |
| 13 | 3127.50 | −6.0628 | 0.0 | | | |
| 31 | −2420.70 | 18.0620 | −0.026791 | | | |
| 23 | 777.45 | −1.7247 | 0.0 | | | |
| 32 | −540.06 | 1.7357 | 0.0 | | | |
| | Pentane (1) + 2-Methyl-2-propanol (2) + Water (3) | | | | | |
| 12 | 513.48 | −0.71825 | 0.0 | −6.84 | 6.00 | −7.52 |
| 21 | −150.558 | 0.20845 | 0.0 | | | |
| 13 | 3051.6 | −5.7158 | 0.0 | | | |
| 31 | −1709.94 | 13.065 | −0.017814 | | | |
| 23 | 777.45 | −1.7247 | 0.0 | | | |
| 32 | −540.06 | 1.7357 | 0.0 | | | |

presented model parameters are not able to describe such behavior of $C_p{}^{\text{E}}$.

Descriptions of binary systems 2-methylbutane (1) + 2-methyl-2-propanol (2) and pentane (1) + 2-methyl-2-propanol (2) were based on correlation of the VLE data only. Pressures in vapor−liquid equilibrium data for the 2-methylbutane (1) + 2-methyl-2-propanol (2) system at 373 K rise up to 700 kPa.[7] Consequently, the absolute value of the root-mean-square deviation in pressure is a bit higher.

Binodal curves in the ternary systems calculated using binary parameters only are outlined in Figures 1 and 2 by dotted lines. The predicted heterogeneous regions are wider than the experimental ones. To correct this discrepancy, the ternary parameters had to be used. The term $Q_{\text{ter}}$ in eq 1 was applied in the form[20]

$$Q_{\text{ter}} = x_1 x_2 x_3 (x_1 d_1 + x_2 d_2 + x_3 d_3) \tag{4}$$

where $d_1$, $d_2$, and $d_3$ are the ternary parameters. Their values were determined by minimization of the objective function

$$F(d_1, d_2, d_3) = \sum_{i=1}^{n} \sum_{k=1}^{3} [(x'_{k,i} - x'_{k,i,\text{calc}})^2 + (x''_{k,i} - x''_{k,i,\text{calc}})^2] \tag{5}$$

where $x'_{k,i}$ and $x''_{k,i}$ are the mole fractions of the $k$-th component for the $i$-th experimental point in the first and second liquid phases, respectively; i.e., points $(x'_{1,i}, x'_{2,i}, x'_{3,i})$ and $(x''_{1,i}, x''_{2,i}, x''_{3,i})$ are end points of the $i$-th experimental tie-line. Similarly, points $(x'_{1,i,\text{calc}}, x'_{2,i,\text{calc}}, x'_{3,i,\text{calc}})$ and $(x''_{1,i,\text{calc}}, x''_{2,i,\text{calc}}, x''_{3,i,\text{calc}})$ are end points of the $i$-th calculated tie-line which lies closest to the above-mentioned $i$-th experimental tie-line. Single points of the binodal curve determined by the titration method were not included into the fit.

The function $F$ is a nonlinear function which could have more than one point of minimum. Therefore, the nonderivative numerical method based on the construction of a sequence of three-dimensional rectangular grids (having decreasing distance between two neighboring lattice points $(d_1, d_2, d_3)$) was used to determine the point of minimum of function $F$. The value of the function $F$ is calculated in each lattice point. Although such a numerical process is relatively slow (it is necessary to determine the binodal curve in each lattice point), it is reliably convergent to the point of the absolute minimum of the objective function $F$. The standard deviation

$$\sigma = \sqrt{\frac{\min F}{6n}} \tag{6}$$

was used as a measure of goodness of fit. The calculated ternary parameters are given in Table 5. They were obtained at 293.15 K, but they can be used together with presented (temperature-dependent) binary parameters for estimation of thermodynamic behavior in the ternary systems up to about 333 K.

As was expected, both ternary systems exhibited similar behavior related to the LLE. The experimental tie-lines as well as binodal lines predicted by the UNIQUAC model without a ternary term are very alike for both systems. The predicted liquid−liquid equilibria exhibit wider regions of limited miscibility than that experimentally determined (see Figures 1 and 2). For the prediction (i.e., for the case $d_1 = d_2 = d_3 = 0$), the standard deviations calculated according to eq 6 were $\sigma = 0.042$ for the 2-methylbutane (1) + 2-methyl-2-propanol (2) + water (3) system and $\sigma = 0.046$ for the pentane (1) + 2-methyl-2-propanol (2) + water (3) system. After the optimization of the ternary parameters, the calculated liquid−liquid equilibria were significantly improved. A slightly better fit was achieved for the 2-methylbutane (1) + 2-methyl-2-propanol (2) + water (3) system ($\sigma = 0.0105$) than for the second one ($\sigma = 0.0134$). Calculated compositions of critical points of the liquid−liquid equilibria were $x_{1\text{c}} = 0.0057$, $x_{2\text{c}} = 0.2351$, and $x_{3\text{c}} = 0.7592$ in the 2-methylbutane (1) + 2-methyl-2-propanol (2) + water (3) system, and $x_{1\text{c}} = 0.0057$, $x_{2\text{c}} = 0.2282$, $x_{3\text{c}} = 0.7661$ in the pentane (1) + 2-methyl-2-propanol (2) + water (3) system. Since the melting temperature of 2-methyl-2-propanol is higher than the temperature of measurement, solid−liquid equilibrium lines are also drawn within the phase diagrams in Figures 1 and 2. These lines were calculated using the presented model, the melting temperature of 2-methyl-2-propanol (298.80 K), and the enthalpy of fusion (6706 J·mol$^{-1}$).[19]

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