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# Phase Equilibria in the Ternary System Methyl 1,1-Dimethylethyl Ether + Hexane + Octane

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Vapor−liquid equilibrium at 94 kPa has been determined for the ternary system methyl 1,1-dimethylethyl ether (MTBE) + hexane + octane. The system deviates positively from ideality, and no azeotrope is present. The ternary activity coefficients and the boiling points of the system have been correlated with the composition using the Redlich−Kister, Wilson, NRTL, UNIQUAC, UNIFAC, and Wisniak−Tamir relations. Most of the models allow a very good prediction of the activity coefficients of the ternary system from those of the pertinent binary systems.

## Introduction

Ethers are usually added to gasolines in order to improve their combustion and reduce pollution; the commonly used oxygenating additives are methyl 1,1-dimethylethyl ether (MTBE), methanol, and ethanol. MTBE is the primary oxygenated compound being used to improve the octane rating and pollution-reducing capability of gasolines. Phase-equilibrium data of oxygenated mixtures are important for predicting the vapor-phase composition that would be in equilibrium with hydrocarbon mixtures, and the system reported here constitutes an example of such mixtures. Vapor−liquid equilibrium data for the two binary systems methyl 1,1-dimethylethyl ether + hexane and methyl 1,1-dimethylethyl ether + octane have already been reported at 94 kPa by Wisniak et al. (1997, 1998), and the two systems present slight to moderate positive deviations from ideality and do not have azeotropic points. Vapor−liquid equilibrium data for the system hexane + octane have been reported by Leslie and Carr (1925) at (12.3, 19.9, 31.1, 47.3, 70.1, and 101.325) kPa, by Kirss et al. (1975) at 328.1 K and by Li et al. (1990) and Weigno et al. (1990) at 298.1 K. According to the data of the last two reports, the system behaves essentially ideal. The present work was undertaken to measure vapor−liquid equilibrium (VLE) data for the ternary system for which no data are available.

## Experimental Section

***Chemicals.*** Methyl *tert*-butyl ether (99.93 mass %), hexane (99.57 mass %), and octane (99.80 mass %) were purchased from Aldrich. The reagents were used without further purification after gas chromatography failed to show any significant impurities. The properties and purity (as determined by GLC) of the pure components appear in Table 1.

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

| component (purity/mass %) | $n_D$ (298.15 K) | *T*/K |
|---|---|---|
| methyl 1,1-dimethylethyl ether (99.93) | 1.3661[a] | 328.29[a] |
| | 1.3663[b] | 328.35[b] |
| hexane (99.57) | 1.3730[a] | 341.84[a] |
| | 1.37226[c] | 341.89[c] |
| octane (99.8) | 1.3948[a] | 398.50[a] |
| | 1.39512[d] | 398.83[d] |

[a] Measured. [b] TRC Tables, a-6040. [c] TRC Tables, fa-1460. [d] TRC Tables, fa-1490. [e] TRC Tables, k-1490.

***Apparatus and Procedure.*** An all-glass vapor−liquid equilibrium apparatus model 602, manufactured by Fischer Labor-und Verfahrenstechnik (Germany), was used in the equilibrium determinations. In this circulation method apparatus, about 100 mL of the solution is heated to its boiling point by a 250-W immersion heater (Cottrell pump). The vapor−liquid mixture flows through an extended contact line 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 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. Temperature control is achieved by a Lauda thermometer, model R42/2, provided with a 4-mm diameter Pt-100 temperature sensor, with an accuracy of 0.01 K. The total pressure of the system is controlled by a vacuum pump capable of working under pressures down to 0.25 kPa. The pressure is measured by a Vac Probs pressure transducer with an accuracy of 0.1 kPa. On the average the system reaches equilibrium conditions after 0.5−1 h of operation. Samples, taken by syringing 0.7 $\mu$L after the system had achieved equilibrium, were analyzed by gas chromatography on a Gow-Mac series 550P apparatus provided with a thermal conductivity detector and a Spectra Physics model SP 4290 electronic integrator. The column was 3 m long and 0.2 cm in diameter, packed with SE-30. The column, injector, and detector temperatures were (338.15, 493.15, and 543.15) K. Very good separation was achieved under these conditions, and calibration analyses using synthetic mixtures were carried out to convert the peak ratio to the mass composition of the

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**Table 2. Experimental Vapor−Liquid Equilibria Data for Methyl 1,1-Dimethylethyl Ether (1) + Hexane (2) + Octane (3) at 94 KPa**

| experimental data | | | | | activity coefficients | | | virial coefficients/cm$^3$·mol$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $T$/K | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ | $-B_{11}$ | $-B_{22}$ | $-B_{33}$ | $-B_{12}$ | $-B_{13}$ | $-B_{23}$ |
| 328.20 | 0.844 | 0.106 | 0.905 | 0.089 | 0.986 | 1.204 | 1.150 | 1125 | 1459 | 3163 | 1265 | 1799 | 2107 |
| 328.94 | 0.820 | 0.094 | 0.917 | 0.074 | 1.004 | 1.103 | 1.100 | 1125 | 1450 | 3139 | 1258 | 1787 | 2093 |
| 329.23 | 0.779 | 0.151 | 0.864 | 0.128 | 0.987 | 1.176 | 1.114 | 1125 | 1447 | 3130 | 1255 | 1783 | 2087 |
| 331.65 | 0.662 | 0.227 | 0.789 | 0.198 | 0.984 | 1.115 | 1.078 | 1104 | 1418 | 3055 | 1231 | 1746 | 2042 |
| 333.10 | 0.481 | 0.450 | 0.599 | 0.393 | 0.984 | 1.068 | 0.965 | 1092 | 1401 | 3012 | 1217 | 1724 | 2016 |
| 333.21 | 0.754 | 0.011 | 0.962 | 0.010 | 1.004 | 1.109 | 0.990 | 1092 | 1400 | 3008 | 1216 | 1723 | 2014 |
| 333.90 | 0.697 | 0.070 | 0.906 | 0.065 | 1.001 | 1.113 | 1.010 | 1086 | 1392 | 2988 | 1210 | 1713 | 2001 |
| 334.10 | 0.555 | 0.284 | 0.718 | 0.264 | 0.991 | 1.101 | 0.894 | 1084 | 1390 | 2982 | 1208 | 1710 | 1998 |
| 334.30 | 0.647 | 0.140 | 0.837 | 0.134 | 0.985 | 1.127 | 1.080 | 1083 | 1388 | 2976 | 1206 | 1707 | 1994 |
| 334.51 | 0.625 | 0.168 | 0.826 | 0.150 | 1.000 | 1.044 | 0.931 | 1081 | 1386 | 2970 | 1204 | 1704 | 1991 |
| 334.77 | 0.477 | 0.373 | 0.641 | 0.340 | 1.009 | 1.057 | 0.984 | 1079 | 1383 | 2963 | 1202 | 1700 | 1986 |
| 334.83 | 0.397 | 0.504 | 0.537 | 0.451 | 1.014 | 1.035 | 0.939 | 1079 | 1382 | 2961 | 1201 | 1699 | 1985 |
| 334.87 | 0.441 | 0.435 | 0.598 | 0.387 | 1.015 | 1.028 | 0.936 | 1078 | 1382 | 2960 | 1201 | 1699 | 1984 |
| 334.95 | 0.700 | 0.020 | 0.944 | 0.019 | 1.007 | 1.096 | 1.021 | 1078 | 1381 | 2957 | 1200 | 1698 | 1983 |
| 334.97 | 0.613 | 0.145 | 0.832 | 0.140 | 1.013 | 1.110 | 0.918 | 1077 | 1380 | 2957 | 1200 | 1697 | 1983 |
| 335.58 | 0.436 | 0.410 | 0.597 | 0.385 | 1.004 | 1.061 | 0.878 | 1073 | 1374 | 2939 | 1194 | 1689 | 1972 |
| 336.35 | 0.252 | 0.686 | 0.372 | 0.620 | 1.058 | 0.996 | 0.996 | 1067 | 1365 | 2917 | 1187 | 1678 | 1959 |
| 336.60 | 0.660 | 0.030 | 0.932 | 0.028 | 1.004 | 1.022 | 0.932 | 1065 | 1362 | 2910 | 1185 | 1674 | 1954 |
| 336.65 | 0.309 | 0.581 | 0.445 | 0.542 | 1.023 | 1.019 | 0.881 | 1064 | 1362 | 2909 | 1185 | 1674 | 1954 |
| 336.70 | 0.335 | 0.533 | 0.481 | 0.502 | 1.020 | 1.026 | 0.944 | 1064 | 1361 | 2907 | 1184 | 1673 | 1953 |
| 336.86 | 0.212 | 0.738 | 0.320 | 0.673 | 1.066 | 0.990 | 0.996 | 1063 | 1360 | 2903 | 1183 | 1671 | 1950 |
| 338.02 | 0.398 | 0.374 | 0.591 | 0.379 | 1.013 | 1.061 | 0.895 | 1054 | 1347 | 2871 | 1172 | 1655 | 1930 |
| 340.13 | 0.509 | 0.130 | 0.812 | 0.134 | 1.024 | 1.015 | 0.924 | 1038 | 1325 | 2813 | 1154 | 1626 | 1895 |
| 340.30 | 0.097 | 0.814 | 0.168 | 0.818 | 1.106 | 0.981 | 0.981 | 1036 | 1323 | 2809 | 1152 | 1624 | 1893 |
| 340.50 | 0.350 | 0.342 | 0.575 | 0.380 | 1.043 | 1.079 | 0.900 | 1035 | 1321 | 2804 | 1151 | 1621 | 1889 |
| 340.55 | 0.137 | 0.735 | 0.236 | 0.745 | 1.091 | 0.982 | 0.930 | 1034 | 1321 | 2802 | 1150 | 1621 | 1889 |
| 340.65 | 0.553 | 0.020 | 0.911 | 0.023 | 1.041 | 1.112 | 0.949 | 1034 | 1320 | 2800 | 1149 | 1619 | 1887 |
| 341.10 | 0.204 | 0.601 | 0.345 | 0.625 | 1.056 | 0.991 | 0.921 | 1030 | 1315 | 2788 | 1145 | 1613 | 1880 |
| 341.45 | 0.364 | 0.334 | 0.589 | 0.367 | 0.999 | 1.037 | 0.865 | 1028 | 1311 | 2779 | 1142 | 1609 | 1874 |
| 342.30 | 0.275 | 0.435 | 0.470 | 0.480 | 1.031 | 1.015 | 0.989 | 1022 | 1303 | 2757 | 1135 | 1598 | 1861 |
| 343.30 | 0.348 | 0.294 | 0.590 | 0.347 | 0.994 | 1.052 | 0.979 | 1014 | 1293 | 2731 | 1127 | 1585 | 1845 |
| 343.95 | 0.318 | 0.292 | 0.570 | 0.362 | 1.032 | 1.086 | 0.938 | 1010 | 1286 | 2714 | 1121 | 1576 | 1835 |
| 344.30 | 0.146 | 0.595 | 0.282 | 0.670 | 1.101 | 0.976 | 0.982 | 1007 | 1283 | 2706 | 1118 | 1572 | 1829 |
| 345.15 | 0.435 | 0.099 | 0.789 | 0.130 | 1.009 | 1.111 | 0.896 | 1001 | 1274 | 2684 | 1111 | 1561 | 1816 |
| 346.53 | 0.436 | 0.032 | 0.847 | 0.043 | 1.041 | 1.092 | 1.010 | 991 | 1261 | 2651 | 1100 | 1544 | 1796 |
| 347.50 | 0.274 | 0.260 | 0.545 | 0.360 | 1.038 | 1.093 | 0.958 | 985 | 1252 | 2627 | 1093 | 1532 | 1781 |
| 348.33 | 0.129 | 0.508 | 0.275 | 0.645 | 1.088 | 0.979 | 1.003 | 979 | 1244 | 2607 | 1086 | 1522 | 1769 |
| 350.93 | 0.115 | 0.452 | 0.270 | 0.630 | 1.118 | 0.998 | 0.954 | 962 | 1220 | 2547 | 1066 | 1492 | 1732 |
| 351.98 | 0.340 | 0.070 | 0.749 | 0.105 | 1.019 | 1.039 | 0.989 | 955 | 1210 | 2523 | 1058 | 1480 | 1717 |
| 352.35 | 0.228 | 0.211 | 0.520 | 0.343 | 1.045 | 1.119 | 0.959 | 952 | 1207 | 2515 | 1055 | 1475 | 1712 |
| 353.73 | 0.103 | 0.402 | 0.256 | 0.620 | 1.100 | 1.022 | 0.935 | 943 | 1194 | 2485 | 1045 | 1460 | 1693 |
| 356.20 | 0.071 | 0.402 | 0.188 | 0.667 | 1.100 | 1.028 | 0.940 | 928 | 1173 | 2431 | 1027 | 1432 | 1660 |
| 357.25 | 0.189 | 0.173 | 0.495 | 0.321 | 1.058 | 1.117 | 0.950 | 921 | 1164 | 2409 | 1019 | 1421 | 1646 |
| 359.11 | 0.081 | 0.320 | 0.238 | 0.575 | 1.134 | 1.029 | 0.963 | 910 | 1148 | 2371 | 1006 | 1401 | 1622 |
| 360.25 | 0.231 | 0.036 | 0.680 | 0.076 | 1.103 | 1.174 | 0.989 | 903 | 1139 | 2348 | 998 | 1389 | 1608 |
| 364.35 | 0.191 | 0.038 | 0.610 | 0.085 | 1.084 | 1.119 | 1.022 | 879 | 1106 | 2268 | 971 | 1348 | 1558 |
| 365.99 | 0.122 | 0.120 | 0.415 | 0.283 | 1.110 | 1.131 | 0.974 | 870 | 1093 | 2237 | 960 | 1332 | 1538 |
| 369.55 | 0.149 | 0.040 | 0.530 | 0.098 | 1.068 | 1.076 | 0.999 | 850 | 1066 | 2173 | 937 | 1298 | 1498 |
| 378.85 | 0.064 | 0.064 | 0.289 | 0.198 | 1.103 | 1.089 | 0.958 | 801 | 1001 | 2017 | 882 | 1216 | 1399 |
| 390.90 | 0.016 | 0.019 | 0.090 | 0.072 | 1.074 | 1.023 | 0.996 | 745 | 925 | 1840 | 817 | 1120 | 1285 |

sample. The pertinent polynomial fits had a correlation coefficient $R^2$ better than 0.99. Concentration measurements were accurate to better than 0.005 mole fraction.

## Results

The temperature $T$ and liquid-phase $x_i$ and vapor-phase $y_i$ mole fraction measurements at $P = 94$ kPa are reported in Table 2, together with the activity coefficients $\gamma_i$, which were calculated from the following equation (Van Ness and Abbott, 1982)

$$\ln \gamma_i = \ln\left(\frac{Py_i}{P_i^0 x_i}\right) + \frac{(B_{ii} - V_i^{\mathrm{L}})(P - P_i^0)}{RT} + \frac{P}{2RT}\sum\sum y_j y_k (2\delta_{ji} - \delta_{jk}) \tag{1}$$

where $T$ and $P$ are the boiling point and the total pressure, $V_i^{\mathrm{L}}$ is the molar liquid volume of component $i$, $P_i^0$ is the pure component vapor pressure, $B_{ii}$ and $B_{jj}$ are the second virial coefficients of the pure gases, $B_{ij}$ is the cross second virial coefficient, and

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \tag{2}$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. The pure component vapor pressures $P_i^0$

**Table 3. Antoine Coefficients, Eq 3**

| compound | $A_i$ | $B_i$ | $C_i$ |
|---|---|---|---|
| methyl 1,1-dimethylethyl ether[a] | 5.860 78 | 1032.988 | 59.876 |
| hexane[b] | 6.000 91 | 1171.170 | 48.740 |
| octane[a] | 6.051 41 | 1354.107 | 63.888 |

[a] Reich et al. (1998). [b] TRC Tables, k-1490.

**Table 4. Constants for the Redlich–Kister Model**

A. Binaries

| system | $b_{ij} \times 10^2$ | $c_{ij} \times 10^2$ | $d_{ij} \times 10^2$ | rmsd | % dev[a] | max % dev[b] |
|---|---|---|---|---|---|---|
| MTBE (1) + hexane (2)[c] | 8.36 | 0.28 | 0.00 | 0.004 | 1.3 | 2.8 |
| MTBE (1) + octane (2)[d] | 4.61 | 0.07 | 0.00 | 0.007 | 2.6 | 4.7 |
| hexane (2) + octane (3)[e] | 0.00 | 0.00 | 0.00 | | | |

B. Ternary

| | | | | $\gamma_1/\gamma_2$ | | | $\gamma_1/\gamma_3$ | | |
|---|---|---|---|---|---|---|---|---|---|
| system | $C \times 10^2$ | $D_1 \times 10^2$ | $D_2 \times 10^2$ | rmsd × $10^3$ | max dev/% | dev/% | rmsd × $10^3$ | max dev/% | dev/% |
| MTBE (1) | 0 | 0 | 0 | 8.0 | 9.7 | 4.7 | 9.0 | 10.3 | 4.9 |
| + hexane (2) | 3.546 | 0 | 0 | 8.0 | 9.6 | 4.6 | 9.0 | 10.9 | 4.9 |
| + octane (3) | 7.588 | −11.944 | 0 | 7.0 | 9.4 | 4.3 | 9.0 | 11.3 | 5.0 |
| | −2.721 | −0.263 | 21.49 | 7.0 | 9.3 | 4.3 | 9.0 | 11.6 | 5.1 |

[a] Percent average deviation. [b] Maximum percent deviation. [c] Wisniak et al. (1997a). [d] Wisniak et al. (1997b). [e] Calculated assuming ideal behavior in the liquid phase.

**Table 5. Parameters and Prediction Statistics for Different $G^E$ Models**

| | | | | | bubble-point pressures | | | dew-point pressures | | |
|---|---|---|---|---|---|---|---|---|---|---|
| model | ij | $A_{ij}$/J mol$^{-1}$ | $A_{ij}$/J mol$^{-1}$ | $\alpha_{ij}$ | $\Delta P$(%) | $\Delta y_1$ | $\Delta y_2$ | $\Delta P$(%) | $\Delta x_1$ | $\Delta x_2$ |
| Redlich–Kister[a] | | | | | 2.50 | 0.0103 | 0.0100 | 1.45 | 0.0108 | 0.0114 |
| | 1–2 | 259.30 | 353.35 | 0.358 | | | | | | |
| NRTL | 1–3 | −1150.49 | 1503.98 | 0.300 | 2.14 | 0.0065 | 0.0079 | 2.22 | 0.0074 | 0.0083 |
| | 2–3 | 0.00 | 0.00 | | | | | | | |
| | 1–2 | 901.71 | −244.70 | | | | | | | |
| Wilson[b] | 1–3 | 1879.95 | −1558.65 | | 2.20 | 0.0064 | 0.0077 | 2.28 | 0.0073 | 0.0080 |
| | 2–3 | 207.75 | −192.35 | | | | | | | |
| | 1–2 | 51.36 | 131.29 | | | | | | | |
| UNIQUAC[c] | 1–3 | −774.74 | 982.98 | | 2.22 | 0.0048 | 0.0052 | 1.72 | 0.0062 | 0.0060 |
| | 2–3 | 0.00 | 0.00 | | | | | | | |
| UNIFAC[d] | | | | | 4.31 | 0.0163 | 0.0168 | 4.62 | 0.0138 | 0.0147 |

[a] Parameters have been included in Table 4. [b] Liquid volumes have been estimated from the Rackett equation. [c] Molecular parameters are those calculated from UNIFAC. [d] Calculations based on modified UNIFAC (Larsen, 1987).

were calculated according to the Antoine equation

$$\log (P_i^0/\mathrm{kPa}) = A_i - \frac{B_i}{(T/\mathrm{K}) - C_i} \qquad (3)$$

where the Antoine constants $A_i$, $B_i$, and $C_i$ are reported in Table 3. The molar virial coefficients $B_{ii}$ and $B_{ij}$ were estimated by the method of Hayden and O'Connell (1975) assuming the association parameter $\eta$ to be negligible. Critical properties of the pure components were taken from DIPPR (Daubert and Danner, 1989). The last two terms in eq 1 contributed less than 7% to the activity coefficients, and their influence was important only at very dilute concentrations. The ternary activity coefficients reported in Table 2 are estimated accurate to within 3% and were found to be thermodynamically consistent as tested by the $L-W$ method of Wisniak (1993) and the McDermot–Ellis method (1965) modified by Wisniak and Tamir (1977). According to these references two experimental points $a$ and $b$ are considered thermodynamically consistent if the following condition is fulfilled:

$$D < D_{\max} \qquad (4)$$

Details of the calculation procedure of $D$ and $D_{\max}$ appear in a previous publication (Wisniak, 1996). For the experimental points reported here, $D$ never exceeded 0.145 while the smallest value of $D_{\max}$ was 0.184.

The activity coefficients for the ternary system were correlated from the following Redlich–Kister expansion (1948):

$$\begin{aligned}\frac{G^E}{RT} = {} & x_1x_2[b_{12} + c_{12}(x_1 - x_2) + d_{12}(x_1 - x_2)^2] + \\ & x_1x_3[b_{13} + c_{13}(x_1 - x_3) + d_{13}(x_1 - x_3)^2] + \\ & x_2x_3[b_{23} + c_{23}(x_2 - x_3) + d_{23}(x_2 - x_3)^2] + \\ & x_1x_2x_3(C + D_1x_1 + D_2x_2) \qquad (5)\end{aligned}$$

The following relationships can be derived from from eq 5

$$\begin{aligned}\ln \frac{\gamma_1}{\gamma_2} = {} & (b_{13} - b_{23})x_3 + (b_{12} + Cx_3)(x_2 - x_1) - \\ & c_{13}x_3(x_3 - 2x_1) + c_{12}[2x_1x_2 - (x_1 - x_2)^2] - \\ & c_{23}x_3(2x_2 - x_3) + D_1x_1x_3(2x_2 - x_1) - \\ & d_{13}x_3(x_3 - 3x_1)\,(x_1 - x_3) + D_2x_3x_2(x_2 - 2x_1) + \\ & d_{12}(x_2 - x_1)[(x_2 - x_1)^2 - 4x_1x_2] - \\ & d_{23}x_3(x_2 - x_3)\,(3x_2 - x_3) \qquad (6)\end{aligned}$$

$$\begin{aligned}\ln \frac{\gamma_1}{\gamma_3} = {} & (b_{13} + D_2x_2^2 + Cx_2)(x_3 - x_1) + x_2(b_{12} - b_{23}) + \\ & c_{23}x_2(2x_3 - x_2) + c_{13}[6x_1x_3 - (1 - x_2)^2] + \\ & c_{12}x_2(2x_1 - x_2) + D_1x_1x_2(2x_3 - xx) + \\ & d_{23}x_2(3x_3 - x_2)(x_2 - x_3) + d_{13}(x_1 - x_3)[8x_1x_3 - \\ & (1 - x_2)^2] + d_{12}x_2(x_2 - 3x_1)(x_2 - x_1) \qquad (7)\end{aligned}$$

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 eqs 6 and 7 are assumed to be independent of the temperature. Data and constants for two of the binary systems have already been reported (Wisniak et al., 1977,

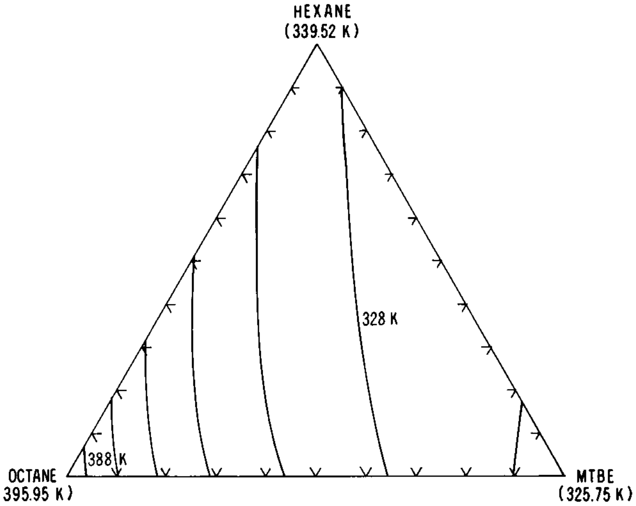

**Figure 1.** Isothermals for the ternary system MTBE (1) + hexane (2) + octane (3) at 94 kPa from 328 K to 378 K, every 10 K. Coefficients from eq 9.

1998), and the system hexane (2) + octane (3) was assumed to be ideal. The ternary Redlich−Kister coefficient was obtained by a Simplex optimization technique, and the results indicated that terms such as $d_{ij}$ were null. The differences between the values of the root-mean-square deviation for the activity coefficient for the two cases—with and without the ternary constants $C$, $D_1$, and $D_2$ (Table 4)—are statistically not significant, suggesting that ternary data can be predicted directly from the binary systems. In fact, equilibrium vapor pressures were correlated very well by the NRTL, Wilson, and UNIQUAC models (the binary parameters have been reported by Wisniak et al. (1997a,b)), and somewhat less by the UNIFAC model (Fredenslund et al., 1977; Larsen et al., 1985) using only binary parameters, both for bubble-point pressure and dew-point pressure calculations, as shown by the statistics and parameters given in Table 5. The boiling points of the systems were correlated by the equation proposed by Wisniak and Tamir (1976):

$$T/\mathrm{K} = \sum_{i=1}^{n} x_i T_i^0/\mathrm{K} + \sum_{i,j=1}^{n} \{x_i x_j \sum_{k=0}^{m} C_k (x_i - x_j)^k\} + x_1 x_2 x_3\{A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3)\} \quad (8)$$

In this equation $n$ is the number of components ($n = 2$ or 3), $T_i^0$ is the boiling point of the pure component $i$, and $m$ is the number of terms in the series expansion of $(x_i - x_j)$. $C_k$ are the binary constants, where $A$, $B$, $C$, and $D$ are ternary constants. The following equation, of the same structure, has been suggested by Tamir (1981) for the direct correlation of ternary data, without use of binary data:

$$T/\mathrm{K} = \sum_{i=1}^{3} x_i T_i^0 + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2 + ...] + x_1 x_3 [A_{13} + B_{13}(x_1 - x_3) + C_{13}(x_1 - x_3)^2 + ...] + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2 + ...] \quad (9)$$

In eq 9 coefficients $A_{ij}$, $B_{ij}$, and $C_{ij}$ are not binary constants; they are multicomponent parameters determined directly from the data. Direct correlation of $T(x)$ for ternary mixtures can be very efficient as reflected by a lower % average deviation and root-mean-square deviation (rmsd) and a smaller number of parameters than those for eq 8. Both equations may require a similar number of constants for similar accuracy, but the direct correlation allows an easier calculation of boiling isotherms (Figures 1 and 2). The various constants of eqs 8 and 9 are reported in Table 6, which also contains information indicating the degree of goodness of the correlation. It is clear that for the ternary system in question a direct fit of the data gives a much better fit.

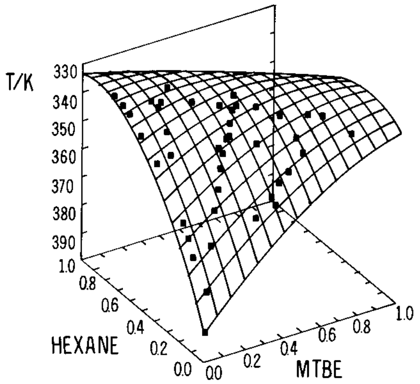

**Figure 2.** Three-dimensional graph $T-x_1-x_2$.

**Table 6. Coefficients in Correlation of Boiling Points, Eqs 10 and 11, Average Deviation, and Root-Mean-Square Deviations in Temperature, rmsd (*T*/K)**

A. Eq 10 (Fit from Binary Constants)

| *A* | *B* | *C*, *D* | max dev/K[a] | avg dev/K[b] | rmsd[c] |
|---|---|---|---|---|---|
| 52.210 | −82.334 | 0 | 1.41 | 0.54 | 0.09 |

Binary Constants

| system | $C_0$ | $C_1$ | $C_2$ | $C_3$ |
|---|---|---|---|---|
| MTBE (1) + hexane (2)[d] | −9.2092 | 3.39392 | −12.0157 | |
| MTBE (1) + octane (2)[e] | −65.0826 | 21.8543 | −13.3961 | 28.4200 |
| hexane (2) + octane (3)[f] | −41.4730 | 16.5117 | −7.4023 | 2.8684 |

B. Eq 11 (Direct Fit)

| *ij* | $A_{ij}$ | $B_{ij}$ | $C_{ij}$ | max dev/K[a] | avg dev/K[b] | rmsd[c] |
|---|---|---|---|---|---|---|
| 1−2 | −4.482 | 6.810 | 0.094 | 0.99 | 0.25 | 0.05 |
| 1−3 | −63.093 | 38.802 | −32.608 | | | |
| 2−3 | −36.603 | 21.129 | 0.496 | | | |

[a] Maximum deviations. [b] Average deviations. [c] rmsd (*T*/K): root-mean-square deviation, $\{\Sigma(T_{\mathrm{exptl}} - T_{\mathrm{obsd}})^2\}^{0.5}/N$. [d] Wisniak et al. (1997a). [e] Wisniak et al. (1997b). [f] Calculated assuming ideal behavior in the liquid phase.

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