# Articles

## Phase Equilibria in the Systems 1-Hexene + Benzene and 1-Hexene + Ethyl 1,1-Dimethylethyl Ether + Benzene at 94.00 kPa

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Consistent vapor−liquid equilibria data at 94.00 kPa have been determined for the ternary system 1-hexene + ethyl 1,1-dimethylethyl ether + benzene and for its constituent binary 1-hexene + benzene, in the temperature range 334−351 K. According to the experimental results, the systems exhibit slight positive deviations from ideal behavior and no azeotrope is present. The VLE data have been correlated with the mole fraction using the Redlich−Kister, Wilson, NRTL, UNIQUAC, and Tamir relations. These models, in addition to UNIFAC, allow good prediction of the VLE properties of the ternary system from those of the pertinent binary systems.

### Introduction

The use of reformulated gasoline is now required in those areas of the U.S. with the most severe ozone air pollution. As part of the reformulation process, oxygenates, such as methyl *tert*-butyl ether (MTBE) or ethanol, are added to gasoline to enhance combustion and reduce the emissions that cause ground level ozone problems as well as reduce air toxic emissions. Oxygenates have been used as octane enhancers since the late 1970s, due to the phaseout of tetraethyl lead. MTBE was introduced in the 1970s and today is the primary oxygenated compound being used to improve the octane rating of gasoline, but it has the drawbacks of easily dissolving in water and of difficult removal from water. These drawbacks are behind the recent decision by the state of California to phase out its use in the near future. It is important, then, to research the possible use of other ethers of higher molecular weights, like ethyl *tert*-butyl ether (ETBE), which may be less harmful to the environment. Among the potential oxygenates ETBE shows good characteristics for unleaded gasoline formulation, including low volatility, high-octane value, and low water solubility. Phase equilibrium data of oxygenated mixtures are important for predicting the vapor-phase concentration that would be in equilibrium with gasoline mixtures. Although aromatics such as benzene may be present in small concentrations in typical gasolines, they represent fundamental examples of mixtures of ethers with an aromatic compound. In addition, alkenes are unstable and are limited to low volume percentages, but they are used in gasoline blending in order to improve octane ratings.

Vapor−liquid equilibrium (VLE) data for the binary systems 1-hexene + ETBE and ETBE + benzene have been reported at 94 kPa by Segura et al.[1,2] These two binaries exhibit slight to moderate positive deviations from ideality and do not present azeotropes. Vapor−liquid equilibrium data for the system 1-hexene + benzene have been reported by Dojcanski et al.[3] at 298.15 K, by Lesteva et al.[4] at (293.15 and 313.15) K, and by Vera and Prausnitz[5] at (283.15, 303.15, and 323.15) K. According to these sources, the binary system 1-hexene + benzene exhibits positive deviation from ideal behavior and no azeotrope is present. The present work was undertaken to measure VLE data for the system 1-hexene + ETBE + benzene and for its constituent binary benzene + 1-hexene at 94 kPa, for which isobaric data have not been determined.

### Experimental Section

***Materials.*** ETBE (96.0+ mass %) was purchased from TCI (Tokyo Chemical Industry Co. Ltd., Japan), and 1-hexene (99.0 mass %) and benzene (99.9 mass %) were purchased from Aldrich. 1-Hexene and ETBE were further purified to more than 99.7+ mass % by rectification in a 1-m height by 30 mm diameter Normschliffgerätebau adiabatic distillation column (packed with 3 mm by 3 mm stainless steel spirals), working at a 1:100 reflux ratio. After this step, gas chromatography failed to show any significant impurity. The properties and purity (as determined by gas liquid chromatography) of the pure components appear in Table 1. Appropriate precautions were taken when handling ETBE in order to avoid peroxide formation, as well as that of benzene, a human carcinogen.

***Apparatus and Procedure.*** An all glass vapor−liquid equilibrium apparatus model 601, manufactured by Fischer Labor und Verfahrenstechnik (Germany), was used in the equilibrium determinations. In this circulation-method apparatus, the mixture is heated to its boiling point by a 250 W immersion heater. The vapor−liquid mixture flows through an extended contact line (Cottrell pump) that guarantees an intense phase exchange and then enters a separation chamber whose construction prevents an entrainment of liquid particles into the vapor phase. The

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**Table 1. Mole Percent Purities (mass %), Refractive Index, $n_D$, at the Na D Line, and Normal Boiling Points, $T$, of Pure Components**

| component (purity/mass %) | $n_D$ (293.15 K) |  | $T_b$ (101.3 kPa)/K |  |
|---|---|---|---|---|
|  | exptl | lit. | exptl | lit. |
| 1-hexene (99.7+) | 1.388 06[a] | 1.387 88[b] | 336.61[a] | 336.635[b] |
| ethyl 1,1-dimethylethyl ether (99.9+) | 1.375 94[a] | 1.375 64[c] | 345.85[a] | 345.86[d] |
| benzene (99.9+) | 1.501 13[a] | 1.501 11[e] | 353.20[a] | 353.21[e] |

[a] Measured. [b] *TRC Tables* a-2630.[17] [c] DIPPR (Daubert and Danner).[18] [d] Krähenbühl and Gmehling.[19] [e] *TRC Tables*, a-3200.[17]

**Table 2. Experimental Vapor−Liquid Equilibrium Data for the Binary System 1-Hexene (1) + Benzene (3) at 94.00 kPa**

| $T$/K | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_3$ |
|---|---|---|---|---|
| 350.76 | 0.000 | 0.000 |  | 1.000 |
| 348.80 | 0.051 | 0.111 | 1.391 | 0.997 |
| 347.69 | 0.085 | 0.170 | 1.321 | 1.000 |
| 346.20 | 0.137 | 0.251 | 1.265 | 1.004 |
| 344.84 | 0.190 | 0.322 | 1.219 | 1.012 |
| 343.80 | 0.237 | 0.376 | 1.177 | 1.023 |
| 342.92 | 0.279 | 0.425 | 1.161 | 1.027 |
| 341.90 | 0.334 | 0.479 | 1.128 | 1.042 |
| 341.08 | 0.382 | 0.525 | 1.108 | 1.052 |
| 340.46 | 0.421 | 0.559 | 1.092 | 1.064 |
| 339.71 | 0.473 | 0.601 | 1.069 | 1.085 |
| 338.90 | 0.535 | 0.651 | 1.050 | 1.106 |
| 338.08 | 0.599 | 0.701 | 1.036 | 1.130 |
| 337.55 | 0.646 | 0.736 | 1.026 | 1.150 |
| 337.04 | 0.692 | 0.772 | 1.021 | 1.162 |
| 336.41 | 0.753 | 0.816 | 1.012 | 1.195 |
| 336.02 | 0.794 | 0.847 | 1.008 | 1.208 |
| 335.53 | 0.847 | 0.886 | 1.005 | 1.232 |
| 335.10 | 0.896 | 0.922 | 1.002 | 1.259 |
| 334.68 | 0.949 | 0.962 | 1.000 | 1.269 |
| 334.27 | 1.000 | 1.000 | 1.000 |  |

**Table 3. Experimental Vapor−Liquid Equilibrium Data for the Ternary System 1-Hexene (1) + ETBE (2) + Benzene (3) at 94.00 kPa**

| $T$/K | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ |
|---|---|---|---|---|---|---|---|
| 335.33 | 0.866 | 0.080 | 0.897 | 0.062 | 1.001 | 1.016 | 1.266 |
| 336.19 | 0.763 | 0.133 | 0.815 | 0.106 | 1.004 | 1.009 | 1.234 |
| 336.97 | 0.668 | 0.235 | 0.734 | 0.191 | 1.009 | 1.004 | 1.212 |
| 337.24 | 0.628 | 0.316 | 0.696 | 0.261 | 1.007 | 1.010 | 1.228 |
| 337.37 | 0.649 | 0.123 | 0.728 | 0.100 | 1.015 | 0.988 | 1.176 |
| 337.85 | 0.567 | 0.329 | 0.643 | 0.275 | 1.013 | 1.004 | 1.194 |
| 338.39 | 0.537 | 0.236 | 0.626 | 0.199 | 1.022 | 0.992 | 1.161 |
| 338.42 | 0.555 | 0.119 | 0.653 | 0.100 | 1.030 | 0.988 | 1.137 |
| 338.73 | 0.469 | 0.431 | 0.550 | 0.371 | 1.017 | 1.003 | 1.175 |
| 339.04 | 0.423 | 0.526 | 0.500 | 0.459 | 1.016 | 1.007 | 1.180 |
| 339.34 | 0.462 | 0.215 | 0.565 | 0.186 | 1.040 | 0.986 | 1.124 |
| 339.34 | 0.438 | 0.336 | 0.530 | 0.293 | 1.029 | 0.994 | 1.142 |
| 339.61 | 0.376 | 0.523 | 0.456 | 0.463 | 1.024 | 1.003 | 1.155 |
| 339.90 | 0.440 | 0.115 | 0.556 | 0.102 | 1.057 | 0.988 | 1.097 |
| 340.27 | 0.347 | 0.432 | 0.434 | 0.388 | 1.034 | 0.997 | 1.130 |
| 340.30 | 0.370 | 0.314 | 0.468 | 0.282 | 1.045 | 0.993 | 1.114 |
| 340.60 | 0.279 | 0.613 | 0.351 | 0.560 | 1.030 | 1.002 | 1.142 |
| 340.75 | 0.357 | 0.226 | 0.466 | 0.206 | 1.062 | 0.991 | 1.093 |
| 340.82 | 0.238 | 0.708 | 0.301 | 0.653 | 1.028 | 1.006 | 1.149 |
| 341.13 | 0.265 | 0.524 | 0.342 | 0.485 | 1.041 | 0.998 | 1.116 |
| 341.19 | 0.353 | 0.112 | 0.477 | 0.104 | 1.086 | 0.996 | 1.069 |
| 341.40 | 0.273 | 0.410 | 0.361 | 0.383 | 1.057 | 0.997 | 1.095 |
| 341.50 | 0.192 | 0.698 | 0.251 | 0.657 | 1.039 | 1.003 | 1.128 |
| 341.70 | 0.273 | 0.324 | 0.369 | 0.306 | 1.068 | 0.998 | 1.083 |
| 341.92 | 0.186 | 0.612 | 0.249 | 0.583 | 1.049 | 1.002 | 1.107 |
| 342.25 | 0.267 | 0.206 | 0.377 | 0.198 | 1.099 | 1.001 | 1.060 |
| 342.34 | 0.189 | 0.500 | 0.260 | 0.483 | 1.065 | 1.002 | 1.087 |
| 342.34 | 0.090 | 0.853 | 0.120 | 0.831 | 1.039 | 1.009 | 1.130 |
| 342.37 | 0.104 | 0.795 | 0.140 | 0.773 | 1.044 | 1.008 | 1.125 |
| 342.69 | 0.188 | 0.416 | 0.265 | 0.407 | 1.082 | 1.004 | 1.073 |
| 342.77 | 0.104 | 0.707 | 0.144 | 0.695 | 1.060 | 1.006 | 1.100 |
| 342.87 | 0.253 | 0.117 | 0.375 | 0.116 | 1.130 | 1.012 | 1.042 |
| 343.29 | 0.105 | 0.590 | 0.149 | 0.591 | 1.069 | 1.008 | 1.084 |
| 343.44 | 0.176 | 0.300 | 0.262 | 0.303 | 1.117 | 1.011 | 1.051 |
| 343.72 | 0.104 | 0.502 | 0.153 | 0.512 | 1.097 | 1.012 | 1.065 |
| 344.03 | 0.170 | 0.210 | 0.263 | 0.218 | 1.142 | 1.020 | 1.038 |
| 344.51 | 0.095 | 0.390 | 0.148 | 0.411 | 1.128 | 1.018 | 1.048 |
| 344.56 | 0.173 | 0.107 | 0.282 | 0.115 | 1.183 | 1.038 | 1.021 |
| 345.02 | 0.097 | 0.299 | 0.156 | 0.323 | 1.153 | 1.027 | 1.036 |
| 345.87 | 0.093 | 0.189 | 0.161 | 0.214 | 1.202 | 1.048 | 1.018 |
| 345.98 | 0.127 | 0.057 | 0.228 | 0.066 | 1.245 | 1.071 | 1.008 |
| 346.64 | 0.089 | 0.103 | 0.165 | 0.122 | 1.256 | 1.073 | 1.007 |
| 347.33 | 0.068 | 0.092 | 0.129 | 0.113 | 1.270 | 1.085 | 1.006 |

separated gas and liquid phases are condensed and returned to a mixing chamber, where they are stirred by a magnetic stirrer, and returned again to the immersion heater. The temperature in the VLE still has been determined with a Systemteknik S1224 digital temperature meter and a Pt 100 Ω probe calibrated at the Swedish Statens Provningsanstält. The accuracy is estimated to be ±0.02 K. The total pressure of the system is controlled by a vacuum pump capable of pressures as low as 0.25 kPa. The pressure has been measured with a Fischer pressure transducer calibrated against an absolute mercury-in-glass manometer (22 mm diameter precision tubing with cathetometer reading); the overall accuracy is estimated to be ±0.03 kPa. On the average the system reaches equilibrium conditions after 2−3 h of operation. Samples, taken by syringing 1.0 μL after the system had achieved equilibrium, were analyzed by gas chromatography on a Varian 3400 apparatus provided with a thermal conductivity detector and a Thermo Separation Products model SP4400 electronic integrator. The column was 3 m long and 0.3 cm in diameter, packed with SE-30. The carrier gas was helium flowing at 26 $cm^3\ min^{-1}$. Column, injector, and detector temperatures were (323.15, 383.15, and 473.15) K, respectively, for all the systems. Very good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the mass composition of the sample. The pertinent polynomial fits had a correlation coefficient $R^2$ better than 0.99. At least three analyses were made of each composition. Concentration measurements were accurate to better than ±0.001 mole fraction.

## Results and Discussion

The temperature, $T$, and liquid-phase, $x_i$, and vapor-phase, $y_i$, mole fraction measurements at $P = 94.00$ kPa are reported in Tables 2 and 3 and in Figures 1−3, together with the activity coefficients $\gamma_i$, which were calculated from the equation (Van Ness and Abbott [6])

$$\gamma_i = \frac{P y_i}{P_i^\circ x_i} \tag{1}$$

where $P$ is the total pressure and $P_i^\circ$ is the pure component vapor pressure. In eq 1 the vapor phase is assumed to be an ideal gas and the pressure dependence of the liquid-phase fugacity is neglected. Equation 1 was selected to calculate activity coefficients because the low pressures observed in the present VLE data make these simplifications reasonable. In addition, and as discussed by Reich et al.[7] and by Aucejo et al.,[8] the scarce physical information available for mixtures of ETBE with hydrocarbons does not allow a reliable estimation of second virial coefficients, thus introducing uncertainty in the estimation of vapor-phase corrections. The temperature dependence of the pure

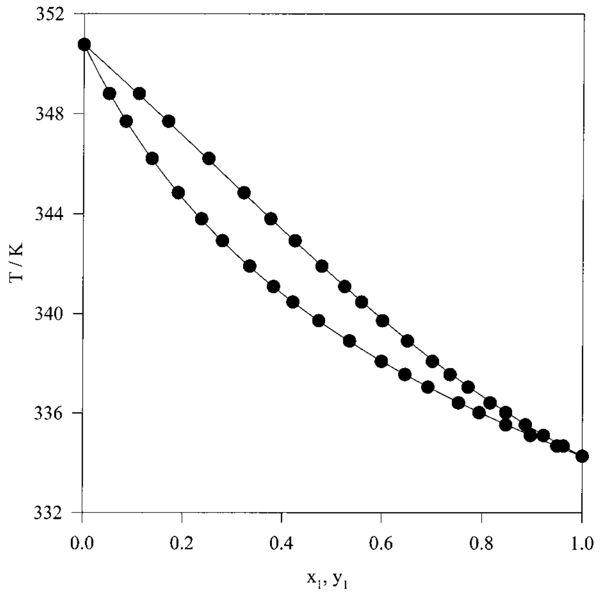

**Figure 1.** Experimental data for the system 1-hexene (1) + benzene (3) at 94.00 kPa: (●) experimental data reported in this work; (—) smoothed data using the regular model, eq 3, with the *A* parameter given in Table 5.

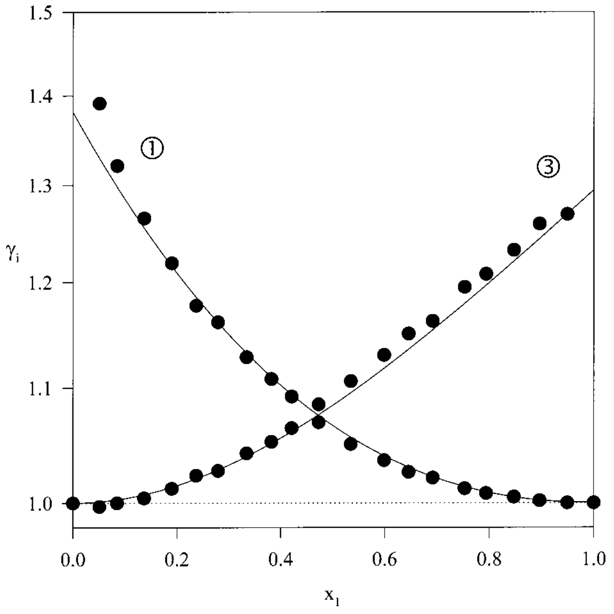

**Figure 2.** Activity coefficient plot of the system 1-hexene (1) + benzene (3) at 94.00 kPa: (●) experimental data reported in this work; (—) smoothed data using the regular model, eq 3, with the *A* parameter given in Table 5.

component vapor pressure $P_i^\circ$ was calculated using the Antoine equation

$$\log(P_i^\circ/\mathrm{kPa}) = A_i - \frac{B_i}{(T/\mathrm{K}) - C_i} \qquad (2)$$

where the Antoine constants $A_i$, $B_i$, and $C_i$ are reported in Table 4. The activity coefficients presented in Tables 2 and 3 are estimated to be accurate within ±2%. The results reported in these tables indicate that the measured systems exhibit moderate positive deviations from ideal behavior and that no azeotrope is present.

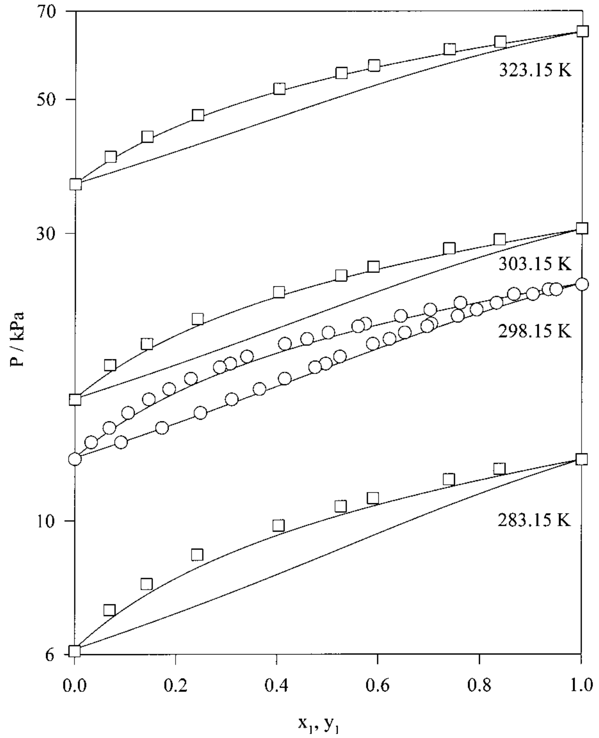

**Figure 3.** Prediction of isothermal VLE data for the system 1-hexene (1) + benzene (3): (○) experimental data of Dojcanski et al.;[3] (□) experimental data of Vera and Prausnitz;[5] (—) predicted from the model in eq 3, with the parameters given in Table 5.

**Table 4. Antoine Coefficients, Eq 2**

| compound | $A_i$ | $B_i$ | $C_i$ |
|---|---|---|---|
| 1-hexene[a] | 6.060 06 | 1189.666 | 43.18 |
| ETBE[b] | 5.966 51 | 1151.730 | 55.06 |
| benzene[c] | 6.088 17 | 1243.260 | 48.64 |

[a] Segura et al.[1] [b] Reich et al.[7] [c] Reich et al.[20]

**Table 5. Consistency Test Statistics for the Binary System 1-Hexene (1) + Benzene (3)**

| $A_0$[a] | $A_1$[a] | $100\Delta y$[b] | $\Delta P$[c]/kPa |
|---|---|---|---|
| 0.291 | −0.032 | 0.2 | 0.05 |

[a] Parameters for the Legendre polynomial in eq 3. [b] Average absolute deviation in vapor-phase mole fractions: $\Delta y = 1/N\sum_{i=1}^{N}|y_1^{\mathrm{exptl}} - y_1^{\mathrm{calc}}|$ ($N$: number of data points). [c] Average absolute deviation in pressure $\Delta P = 1/N\sum_{i=1}^{N}|P^{\mathrm{exptl}} - P^{\mathrm{calc}}|$.

The VLE data reported in Table 2 for the binary system 1-hexene (1) + benzene (3) were found to be thermodynamically consistent by the point-to-point test of Van Ness et al.,[9] as modified by Fredenslund et al.[10] Consistency criteria ($\Delta y \leq 0.01$) were met using a two-parameter Legendre polynomial, which reduces the functionality of the excess Gibbs energy $G^E$ to the relation

$$\frac{G^E}{RT} = x_1x_2(A_0 + A_1[2x_1 - 1]) \qquad (3)$$

Table 5 presents the values of parameters $A_0$ and $A_1$ and the pertinent deviations. The statistics show that eq 3 gives a very good fit of the data and a reasonable fit of the activity coefficients, as shown in Figure 2. In addition, as shown in Figure 3, the model in eq 3 with the parameters given in Table 5 allows a fair prediction of the isothermal data reported by Dojcanski et al.[3] and by Vera and Prausnitz.[5]

The vapor−liquid equilibrium data reported in Table 3 for the ternary system 1-hexene + ETBE (1) + benzene (3) were found to be thermodynamically consistent by the

**Table 6. Constants for the Redlich−Kister Model, Fit, Correlation, and Prediction Statistics**

Binary Data

| system | $10b_{ij}$ | $10c_{ij}$ | $d_{ij}$ | rmsd[a] × $10^{-2}$ | % dev[b] | max % dev[c] |
|---|---|---|---|---|---|---|
| 1-hexene (1) + ETBE (2)[d] | 0.45 | 0.00 | 0.00 | 0.9 | 0.5 | 3.6 |
| 1-hexene (1) + benzene (3)[e] | 2.91 | −0.32 | 0.00 | 1.0 | 0.5 | 4.4 |
| ETBE (2) + benzene (3) | 1.46 | 0.00 | 0.00 | 1.2 | 0.9 | 5.2 |

Ternary Data

| $\gamma_1/\gamma_2$ | | | $\gamma_1/\gamma_3$ | | |
|---|---|---|---|---|---|
| rmsd | max % dev | % dev | rmsd | max % dev | % dev |
| 2 × $10^{-2}$ | 2.4 | 1.2 | 1 × $10^{-2}$ | 1.5 | 0.8 |

VLE Correlations and Predictions

| | bubble-point pressures | | | dew-point pressures | | |
|---|---|---|---|---|---|---|
| system | $\Delta P$[f]/% | $100\Delta y_1$[g] | $100\Delta y_2$ | $\Delta P$/% | $100\Delta x_1$ | $100\Delta x_2$ |
| 1 + 2[d] | 0.09 | 0.1 | 0.1 | 0.12 | 0.1 | 0.1 |
| 1 + 3[e] | 0.05 | 0.2 | | 0.05 | 0.2 | |
| 2 + 3 | 0.11 | | 0.3 | 0.10 | | 0.3 |
| 1 + 2 + 3[h] | 0.34 | 0.1 | 0.2 | 0.32 | 0.1 | 0.2 |

[a] Root-mean-square deviation in activity coefficients $\{\sum_i^N\{\gamma_i^{\text{exptl}} - \gamma_i^{\text{calc}}\}^2/N\}^{0.5}$ ($N$: number of data points). [b] Average percentage deviation in activity coefficients. [c] Maximum percentage deviation in activity coefficients. [d] Calculated from the data of Segura et al.[1] [e] Calculated from the data of Segura et al.[2] [f] Average percentage deviation in pressure $\Delta P = 100/\mathrm{N}\sum_i^N|P_i^{\text{exptl}} - P_i^{\text{calc}}|/P_i^{\text{exptl}}$. [g] Average absolute deviation in mole fraction $\Delta y = 1/N\sum_i^N|y_i^{\text{exptl}} - y_i^{\text{calc}}|$. [h] Prediction from binary parameters.

McDermott−Ellis method,[11] as modified by Wisniak and Tamir.[12] According to these references, two experimental points *a* and *b* are considered thermodynamically consistent if the following condition is fulfilled

$$D < D_{\max} \tag{4}$$

where the local deviation $D$ is given by

$$D = \sum_{i=1}^{N}(x_{ia} - x_{ib})(\ln \gamma_{ia} - \ln \gamma_{ib}) \tag{5}$$

and $N$ is the number of components. The maximum deviation $D_{\max}$ is given by

$$D = \sum_{i=1}^{N}(x_{ia} - x_{ib})\left(\frac{1}{x_{ia}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ib}}\right)\Delta x + \sum_{i=1}^{N}(x_{ia} - x_{ib})\frac{\Delta P}{P} + 2\sum_{i=1}^{N}|\ln \gamma_{ib} - \ln \gamma_{ia}|\Delta x + \sum_{i=1}^{N}(x_{ia} - x_{ib})B_j\{(T_a + C_j)^{-2} + (T_b + C_j)^{-2}\}\Delta T \tag{6}$$

The errors in the measurements $\Delta x$, $\Delta P$, and $\Delta T$ were as previously indicated. The first term in eq 6 was the dominant one. For the experimental points reported here, $D$ never exceeded 0.020 while the smallest value of $D_{\max}$ was 0.024.

The activity coefficients for the ternary system were correlated with the Redlich−Kister expansion[13]

$$\frac{G^{\mathrm{E}}}{RT} = \sum_{i=1}^{3}\sum_{j>i}^{3}x_ix_j[b_{ij} + c_{ij}(x_i - x_j) + d_{ij}(x_i - x_j)^2] + x_1x_2x_3[C + D_1x_1 + D_2x_2] \tag{7}$$

where $b_{ij}$, $c_{ij}$, and $d_{ij}$ are the constants for the pertinent *ij* binary and $C$, $D_1$, and $D_2$ are ternary constants. All the constants in eq 7 are assumed to be independent of the temperature. Data and constants for the binary system 1-hexene (1) + ETBE (2) and ETBE (2) + benzene (3) have been calculated from the data reported by Segura et al.[1,2] The Redlich−Kister coefficients for the binaries 1-hexene (1) + benzene (2) and the values of the constants $C$, $D_1$, and $D_2$ for the ternary mixture were obtained by a Simplex optimization technique; the results are shown in Table 6. Analysis of the correlation indicated that the binary constant $d_{13}$ is negligible, which is consistent with the previous discussion about eq 3. In addition, the ternary constants $C$, $D_1$, and $D_2$ were not statistically significant, suggesting that the ternary data can be predicted directly from the binary systems. In fact, activity coefficients and equilibrium vapor pressures of the ternary system were predicted very well by the Redlich−Kister equation when using only the binary constants, as shown in Table 6, where $C$, $D_1$, and $D_2$ are zero. Equilibrium vapor pressures and VLE mole fractions were also predicted well for the ternary system using the NRTL, Wilson, and UNIQUAC models (Walas[14]) but somewhat worse by the UNIFAC model (Fredenslund et al.;[10] Hansen et al.[15]) using parameters

**Table 7. Parameters and Correlation and Prediction Statistics for Different $G^{\mathrm{E}}$ Models**

| | | $a_{ij}$ | $a_{ji}$ | $\alpha_{ij}$ | bubble-point pressures | | | dew-point pressures | | |
|---|---|---|---|---|---|---|---|---|---|---|
| model | *ij* | J·mol$^{-1}$ | J·mol$^{-1}$ | | $\Delta P$[f]/% | $100\Delta y_1$[g] | $100\Delta y_2$ | $\Delta P$/% | $100\Delta x_1$ | $100\Delta x_2$ |
| NRTL | 1 + 2[d] | −1139.22 | 1433.47 | 0.3 | 0.05 | 0.1 | 0.1 | 0.05 | 0.1 | 0.1 |
| | 1 + 3[e] | −857.26 | 1929.35 | 0.3 | 0.12 | 0.1 | | 0.16 | 0.1 | |
| | 2 + 3 | 92.84 | 314.46 | 0.3 | 0.14 | | 0.2 | 0.18 | | 0.2 |
| | 1 + 2 + 3[h] | | | | 0.34 | 0.1 | 0.2 | 0.33 | 0.1 | 0.2 |
| Wilson[a] | 1 + 2[d] | −78.13 | 208.22 | | 0.12 | 0.1 | 0.1 | 0.13 | 0.1 | 0.1 |
| | 1 + 3[e] | 389.30 | 639.39 | | 0.09 | 0.1 | | 0.14 | 0.1 | |
| | 2 + 3 | 320.98 | 341.04 | | 0.27 | | 0.1 | 0.27 | | 0.1 |
| | 1 + 2 + 3[h] | | | | 0.19 | 0.1 | 0.1 | 0.20 | 0.1 | 0.1 |
| UNIQUAC[b] | 1 + 2[d] | −146.16 | 175.08 | | 0.11 | 0.1 | 0.1 | 0.12 | 0.1 | 0.1 |
| | 1 + 3[e] | 436.95 | −200.41 | | 0.13 | 0.1 | | 0.16 | 0.1 | |
| | 2 + 3 | 31.50 | −20.96 | | 0.30 | | 0.1 | 0.29 | | 0.1 |
| | 1 + 2 + 3[h] | | | | 0.24 | 0.1 | 0.1 | 0.27 | 0.1 | 0.1 |
| UNIFAC[c] | 1 + 2 + 3[h] | | | | 2.17 | 1.3 | 0.7 | 1.65 | 1.2 | 0.5 |

[a] Liquid volumes have been estimated from the Rackett equation,[21] with critical parameters taken from ref 18. [b] Molecular parameters are those calculated from UNIFAC.[10] [c] Calculations based on original UNIFAC.[11,15] [d] Data of Segura et al.[1] [e] Data of Segura et al.[2] [f] Average percentage deviation in pressure: $\Delta P = 100/N\sum_i^N|P_i^{\text{exptl}} - P_i^{\text{calc}}|/P_i^{\text{exptl}}$ ($N$: number of data points). [g] Average absolute deviation in mole fraction: $\Delta y = 1/N\sum_i^N|y_i^{\text{exptl}} - y_i^{\text{calc}}|$. [h] Ternary prediction from binary parameters.

**Table 8. Coefficients in Correlation of Boiling Points, Eq 8, Average Deviation, and Root Mean Square Deviations in Temperature**

| $ij$ | $A_{ij}$ | $B_{ij}$ | $C_{ij}$ | max dev[a]/K | avg dev[b]/K | rmsd[c] |
|---|---|---|---|---|---|---|
| 1 + 2[d] | −2.2840 | 0.7668 | −1.5695 | | | |
| 1 + 3 | −12.0483 | 6.2992 | −3.1669 | 0.08 | 0.03 | 0.03 |
| 2 + 3 | −4.4788 | 1.0899 | −3.4706 | | | |

[a] Maximum deviations. [b] Average deviations. [c] rmsd ($T$/K): Root-mean-square deviation, $\{\sum(T_{\mathrm{exptl}} - T_{\mathrm{calc}})^2/N\}^{0.5}$.

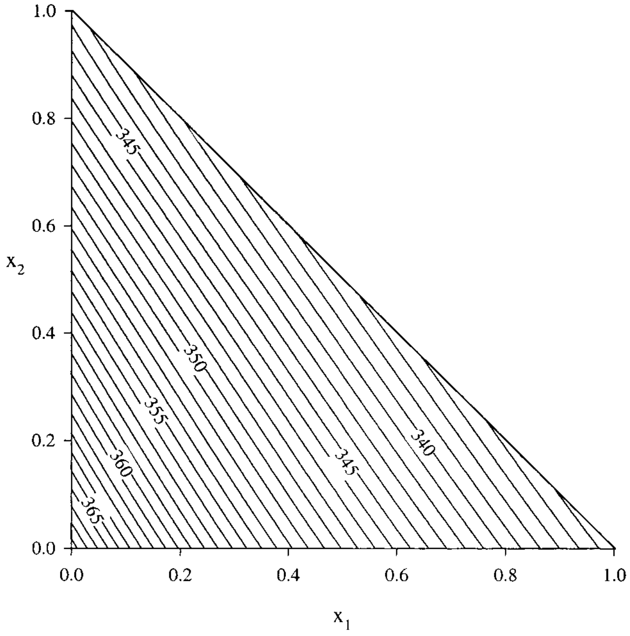

**Figure 4.** Boiling temperatures for the ternary system 1-hexene (1) + ETBE (2) + benzene (3) at 94.00 kPa: (—) smoothed with eq 8 and the coefficients given in Table 8.

previously fitted to the binaries. Table 7 reports results of the pertinent bubble-point pressure and dew-point pressure calculations, together with statistics and parameters. From these results it can be concluded again that the binary contributions allow a good prediction of the ternary system.

The boiling points of the systems were correlated by the equation proposed by Tamir[16]

$$T/\mathrm{K} = \sum_{i=1}^{3} x_i T_i^\circ + x_1x_2[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2 + ...] + x_1x_3[A_{13} + B_{13}(x_1 - x_3) + C_{13}(x_1 - x_3)^2 + ...] + x_2x_3[A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2 + ...] \quad (8)$$

where the coefficients $A_{ij}$, $B_{ij}$, and $C_{ij}$ are multicomponent parameters determined directly from the data. The various constants of eq 8 are reported in Table 8, together with information regarding the quality of the correlation. In addition, Figure 4 shows the isotherms of the ternary system as calculated from eq 8. Inspection of Figure 4 reveals that no stationary point appears in boiling temperature, indicating that the ternary system is not azeotropic.

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