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# Phase Equilibria of the Ternary System Benzene + Cyclohexane + 1-Pentanol at 101.3 kPa

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Vapor−liquid equilibrium at 101.3 kPa has been measured for the ternary system benzene + cyclohexane + 1-pentanol in an isobaric equilibrium still with secondary recirculation of both vapor and liquid phases. Satisfactory results were obtained for the prediction of activity coefficients and the equilibrium compositions with the ASOG and UNIFAC group contribution models; low standard deviations of vapor mole fraction and temperature were computed. Azeotropic behavior was observed only in the benzene + cyclohexane mixture. The correlation parameters for the Tamir−Wisniak and UNIQUAC equations are presented.

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## Introduction

Experimental data collections of phase equilibria for ternary or higher order complexity are scarce because of the time-consuming experimental procedures to obtain a complete description of every mixture. As an extension of our earlier work concerning vapor−liquid or liquid−liquid equilibria (VLE or LLE)[1−3] and thermochemical properties,[4−6] we present new phase equilibrium data concerning 1-pentanol as an alternative extractive rectification solvent for the azeotropic mixture benzene + cyclohexane. This paper presents VLE data for the mixture benzene + cyclohexane + 1-pentanol at a pressure of 101.3 kPa; no literature data are available for this system. Such thermodynamic data can be obtained from available predictive models of functional molecular group contribution, as the well-known UNIFAC method.[7] These models require complete and fully updated experimental data in order to compute group interaction parameters and reproduce the behavior of systems at other mixing or operation conditions. The application of the ASOG, UNIFAC, and their modification group contribution methods leads to satisfactory predictions in terms of activity coefficients and compositions for this mixture. Fitting parameters corresponding to boiling temperatures and activity coeficient mole fraction dependence are presented.

## Experimental Section

***Chemicals.*** All chemicals were Merck chromatographic grade. Purification was attempted by ultrasonic degassing and molecular sieve drying (4 Å, $^1/_{16}$ in.). The purity of materials was checked by gas chromatography and found to be better than 99.9 mass % for benzene and cyclohexane and 99.0 mass % for 1-pentanol, and the maximun water contents of the pure liquids (Metrohm 737 Coulometer) were $3.0 \times 10^{-2}$, $4.9 \times 10^{-3}$, and $2.3 \times 10^{-1}$ mass % for benzene, cyclohexane, and 1-pentanol, respectively. Their purity was also checked by determining their densities and refractive indices at 298.15 K and their normal boiling temperatures $T_b$ (Table 1), prior to the measurements.

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

| | $\rho$(298.15 K)/(g·cm$^{-3}$) | | $n_D$(298.15 K) | | $T_b$/K | |
|---|---|---|---|---|---|---|
| component | exptl | lit.[a] | exptl | lit.[a] | exptl | lit.[a] |
| benzene | 0.8736 | 0.87370 | 1.49692 | 1.49792 | 353.16 | 353.250 |
| cyclohexane | 0.7737 | 0.77389 | 1.42320 | 1.42354 | 353.79 | 353.888 |
| 1-pentanol | 0.8110 | 0.8112 | 1.40782 | 1.4079 | 410.78 | 410.95 |

[a] *TRC Thermodynamic Tables*.[8]

***Apparatus and Procedure.*** VLE measurements were carried out under an atmosphere of dry argon (less than 3 ppmv in water) in a modified all-glass Othmer-type ebulliometer with secondary recirculation of both the liquid and vapor phase.[9] Thermal isolation was ensured because the whole apparatus was insulated except for the part corresponding to the vapor condenser. Boiling temperatures of mixtures were measured with a Yokogawa 7563 digital thermometer with a precision of $\pm 10^{-2}$ K (temperature scale IPTS-75), calibrated with an Anton Paar MKT-100 digital thermometer (precision $\pm 10^{-3}$ K and temperature scale ITS-90) over the entire range of work temperatures. Pressure was kept constant at (101.3 ± 0.1) kPa by a controller device which introduced argon to the apparatus in order to maintain the pressure difference with respect to the pressure in the laboratory. Each experiment was continued at least for 1 h after the boiling temperature had become stable. Samples of both the liquid and vapor phases were taken at low temperature by a built-in refrigeration device and sealed in ice-cooled graduated test tubes to prevent evaporation leakage. Once the sample temperature became stable using a PolyScience controller bath model 9510 with a temperature stability of $\pm 10^{-2}$ K, the samples were analyzed by measuring their refractive indices and densities at 298.15 K. Densities of the pure liquid and mixtures were measured with an Anton Paar DSA-48 densimeter (accuracy of $\pm 10^{-4}$ g·cm$^{-3}$) and refractive indices with an automatic refractometer ABBEMAT-HP Dr. Kernchen (accuracy of $\pm 5 \times 10^{-5}$). The estimated uncertainty for mole fractions was determined as $\pm 7 \times 10^{-3}$.

## Results and Discussion

***Equilibrium Equation and Activity Coefficients.*** Experimental density ($\rho$) and refractive index ($n_D$) values at 298.15 K for this ternary system as a function of $x_i$ have been published previously.[4] Such physical properties were applied in order to compute the mixing composition by

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**Table 2. Experimental Vapor−Liquid Equilibrium Data: Temperature $T$, Liquid Phase $x_i$ and Vapor Phase $y_i$ Mole Fractions, Activity Coefficient $\gamma_i$ for Benzene (1) + Cyclohexane (2) + 1-Pentanol (3) at 101.3 kPa, and Root-Mean-Square Deviation from the UNIQUAC Correlation (in Parentheses)**

| $T$/K | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ | $T$/K | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 350.85 | 0.519 | 0.472 | 0.522 | 0.476 | 1.070 | 1.097 | 3.479 | 352.83 | 0.143 | 0.797 | 0.167 | 0.803 | 1.172 | 1.034 | 5.674 |
| 350.87 | 0.494 | 0.492 | 0.500 | 0.496 | 1.077 | 1.097 | 3.152 | 352.87 | 0.173 | 0.629 | 0.220 | 0.742 | 1.272 | 1.211 | 2.185 |
| 350.98 | 0.483 | 0.501 | 0.491 | 0.505 | 1.076 | 1.092 | 3.435 | 352.94 | 0.119 | 0.831 | 0.146 | 0.834 | 1.224 | 1.027 | 4.493 |
| 350.98 | 0.468 | 0.521 | 0.476 | 0.520 | 1.076 | 1.084 | 4.315 | 352.98 | 0.578 | 0.239 | 0.653 | 0.319 | 1.125 | 1.367 | 1.753 |
| 350.98 | 0.444 | 0.543 | 0.455 | 0.541 | 1.083 | 1.081 | 4.240 | 353.00 | 0.146 | 0.662 | 0.192 | 0.772 | 1.310 | 1.193 | 2.092 |
| 350.99 | 0.487 | 0.492 | 0.496 | 0.500 | 1.077 | 1.101 | 2.729 | 353.05 | 0.328 | 0.341 | 0.449 | 0.518 | 1.362 | 1.552 | 1.121 |
| 351.07 | 0.456 | 0.525 | 0.467 | 0.525 | 1.081 | 1.081 | 5.382 | 353.05 | 0.674 | 0.189 | 0.729 | 0.250 | 1.076 | 1.352 | 1.700 |
| 351.09 | 0.445 | 0.532 | 0.459 | 0.535 | 1.089 | 1.087 | 3.069 | 353.07 | 0.903 | 0.066 | 0.912 | 0.084 | 1.003 | 1.306 | 1.390 |
| 351.15 | 0.422 | 0.554 | 0.440 | 0.553 | 1.096 | 1.077 | 3.848 | 353.13 | 0.067 | 0.912 | 0.091 | 0.900 | 1.355 | 1.004 | 4.859 |
| 351.23 | 0.399 | 0.576 | 0.419 | 0.572 | 1.103 | 1.070 | 4.620 | 353.15 | 0.126 | 0.705 | 0.160 | 0.798 | 1.257 | 1.152 | 2.796 |
| 351.26 | 0.387 | 0.583 | 0.409 | 0.575 | 1.107 | 1.061 | 6.859 | 353.26 | 0.105 | 0.761 | 0.133 | 0.836 | 1.246 | 1.115 | 2.578 |
| 351.32 | 0.374 | 0.590 | 0.399 | 0.592 | 1.117 | 1.077 | 3.370 | 353.29 | 0.930 | 0.038 | 0.944 | 0.048 | 1.001 | 1.305 | 2.741 |
| 351.42 | 0.503 | 0.437 | 0.516 | 0.468 | 1.073 | 1.145 | 3.249 | 353.34 | 0.622 | 0.199 | 0.703 | 0.274 | 1.113 | 1.389 | 1.488 |
| 351.42 | 0.361 | 0.605 | 0.387 | 0.602 | 1.120 | 1.065 | 3.952 | 353.41 | 0.034 | 0.951 | 0.038 | 0.950 | 1.095 | 1.008 | 9.020 |
| 351.43 | 0.449 | 0.501 | 0.466 | 0.520 | 1.084 | 1.112 | 3.323 | 353.53 | 0.056 | 0.895 | 0.063 | 0.908 | 1.101 | 1.021 | 6.493 |
| 351.44 | 0.486 | 0.458 | 0.501 | 0.485 | 1.076 | 1.134 | 3.033 | 353.66 | 0.811 | 0.078 | 0.870 | 0.116 | 1.047 | 1.483 | 1.384 |
| 351.45 | 0.500 | 0.435 | 0.516 | 0.469 | 1.077 | 1.154 | 2.844 | 353.69 | 0.872 | 0.058 | 0.907 | 0.078 | 1.014 | 1.344 | 2.353 |
| 351.45 | 0.445 | 0.512 | 0.459 | 0.526 | 1.076 | 1.098 | 4.348 | 353.71 | 0.347 | 0.281 | 0.498 | 0.463 | 1.399 | 1.646 | 1.153 |
| 351.48 | 0.371 | 0.589 | 0.396 | 0.592 | 1.110 | 1.075 | 3.786 | 353.76 | 0.068 | 0.826 | 0.083 | 0.882 | 1.189 | 1.067 | 3.647 |
| 351.48 | 0.362 | 0.601 | 0.387 | 0.601 | 1.112 | 1.069 | 4.216 | 353.77 | 0.031 | 0.905 | 0.041 | 0.936 | 1.259 | 1.033 | 4.065 |
| 351.49 | 0.399 | 0.579 | 0.413 | 0.575 | 1.080 | 1.060 | 6.864 | 353.83 | 0.744 | 0.093 | 0.835 | 0.143 | 1.089 | 1.534 | 1.462 |
| 351.51 | 0.421 | 0.542 | 0.433 | 0.549 | 1.072 | 1.082 | 5.915 | 354.18 | 0.100 | 0.505 | 0.155 | 0.790 | 1.492 | 1.543 | 1.482 |
| 351.59 | 0.491 | 0.431 | 0.511 | 0.471 | 1.081 | 1.164 | 2.887 | 354.19 | 0.078 | 0.618 | 0.114 | 0.846 | 1.410 | 1.350 | 1.413 |
| 351.84 | 0.634 | 0.305 | 0.642 | 0.345 | 1.044 | 1.195 | 2.658 | 354.20 | 0.619 | 0.125 | 0.767 | 0.207 | 1.189 | 1.626 | 1.096 |
| 351.86 | 0.584 | 0.347 | 0.596 | 0.385 | 1.051 | 1.175 | 3.311 | 354.22 | 0.084 | 0.552 | 0.130 | 0.823 | 1.483 | 1.471 | 1.381 |
| 351.88 | 0.528 | 0.385 | 0.550 | 0.431 | 1.072 | 1.181 | 2.668 | 354.22 | 0.684 | 0.109 | 0.803 | 0.169 | 1.126 | 1.538 | 1.434 |
| 351.94 | 0.680 | 0.259 | 0.685 | 0.303 | 1.036 | 1.232 | 2.448 | 354.24 | 0.048 | 0.668 | 0.070 | 0.887 | 1.410 | 1.309 | 1.591 |
| 352.01 | 0.439 | 0.457 | 0.459 | 0.508 | 1.073 | 1.168 | 3.802 | 354.28 | 0.036 | 0.695 | 0.059 | 0.904 | 1.552 | 1.280 | 1.497 |
| 352.04 | 0.469 | 0.411 | 0.504 | 0.470 | 1.100 | 1.202 | 2.673 | 354.35 | 0.039 | 0.662 | 0.056 | 0.899 | 1.362 | 1.334 | 1.597 |
| 352.04 | 0.420 | 0.463 | 0.455 | 0.521 | 1.110 | 1.182 | 2.428 | 354.40 | 0.010 | 0.835 | 0.014 | 0.956 | 1.327 | 1.123 | 2.048 |
| 352.08 | 0.432 | 0.453 | 0.470 | 0.504 | 1.114 | 1.169 | 2.644 | 354.44 | 0.026 | 0.761 | 0.035 | 0.929 | 1.269 | 1.197 | 1.770 |
| 352.15 | 0.275 | 0.593 | 0.320 | 0.654 | 1.187 | 1.156 | 2.333 | 354.64 | 0.105 | 0.454 | 0.177 | 0.765 | 1.598 | 1.641 | 1.372 |
| 352.19 | 0.409 | 0.440 | 0.458 | 0.520 | 1.141 | 1.236 | 1.765 | 354.75 | 0.550 | 0.129 | 0.734 | 0.229 | 1.260 | 1.716 | 1.194 |
| 352.21 | 0.363 | 0.497 | 0.407 | 0.569 | 1.142 | 1.198 | 2.041 | 355.14 | 0.212 | 0.363 | 0.333 | 0.612 | 1.462 | 1.616 | 1.333 |
| 352.21 | 0.449 | 0.389 | 0.502 | 0.474 | 1.139 | 1.275 | 1.765 | 355.18 | 0.212 | 0.329 | 0.342 | 0.582 | 1.507 | 1.697 | 1.672 |
| 352.24 | 0.482 | 0.347 | 0.543 | 0.436 | 1.148 | 1.312 | 1.456 | 355.69 | 0.351 | 0.167 | 0.600 | 0.341 | 1.570 | 1.926 | 1.205 |
| 352.31 | 0.325 | 0.568 | 0.360 | 0.616 | 1.125 | 1.131 | 2.666 | 355.85 | 0.112 | 0.388 | 0.200 | 0.737 | 1.640 | 1.789 | 1.229 |
| 352.34 | 0.243 | 0.636 | 0.285 | 0.689 | 1.194 | 1.128 | 2.500 | 357.81 | 0.141 | 0.313 | 0.269 | 0.648 | 1.642 | 1.846 | 1.341 |
| 352.35 | 0.528 | 0.261 | 0.616 | 0.364 | 1.183 | 1.454 | 1.130 | 357.88 | 0.525 | 0.070 | 0.809 | 0.140 | 1.328 | 1.774 | 1.105 |
| 352.38 | 0.215 | 0.676 | 0.255 | 0.718 | 1.204 | 1.106 | 2.850 | 358.58 | 0.459 | 0.080 | 0.767 | 0.170 | 1.411 | 1.850 | 1.166 |
| 352.43 | 0.502 | 0.296 | 0.580 | 0.397 | 1.171 | 1.392 | 1.345 | 359.36 | 0.374 | 0.092 | 0.708 | 0.218 | 1.560 | 2.031 | 1.129 |
| 352.50 | 0.193 | 0.708 | 0.228 | 0.739 | 1.196 | 1.082 | 3.819 | 359.49 | 0.142 | 0.284 | 0.280 | 0.620 | 1.624 | 1.855 | 1.410 |
| 352.55 | 0.246 | 0.480 | 0.328 | 0.638 | 1.344 | 1.378 | 1.456 | 362.24 | 0.267 | 0.132 | 0.566 | 0.320 | 1.612 | 1.914 | 1.335 |
| 352.55 | 0.569 | 0.269 | 0.630 | 0.348 | 1.117 | 1.340 | 1.568 | 363.49 | 0.136 | 0.235 | 0.292 | 0.560 | 1.579 | 1.810 | 1.567 |
| 352.55 | 0.843 | 0.121 | 0.843 | 0.152 | 1.009 | 1.306 | 1.480 | 366.15 | 0.244 | 0.126 | 0.545 | 0.317 | 1.519 | 1.784 | 1.286 |
| 352.57 | 0.225 | 0.528 | 0.292 | 0.670 | 1.307 | 1.312 | 1.815 | 371.67 | 0.204 | 0.109 | 0.504 | 0.300 | 1.446 | 1.684 | 1.304 |
| 352.63 | 0.275 | 0.444 | 0.362 | 0.603 | 1.326 | 1.404 | 1.430 | 372.44 | 0.119 | 0.190 | 0.288 | 0.501 | 1.390 | 1.578 | 1.349 |
| 352.65 | 0.785 | 0.155 | 0.799 | 0.193 | 1.024 | 1.286 | 1.601 | 375.77 | 0.118 | 0.178 | 0.282 | 0.456 | 1.254 | 1.409 | 1.419 |
| 352.73 | 0.731 | 0.179 | 0.758 | 0.227 | 1.041 | 1.304 | 1.988 | 375.96 | 0.181 | 0.107 | 0.464 | 0.306 | 1.335 | 1.559 | 1.225 |
| 352.73 | 0.555 | 0.283 | 0.616 | 0.359 | 1.114 | 1.307 | 1.759 | 380.40 | 0.144 | 0.096 | 0.388 | 0.270 | 1.250 | 1.376 | 1.411 |
| 352.75 | 0.203 | 0.570 | 0.260 | 0.702 | 1.288 | 1.269 | 1.875 | 387.09 | 0.115 | 0.075 | 0.330 | 0.228 | 1.133 | 1.269 | 1.300 |
| 352.75 | 0.152 | 0.790 | 0.186 | 0.784 | 1.230 | 1.021 | 5.885 | 397.75 | 0.073 | 0.054 | 0.240 | 0.169 | 1.001 | 1.025 | 1.078 |
| 352.75 | 0.848 | 0.110 | 0.853 | 0.142 | 1.009 | 1.328 | 1.344 | 402.17 | 0.045 | 0.038 | 0.179 | 0.144 | 1.099 | 1.113 | 1.004 |
| 352.79 | 0.296 | 0.399 | 0.396 | 0.568 | 1.341 | 1.463 | 1.355 | (2.25) |  |  | (0.009) | (0.012) |  |  |  |

application of the corresponding polynomials. The thermodynamic consistency of the measured vapor−liquid equilibrium data have been tested with the McDermott−Ellis method[10] to reject possible inconsistent equilibrium points. According with this test, two experimental points (a and b) are thermodynamically consistent when

$$D < D_{\max} \tag{1}$$

where $D$ is the local deviation, which is expressed as

$$D = \sum_{i=1}^{N_{\text{comp}}} [(x_{i\text{a}} + x_{i\text{b}})(\ln \gamma_{i\text{b}} - \ln \gamma_{i\text{a}})] \tag{2}$$

and $D_{\max}$ is the maximum deviation. McDermott and Ellis proposed a value of 0.01 for $D_{\max}$ if the uncertainty in the mole fraction of the liquid and vapor compositions is between +0.001 and −0.001. The maximum local deviation is not a constant, and Tamir and Wisniak[11] propose the following expression for this magnitude:

$$D_{\max} = \sum_{i=1}^{N_{\text{comp}}} (x_{i\text{a}} + x_{i\text{b}})\left(\frac{1}{x_{i\text{a}}} + \frac{1}{x_{i\text{b}}} + \frac{1}{y_{i\text{a}}} + \frac{1}{y_{i\text{b}}}\right)\Delta x + 2\sum_{i=1}^{N_{\text{comp}}} |\ln \gamma_{i\text{b}} - \ln \gamma_{i\text{a}}|\Delta x + \sum_{i=1}^{N_{\text{comp}}} (x_{i\text{a}} + x_{i\text{b}})\frac{\Delta P}{P} + \sum_{i=1}^{N_{\text{comp}}} (x_{i\text{a}} + x_{i\text{b}})B_i\left(\frac{1}{(t_\text{a} + C_i)^2} + \frac{1}{(t_\text{b} + C_i)^2}\right)\Delta t \tag{3}$$

In eq 3, $B_i$ and $C_i$ are the Antoine constants and $\Delta x$, $\Delta P$, and $\Delta t$ are the uncertainties of mole fraction, pressure, and temperature, respectively.

The experimental VLE data are given in Table 2 with values of the activity coefficients ($\gamma_i$) which were calculated with eq 4:

$$\gamma_i = \phi_i y_i P/\{\phi_i^{\text{S}} x_i P_i^{\text{S}} \exp[v_i^{\text{L}}(P - P_i^{\text{S}})/RT]\} \tag{4}$$

**Table 3. Physical Properties of the Pure Components: Critical Pressure $P_C$, Mean Gyration Radius $R_D$, Dipole Moment $\mu$, Association Parameter ETA, Critical Temperature $T_C$, Critical Compressibility Factor $Z_C$, and Antoine Parameters $A$, $B$, and $C$**

| | | | | | | | Antoine constants$^c$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| compound | $P_C$/kPa$^a$ | $R_D{}^a \times 10^{10}$/m | $\mu^a \times 10^{30}$/(C·m) | ETA$^b$ | $T_C$/K$^a$ | $Z_C{}^a$ | $A$ | $B$ | $C$ | range $T$/K |
| benzene | 4898.051 | 3.0040 | 0.00 | 0.00 | 562.16 | 0.271 | 6.32580 | 1415.800 | −25.122 | 353.15−523.15 |
| cyclohexane | 4075.292 | 3.2420 | 0.00 | 0.00 | 553.54 | 0.273 | 6.24778 | 1418.380 | −19.379 | 354.15−501.15 |
| 1-pentanol | 3879.734 | 3.6790 | 5.67 | 2.20 | 586.15 | 0.260 | 6.30736 | 1287.625 | −111.820 | 347.15−429.15 |

[a] Daubert and Danner.[14] [b] Prausnitz et al.[15] [c] Gmehling and Onken.[16]

**Table 4. Parameters of the Tamir−Wisniak and UNIQUAC Equations for Benzene + Cyclohexane + 1-Pentanol at 101.3 kPa**

| | | | |
|---|---|---|---|
| Parameters of the Tamir−Wisniak Equation | | | |
| $A_{12} = -1.11410 \times 10^1$ | $B_{12} = 8.13019 \times 10^{-1}$ | $C_{12} = 9.27084 \times 10^{-2}$ | $D_{12} = -2.35520$ |
| $A_{13} = -8.76364 \times 10^1$ | $B_{13} = 7.33202 \times 10^1$ | $C_{13} = 3.72218 \times 10^1$ | $D_{13} = -8.82297 \times 10^1$ |
| $A_{23} = -1.05836 \times 10^2$ | $B_{23} = 6.24738 \times 10^1$ | $C_{23} = 7.24165 \times 10^1$ | $D_{23} = -1.11896 \times 10^2$ |
| $E_1 = 6.98015 \times 10^1$ | $E_2 = -3.47709 \times 10^1$ | $E_3 = -2.31314 \times 10^1$ | $E_4 = 5.46241$ |
| Parameters of the UNIQUAC Equation $\Delta u_{ij}$ (cal/mol) | | | |
| $\Delta u_{12} = -193.5314$ | $\Delta u_{13} = -762.6474$ | $\Delta u_{23} = -1099.5871$ | |
| $\Delta u_{21} = 80.2221$ | $\Delta u_{31} = 436.5868$ | $\Delta u_{32} = 465.6431$ | |

where the liquid molar volume, $v_i^L$, was calculated by the Yen and Woods[12] equation and the fugacity coefficients, $\phi_i$ and $\phi_i^S$, were obtained using a value of the second virial coefficient computed by the Hayden and O'Connell method[13] to characterize the vapor phase deviation from ideal behavior. $P_i^S$ is the vapor pressure which was calculated from the Antoine equation

$$\log P_i^S\,(\mathrm{kPa}) = A - \frac{B}{T\,(\mathrm{K}) + C} \tag{5}$$

where $A$, $B$, and $C$ are fitting parameters. The properties of the pure components required to calculate $\gamma_i$ are listed in Table 3. Figure 1 gives the corresponding liquid and vapor compositions for the ternary mixture.

***Temperature Correlation.*** To obtain general parameters of the experimental measured magnitudes, the Tamir−Wisniak equation[11] was applied to correlate the boiling temperatures, which is expressed as follows:

$$T = \sum_{i=1}^{N} x_i T_i^0 + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j [A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2] + x_i x_2 x_3 [D_1 + D_2(x_1 - x_2) + D_3(x_1 - x_3) + D_4(x_2 - x_3)] \tag{6}$$

where $N$ is the number of components ($N = 3$), $T_i^0$ is the boiling temperature of every pure component, and $A_{ij}$, $B_{ij}$, $C_{ij}$, $D_{ij}$, and $E_i$ are correlation parameters, which are gathered in Table 4. The root-mean-square deviation (eq 7) for temperature from eq 6 is $\sigma = 0.5$ K.

$$\sigma(M) = \{\sum (M_{\mathrm{exptl}} - M_{\mathrm{calcd}})^2 / N_D\}^{1/2} \tag{7}$$

In this equation, $M$ is a general magnitude (as temperature, vapor phase composition, etc.) and $N_D$ is the number of experimental data. Figure 2 shows the equilibrium isotherms on the liquid-phase composition diagram calculated with eq 6. The shape of the curves indicates that the system does not exhibit azeotropic behavior out of the binary range composition of the benzene + cyclohexane mixture (unstable node and minimum azeotrope) as previously published literature data[17] show. This type of equilibrium topology leads to simple separations[18] and typical economic distillation sequences in terms of mechanical design and control requirements.

***Activity Coefficient Correlation.*** The activity coefficients play a key role in vapor−liquid equilibrium calculations because Raoult's law provides no more than a rough approximation in common nonideal mixtures. For strongly nonideal mixtures, such as solutions of alcohols, water, etc., the UNIQUAC equation[19] is likely to represent the data successfully. This equation offers three advantages: only two fitting parameters for each pair of compounds; a weaker dependence on temperature for such parameters; and the surface fraction as a primary concentration variable. This equation is applicable to a wide range of mixtures with small or large molecules and to both vapor−liquid or liquid−liquid equilibria. The fitted parameters of this model are presented in Table 4; the root-mean-square deviations of $T$ and $y_i$ are presented in Table 2, after the experimental data. In Figure 3 the corresponding residual curve map is shown where the UNIFAC model was applied to activity coefficient calculations. The capability of the solvent (1-pentanol) as an extractive agent is selectively high for cyclohexane by means of polar interactions between hydroxyl groups and Π electrons and an analogous molecular volume. At first, an adequate topology is observed only one distillation region into the composition diagram, and attending to relatively volatile values obtained from these measurements, a reverse sequence in extractive rectification is necessary (the first column with

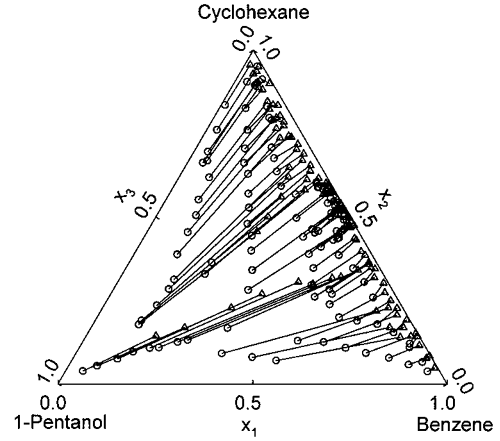

**Figure 1.** Composition (mole fractions) diagram for benzene + cyclohexane + 1-pentanol at 101.3 kPa: ○, liquid phase; △, vapor phase.

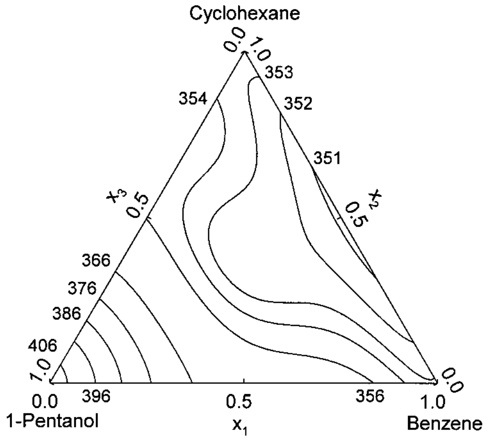

**Figure 2.** Isotherms (temperature in K) for benzene + cyclohexane + 1-pentanol at 101.3 kPa calculated with eq 6 and coefficients from Table 4.

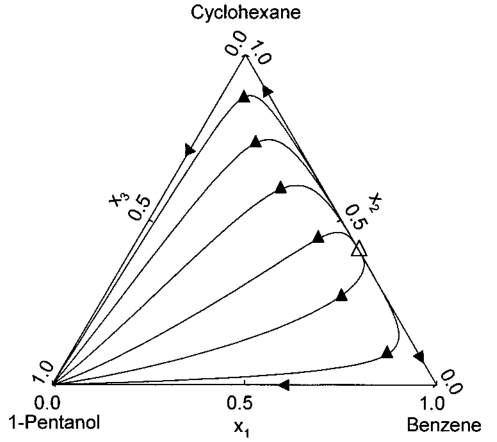

**Figure 3.** Residual curve map for benzene + cyclohexane + 1-pentanol at 101.3 kPa calculated with the UNIFAC method: △, experimental azeotrope.[17]

**Table 5. Root-Mean-Square Deviations from the ASOG, UNIFAC, UNIFAC-Dortmund, and UNIFAC-Lyngby Group Contribution Methods**

| method | $\sigma$ ($T$/K) | $\sigma(y_1)$ | $\sigma(y_2)$ | $\sigma(y_3)$ |
|---|---|---|---|---|
| ASOG | 2.24 | 0.016 | 0.021 | 0.032 |
| UNIFAC | 2.21 | 0.017 | 0.025 | 0.040 |
| UNIFAC-Dortmund | 2.64 | 0.114 | 0.062 | 0.041 |
| UNIFAC-Lyngby | 3.00 | 0.037 | 0.010 | 0.040 |

cyclohexane as the head product and the second column with benzene as the head product in the sequence). Moreover, a relatively low concentration of solvent in the extractive column will be used for high-purity separations and economical operation conditions attending to the position of the isoline $\alpha_{BC} = 1$ with respect to the cyclohexane + 1-pentanol binary mixture.

***Predictive Models.*** Prediction of vapor−liquid equilibrium for the ternary system benzene + cyclohexane + 1-pentanol at 101.3 kPa has been carried out by ASOG[20] and UNIFAC[7] and their modifications UNIFAC-Dortmund[21] and UNIFAC-Lyngby[22] group contribution methods. The group interaction parameters were those published by Tochigi et al.,[23] Hansen et al.,[24] Gmehling et al.,[25] and Larsen et al.,[22] for these methods. The results are compared with the experimental values, and the root-mean-square deviations for the temperature $\sigma(T)$ and the composition of the vapor phase $\sigma(y_i)$ are shown in Table 5. The best results are obtained by the ASOG and the original UNIFAC methods because of the simple topology and the molecular groups enclosed in these solvents.

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