# Isobaric Vapor−Liquid Equilibria of the Ternary System Methylbutyl Ketone + Nonane + Cyclohexanol

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Isobaric vapor−liquid equilibria (VLE) were measured for the ternary system methylbutyl ketone + nonane + cyclohexanol and for the binary methylbutyl ketone + cyclohexanol. Boiling temperature ($T$)−liquid composition ($x$) relations were obtained at (26.66, 53.33, and 79.99) kPa by using a semi-microebulliometer. The modified Wilson model was used to correlate the binary $T-x$ data and to predict VLE in the ternary system.

## Introduction

Multicomponent vapor−liquid equilibrium (VLE) data are important in the design of equipment for separation processes, and it is necessary to test and develop models for the correlation and prediction of thermodynamic properties of mixtures. In previous work, we have reported vapor−liquid equilibria in the ternary systems *o*-xylene + amyl acetate + nonane,[1] *o*-xylene + nonane + cyclohexanol,[2] hexan-2-one + *o*-xylene + nonane,[3] toluene + *p*-xylene + 1,2-dichloroethane,[4] toluene + ethylbenzene + chlorobenzene,[5] and toluene + ethylbenzene + amyl acetate.[6] In this paper, we present vapor−liquid equilibria at pressures of (26.66, 53.33, and 79.99) kPa for the ternary system methylbutyl ketone + nonane + cyclohexanol. The study of the thermodynamics of this system is interesting from a scientific point of view because there exist two different polar components (ketone and alcohol) together with a nonpolar one (hydrocarbon). We have not found information for VLE of this ternary system and of the binary system methylbutyl ketone + cyclohexanol in the literature. For the other binaries, our VLE data have been published earlier.[2,3] Our microcalorimetric experiments at 318.15 K showed that there are quite large positive excess enthalpies in the ternary system methylbutyl ketone + nonane + cyclohexanol and in all constituent binaries.[7] For the correlation of binary VLE data and prediction of ternary VLE, the modified Wilson equation[2] was used as a model, giving in many cases the most reliable results.

## Experimental Section

***Materials.*** All substances were purified twice by vacuum rectification. Their purity, checked by gas chromatography, was better than 99.5 mass %. Densities $\rho$/kg·m$^{-3}$ were measured with a capillary pycnometer, and refractive indices $n_D$ were measured with an Abbé refractometer at 293.15 K. Measurements of normal boiling temperatures $T_b$/K, densities, and refractive indices are compared with literature data in Table 1.

***Apparatus and Procedure.*** The boiling temperature−liquid mole fraction $T-x$ measurements were performed by means of a semi-microebulliometer. The experimental arrangement and the procedure of determining the $T-x$ relation were described previously.[8] The uncertainties of the boiling-temperature measurements were estimated to be less than 0.05 K. The equilibrium pressure was measured with a mercury manometer. The absolute accuracy of these measurements is probably within 13 Pa. All mixtures were prepared by mass. The uncertainties of the mole fraction composition of a liquid mixture ($x_i$) were found to be less than 5 × 10$^{-4}$.

**Table 1. Normal Boiling Temperatures $T_b$, Densities $\rho$, and Refractive Indices $n_D$ of Pure Components**

| | | $T_b$/K | | $\rho$/kg·m$^{-3}$ | | $n_D$ | |
|---|---|---|---|---|---|---|---|
| component | $T$/K | exptl | lit | exptl | lit | exptl | lit |
| methylbutyl ketone | 293.15 | 400.69 | 400.35[a] | 811.2 | 811.3[b] | 1.4008 | 1.4007[b] |
| nonane | 293.15 | 423.97 | 423.95[a] | 717.6 | 717.6[c] | 1.4055 | 1.4054[c] |
| cyclohexanol | 303.15 | 433.89 | 434.25[a] | 941.6 | 941.6[a] | 1.4621 | 1.4629[a] |

[a] Dean.[10] [b] Lide.[11] [c] TRC Thermodynamic Tables.[12]

**Table 2. Isobaric Vapor−Liquid Equilibrium Data: Liquid-Phase Mole Fraction ($x_1$) and Boiling Temperatures ($T$) in the Binary System Methylbutyl Ketone + Cyclohexanol**

| | $T$/K at pressure $P$/kPa | | |
|---|---|---|---|
| $x_1$ | $P$ = 26.66 | $P$ = 53.33 | $P$ = 79.99 |
| 0.000 | 394.86 | 413.79 | 426.16 |
| 0.153 | 384.27 | 404.77 | 417.90 |
| 0.227 | 380.48 | 401.21 | 414.56 |
| 0.357 | 374.48 | 395.33 | 408.76 |
| 0.508 | 369.84 | 390.48 | 404.09 |
| 0.625 | 367.10 | 387.50 | 400.97 |
| 0.795 | 363.45 | 383.45 | 396.74 |
| 0.899 | 361.51 | 381.40 | 394.58 |
| 1.000 | 359.51 | 379.52 | 392.57 |

## Results and Discussion

The experimental values of boiling-temperature measurements for the binary system methylbutyl ketone + cyclohexanol at three pressures (26.66, 53.33, and 79.99) kPa are reported in Table 2 and for all of the binaries at 79.99 kPa in Figure 1.

The $T-x$ data of the binary systems were fit with the Wilson model,[9] writing the expression for the activity coefficients as

$$\ln \gamma_i = -\ln(x_i - \Lambda_{ik}x_k) + x_k\left[\frac{\Lambda_{ik}}{x_i + \Lambda_{ik}x_k} - \frac{\Lambda_{ki}}{x_k + \Lambda_{ki}x_i}\right] \quad (1)$$

where $\gamma_i$ is the activity coefficient of component $i$ in the liquid phase. We have used the modified form of the Wilson

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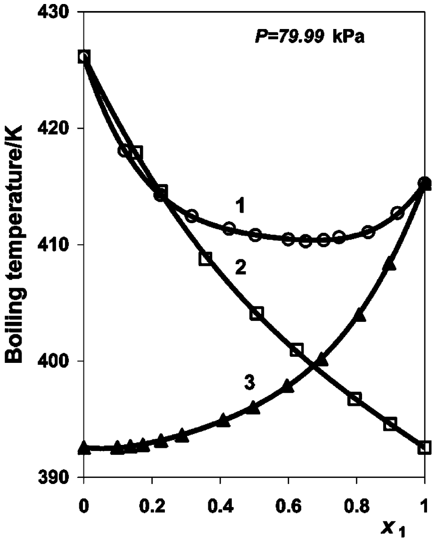

**Figure 1.** Boiling temperature−composition diagram for binaries at 79.99 kPa: ○, nonane (1) + cyclohexanol (2), line 1, Siimer et al.;[2] □, methylbutyl ketone (1) + cyclohexanol (2), line 2, this work; △, nonane (1) + methylbutyl ketone (2), line 3, Siimer et al.[3]

**Table 3. Coefficients for the Antoine Vapor-Pressure Equation (kPa, K) (Eq 4)**

| component | $A_i$ | $B_i$ | $C_i$ | temperature region, K |
|---|---|---|---|---|
| methylbutyl ketone[a] | 14.0050 | 3104.454 | −69.962 | 359 to 401 |
| nonane[b] | 13.8546 | 3224.816 | −74.824 | 380 to 424 |
| cyclohexanol[b] | 13.7219 | 2778.058 | −128.724 | 395 to 426 |

[a] Siimer et al., 2002.[3] [b] Siimer et al., 2002.[2]

model,[2] considering the linear dependence of the parameters $(\lambda_{ij} - \lambda_{ii})$ on temperature. In this case, coefficients $\Lambda_{ik}$ and $\Lambda_{ki}$ can be expressed as

$$\Lambda_{ik} = \exp\left[a_{ik} + \frac{b_{ik}}{T}\right] \tag{2}$$

$$\Lambda_{ki} = \exp\left[a_{ki} + \frac{b_{ki}}{T}\right] \tag{3}$$

including in parameters $a_{ik}$ and $b_{ik}$ the molar volumes of components and the gas constant. Parameters $a_{ik}$ and $b_{ik}$ were calculated by the Newton iteration method.

The vapor pressures of pure components $P_i$ needed for VLE calculations were calculated using the Antoine equation

$$\ln(P_i/\text{kPa}) = A_i - \frac{B_i}{T/\text{K} + C_i} \tag{4}$$

as given by us earlier,[2,3] and the values of $A_i$, $B_i$, and $C_i$ are also given in Table 3.

In Table 4, the optimal values of parameters $a_{ik}$ and $b_{ik}$, standard deviation, and mean relative error in the pressure as a result of correlation are presented. For the systems methylbutyl ketone + nonane and nonane + cyclohexanol, our earlier results[2,3] are given. The standard deviation was calculated using eq 5

$$\sigma(P/\text{kPa}) = \left[\sum \frac{(P_{\text{calcd}} - P_{\text{exptl}})^2}{N - n}\right]^{1/2} \tag{5}$$

where $N$ is the number of experimental points and $n$ is the number of parameters used. In determining parameters $a_{ik}$ and $b_{ik}$, we used $n = 4$.

**Table 4. Fit Parameters of the Modified Wilson Equation and Calculated Standard Deviations ($\sigma P$) and Absolute Mean Errors ($\Delta P$) in Pressure for Binary Systems**

| | Wilson parameter values | | | | | |
|---|---|---|---|---|---|---|
| system | $a_{12}$ | $b_{12}$ | $a_{21}$ | $b_{21}$ | $\sigma P$/kPa | $\Delta P$/% |
| methylbutyl ketone (1) + cyclohexanol (2) | 2.17687 | −839.958 | −0.86126 | 195.303 | 0.25 | 0.31 |
| methylbutyl ketone (1) + nonane (2)[a] | 1.70016 | −728.735 | −1.03432 | 155.701 | 0.19 | 0.22 |
| nonane (1) + cyclohexanol (2)[b] | 0.05676 | −314.903 | 3.58544 | −1774.377 | 0.15 | 0.20 |

[a] Siimer et al., 2002.[3] [b] Siimer et al., 2002.[2]

**Table 5. Experimental Vapor−Liquid Equilibria Data for the Ternary System Methylbutyl Ketone (1) + Nonane (2) + Cyclohexanol (3) at Three Pressures and Values Calculated by the Modified Wilson Equation[2] Activity Coefficients ($\gamma_1$, $\gamma_2$, and $\gamma_3$), Vapor Mole Fractions ($y_1$ and $y_2$), Excess Gibbs Energy ($G^E$), Pressure ($P_{\text{calcd}}$), and Boiling Temperature ($T_{\text{calcd}}$)**

| experimental data | | | calculated values | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| liquid mole fraction | | boiling temp | activity coefficients | | | vapor mole fractions | | Gibbs energy | pressure | boiling temp |
| $x_1$ | $x_2$ | $T_{\text{exptl}}$/K | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ | $y_1$ | $y_2$ | $G^E$/J mol$^{-1}$ | $P_{\text{calcd}}$/kPa | $T_{\text{calcd}}$/K |
| $P = 79.99$ kPa | | | | | | | | | | |
| 0.425 | 0.424 | 398.51 | 1.129 | 1.282 | 1.607 | 0.573 | 0.334 | 757.1 | 79.77 | 398.61 |
| 0.345 | 0.344 | 401.32 | 1.092 | 1.462 | 1.335 | 0.487 | 0.336 | 837.3 | 79.90 | 401.36 |
| 0.225 | 0.225 | 406.30 | 1.087 | 1.853 | 1.119 | 0.362 | 0.323 | 741.6 | 80.05 | 406.28 |
| 0.284 | 0.569 | 401.32 | 1.224 | 1.152 | 1.834 | 0.448 | 0.437 | 758.1 | 80.07 | 401.29 |
| 0.184 | 0.368 | 405.73 | 1.114 | 1.498 | 1.260 | 0.298 | 0.419 | 917.0 | 80.14 | 405.67 |
| 0.128 | 0.256 | 408.88 | 1.103 | 1.818 | 1.115 | 0.225 | 0.389 | 790.7 | 79.91 | 408.92 |
| 0.154 | 0.564 | 405.04 | 1.207 | 1.202 | 1.613 | 0.267 | 0.509 | 900.7 | 79.54 | 405.24 |
| 0.580 | 0.280 | 396.29 | 1.060 | 1.479 | 1.449 | 0.690 | 0.238 | 642.9 | 79.54 | 396.49 |
| 0.753 | 0.165 | 394.24 | 1.022 | 1.688 | 1.409 | 0.812 | 0.150 | 429.6 | 79.66 | 394.38 |
| 0.128 | 0.744 | 405.83 | 1.373 | 1.057 | 2.211 | 0.257 | 0.600 | 619.1 | 80.01 | 405.82 |
| 0.452 | 0.226 | 399.85 | 1.054 | 1.694 | 1.233 | 0.593 | 0.246 | 699.4 | 79.51 | 400.06 |
| 0.334 | 0.167 | 404.20 | 1.069 | 1.980 | 1.109 | 0.498 | 0.240 | 631.7 | 80.21 | 404.11 |
| $P = 53.33$ kPa | | | | | | | | | | |
| 0.425 | 0.424 | 385.05 | 1.138 | 1.310 | 1.690 | 0.580 | 0.333 | 795.7 | 52.98 | 385.26 |
| 0.345 | 0.344 | 387.95 | 1.104 | 1.507 | 1.377 | 0.497 | 0.341 | 885.3 | 53.29 | 387.98 |
| 0.225 | 0.225 | 392.84 | 1.112 | 1.941 | 1.133 | 0.378 | 0.335 | 789.2 | 53.44 | 392.78 |
| 0.284 | 0.569 | 387.68 | 1.241 | 1.169 | 1.948 | 0.458 | 0.435 | 800.7 | 53.13 | 387.80 |
| 0.184 | 0.368 | 392.19 | 1.136 | 1.552 | 1.285 | 0.310 | 0.431 | 970.1 | 53.29 | 392.21 |
| 0.128 | 0.256 | 395.48 | 1.135 | 1.910 | 1.125 | 0.237 | 0.408 | 836.3 | 53.41 | 395.44 |
| 0.154 | 0.564 | 391.58 | 1.228 | 1.226 | 1.680 | 0.277 | 0.514 | 954.0 | 53.04 | 391.76 |
| 0.580 | 0.280 | 383.01 | 1.063 | 1.521 | 1.519 | 0.695 | 0.239 | 673.9 | 52.91 | 383.26 |
| 0.753 | 0.165 | 381.14 | 1.023 | 1.744 | 1.482 | 0.815 | 0.151 | 448.0 | 53.14 | 381.25 |
| 0.128 | 0.744 | 392.12 | 1.407 | 1.065 | 2.396 | 0.267 | 0.596 | 660.1 | 53.32 | 392.13 |
| 0.452 | 0.226 | 386.40 | 1.063 | 1.757 | 1.269 | 0.604 | 0.250 | 743.6 | 52.80 | 386.72 |
| 0.334 | 0.167 | 390.67 | 1.088 | 2.074 | 1.125 | 0.514 | 0.248 | 678.7 | 53.40 | 390.63 |
| $P = 26.66$ kPa | | | | | | | | | | |
| 0.425 | 0.424 | 364.67 | 1.151 | 1.355 | 1.820 | 0.595 | 0.333 | 845.3 | 26.46 | 364.89 |
| 0.345 | 0.344 | 367.52 | 1.125 | 1.577 | 1.441 | 0.517 | 0.347 | 947.4 | 26.65 | 367.53 |
| 0.225 | 0.225 | 372.28 | 1.153 | 2.078 | 1.154 | 0.406 | 0.354 | 851.5 | 26.82 | 372.12 |
| 0.284 | 0.569 | 367.16 | 1.267 | 1.198 | 2.125 | 0.475 | 0.432 | 856.5 | 26.59 | 367.24 |
| 0.184 | 0.368 | 371.62 | 1.173 | 1.636 | 1.323 | 0.332 | 0.449 | 1037.7 | 26.64 | 371.65 |
| 0.128 | 0.256 | 374.83 | 1.190 | 2.054 | 1.140 | 0.261 | 0.440 | 895.1 | 26.70 | 374.79 |
| 0.154 | 0.564 | 371.13 | 1.263 | 1.266 | 1.781 | 0.295 | 0.524 | 1023.2 | 26.60 | 371.20 |
| 0.580 | 0.280 | 362.85 | 1.069 | 1.589 | 1.628 | 0.705 | 0.240 | 713.2 | 26.49 | 363.03 |
| 0.753 | 0.165 | 361.42 | 1.025 | 1.833 | 1.596 | 0.820 | 0.152 | 470.7 | 26.93 | 361.15 |
| 0.128 | 0.744 | 371.14 | 1.459 | 1.079 | 2.697 | 0.284 | 0.591 | 716.4 | 26.53 | 371.29 |
| 0.452 | 0.226 | 365.91 | 1.076 | 1.854 | 1.324 | 0.623 | 0.256 | 800.8 | 26.27 | 366.32 |
| 0.334 | 0.167 | 370.00 | 1.118 | 2.221 | 1.152 | 0.544 | 0.261 | 741.4 | 26.66 | 370.01 |

The isobaric VLE data for the ternary system are given in Table 5. Experimental $T-x$ data are presented together with calculated values of activity coefficients, vapor compositions, excess Gibbs energy, temperatures, and total pressures predicted by the modified Wilson equation using

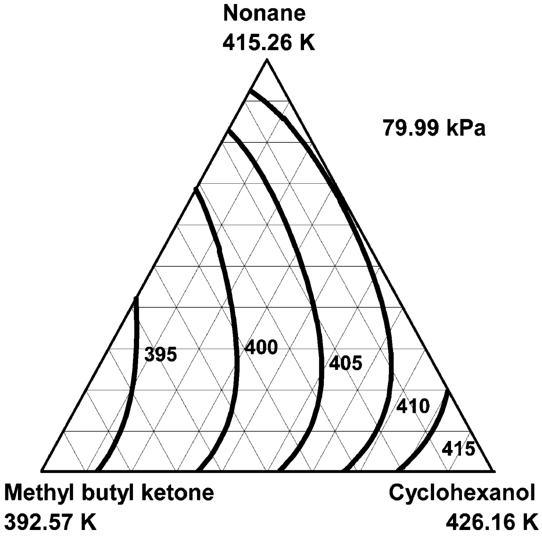

**Figure 2.** Boiling temperature isotherms calculated with the modified Wilson equation for the ternary system methylbutyl ketone (1) + nonane (2) + cyclohexanol (3) at 79.99 kPa.

the binary parameters from Table 4. Mean (absolute) deviations between experimental and calculated temperature and pressure were equal to 0.12 K and 0.18 kPa, respectively, and standard deviation of pressure was 0.25 kPa. Isotherms of the boiling point at a pressure of 79.99 kPa calculated using the modified Wilson equation are presented as (395, 400, 405, 410, and 415) K curves on the Gibbs triangle in Figure 2.

We reported earlier that binaries of nonane + cyclohexanol[2] and nonane + methylbutyl ketone[3] form azeotropes at nonane mole fractions of 0.665 and 0.053 (at a pressure of 79.99 kPa), respectively, as can also be seen from Figure 1. The binary methylbutyl ketone + cyclohexanol has a relatively weak deviation from ideality.

As seen from Figure 2, for the ternary system there exists quite a strong deviation from Raoult's law. This is not surprising, considering the binary VLE data and the quite remarkable positive excess enthalpies in this system,[7] both proving the strong interaction between different component molecules.

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