876 *J. Chem. Eng. Data* **2004,** *49,* 876−880

# Vapor−Liquid Equilibria of Acetone, Diisopropyl Ether, Ethanol, and Methyl Ethyl Ketone with Hydrocarbon Mixtures at 101.3 kPa

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Isobaric vapor−liquid equilibria (VLE) data were measured at 101.3 kPa on four oxygenates (acetone, diisopropyl ether, ethanol, and methyl ethyl ketone) separately with hydrocarbon mixtures. Acetone, ethanol, and methyl ethyl ketone were mixed with a five-component hydrocarbon mixture and diisopropyl ether was mixed with a four-component hydrocarbon mixture. Calculations of nonideality of the vapor phase were made with the Soave−Redlich−Kwong equation of state. The vaporization equilibrium ratio of oxygenate in the hydrocarbon mixture was derived. Analysis of the experimental VLE data exhibits a minimum boiling temperature for the systems containing acetone, ethanol, and methyl ethyl ketone. The experimental data have been correlated with the mole fraction of oxygenate using the Redlich−Kister-type and Wisniak−Tamir equations.

## Introduction

Reformulated gasoline includes certain oxygenated compounds such as alcohols and ethers. These are commonly methanol, ethanol, propanol, and butanols as well as methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), and *tert*-amyl methyl ether (TAME). These oxygenated compounds are added to improve the octane rating and pollution-reducing capability of gasoline. MTBE, the primary oxygenated compound currently used in reformulated gasoline, is being phased out because of groundwater pollution problems. It is important to investigate the possible use of other oxygenates to comply with environmental regulations. In this sense, there has been an increasing interest in the thermodynamic behavior of liquid mixtures of oxygenated compounds in a hydrocarbon mixture.[1−6] However, there are relatively few vapor−liquid equilibrium data on oxygenate + multicomponent hydrocarbon mixtures.

For these reasons, we measured vapor−liquid equilibrium (VLE) data at 101.3 kPa for acetone, ethanol, and methyl ethyl ketone separately with the five-component hydrocarbon mixture of hexane, heptane, 2,2,4-trimethylpentane (isooctane), toluene, and *p*-xylene. The VLE data at 101.3 kPa were also obtained for diisopropyl ether with the four-component hydrocarbon mixture of heptane, 2,2,4-trimethylpentane, toluene, and *p*-xylene. These hydrocarbon liquids are components that generally appear in gasoline. The equilibrium data are used to calculate the vaporization equilibrium ratios of oxygenate in the hydrocarbon mixture. The equilibrium vapor-phase compositions of oxygenate and the boiling temperatures have been fitted with Redlich−Kister and Wisniak−Tamir equations to estimate the coefficients. For these systems, no VLE data have been previously reported.

## Experimental Section

***Materials.*** The chemicals used were of analytical grade and obtained from Showa, Tedia, Acros, and Merck. All oxygenates were dried over molecular sieves (Aldrich, 0.3 nm), and all chemicals were used without further purification. The purity of all chemicals was checked by gas chromatography. In all cases, chemicals with a purity greater than 99.7 mass % were used for the experimental investigations. The purity of solvents was further ascertained by comparing their normal boiling points, densities, and refractive indices at 298.15 K, which agreed reasonably well with the corresponding literature values as shown in Table 1. The boiling point, $T$, of each pure compound at 101.3 kPa was measured with the same VLE apparatus described in this study, with an uncertainty of ±0.04 K. The density, $\rho$, of each pure compound was measured at (298.15 ± 0.01) K using a DMA-58 vibrating-tube densimeter (Anton-Paar; Graz, Austria) with an uncertainty of ±0.02 $\mathrm{kg \cdot m^{-3}}$. The refractive index, $n_D$, of each pure chemical was measured at (298.15 ± 0.1) K by an Abbe refractometer, Atago RX-5000 (ATAGO; Tokyo), with an uncertainty of ±0.00002 units.

***Apparatus and Procedure.*** The vapor−liquid equilibria of oxygenate + hydrocarbon mixtures were measured at 101.3 kPa. The oxygenates are those that are under consideration as possible fuel additive candidates, e.g., ethanol, acetone, diisopropyl ether, and methyl ethyl ketone. Five hydrocarbons were chosen from the major components shown in a gas chromatography analysis of gasoline,[11] and the concentration was roughly assigned to each component according to its peak height. The hydrocarbon mixture consisting of 25 mol % hexane, 10 mol % heptane, 35 mol % 2,2,4-trimethylpentane, 20 mol % toluene, and 10 mol % *p*-xylene was used as a base fuel to mix with acetone, ethanol, and methyl ethyl ketone. The base fuel used to mix with diisopropyl ether excludes hexane because hexane could not be separated from diisopropyl ether with our gas chromatograph (GC); it contains 13 mol % heptane, 47 mol % 2,2,4-trimethylpentane, 27 mol % toluene, and 13 mol % *p*-xylene. The four- and five-component base fuels, respectively, have an average molecular weight of 105.39 and 100.59 and a refractive index of 1.50001 and 1.42108 at 298.15 K.

The VLE measurement apparatus was an all-glass equilibrium still (NGW, Wertheim/Germany) with provisions for both vapor and liquid recirculation as described

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10.1021/je030232o CCC: \$27.50

**Table 1. Comparison of Measured Normal Boiling Points *T*, Densities $\rho$, and Refractive Indices $n_D$ at 298.15 K with Literature Values**

| | $T$/K | | $\rho$/kg·m$^{-3}$ | | $n_D$ | |
|---|---|---|---|---|---|---|
| compound | this work | lit | this work | lit | this work | lit |
| acetone | 329.24 | 329.217 [a] | 785.18 | 784.40 [a]<br>785.47 [c] | 1.35674 | 1.35596 [a] |
| diisopropyl ether | 341.49 | 341.66 [a] | 718.44 | 718.54 [a]<br>718.13 [d] | 1.36542 | 1.3655 [a]<br>1.3658 [d] |
| ethanol | 351.48 | 351.443 [a] | 785.49 | 784.93 [a]<br>785.4 [b] | 1.35791 | 1.35941 [a]<br>1.3605 [b] |
| methyl ethyl ketone | 352.75 | 352.733 [a] | 799.75 | 799.7 [a] | 1.37636 | 1.37685 [a] |
| hexane | 341.87 | 341.886 [a] | 654.89 | 654.84 [a] | 1.37224 | 1.37226 [a] |
| heptane | 371.58 | 371.574 [a] | 679.53 | 679.46 [a] | 1.38513 | 1.38511 [a] |
| 2,2,4-trimethyl pentane | 372.43 | 372.388 [a] | 687.73 | 687.81 [a] | 1.38915 | 1.38898 [a] |
| toluene | 383.76 | 383.78[a] | 862.24 | 862.19 [a] | 1.49409 | 1.49413 [a] |
| *p*-xylene | 411.52 | 411.509 [a] | 856.57 | 856.61 [a] | 1.49299 | 1.49325 [a] |

[a] Riddick et al., 1986.[7] [b] Aralaguppi et al., 1999.[8] [c] TRC Tables, 1996.[9] [d] Montón et al., 1999.[10]

**Table 2. Experimental VLE Data at 101.3 kPa for the System Acetone (1) + Hexane (2) + Heptane (3) + 2,2,4-Trimethyl Pentane (4) + Toluene (5) + *p*-Xylene (6)**

| $i$ | $x_i$ | $y_i$ | $\gamma_i$ | $x_i$ | $y_i$ | $\gamma_i$ | $x_i$ | $y_i$ | $\gamma_i$ |
|---|---|---|---|---|---|---|---|---|---|
| | | 359.46 K | | | 334.50 K | | | 328.94 K | |
| 1 | 0.011 | 0.117 | 4.532 | 0.167 | 0.566 | 2.865 | 4.532 | 0.848 | 1.092 |
| 2 | 0.145 | 0.303 | 1.302 | 0.116 | 0.165 | 1.797 | 0.028 | 0.069 | 3.660 |
| 3 | 0.136 | 0.114 | 1.198 | 0.103 | 0.044 | 1.408 | 0.023 | 0.016 | 2.830 |
| 4 | 0.341 | 0.296 | 1.248 | 0.301 | 0.148 | 1.585 | 0.092 | 0.044 | 1.890 |
| 5 | 0.175 | 0.110 | 1.299 | 0.144 | 0.048 | 1.665 | 0.038 | 0.016 | 2.620 |
| 6 | 0.193 | 0.060 | 1.523 | 0.170 | 0.030 | 2.323 | 0.033 | 0.008 | 4.080 |
| | | 353.16 K | | | 332.05 K | | | 328.63 K | |
| 1 | 0.024 | 0.196 | 3.900 | 0.244 | 0.644 | 2.410 | 0.841 | 0.870 | 1.058 |
| 2 | 0.142 | 0.283 | 1.447 | 0.105 | 0.131 | 1.702 | 0.021 | 0.063 | 4.360 |
| 3 | 0.132 | 0.106 | 1.396 | 0.090 | 0.035 | 1.404 | 0.016 | 0.012 | 3.088 |
| 4 | 0.338 | 0.268 | 1.378 | 0.278 | 0.126 | 1.596 | 0.068 | 0.037 | 2.176 |
| 5 | 0.173 | 0.095 | 1.398 | 0.133 | 0.041 | 1.694 | 0.027 | 0.011 | 2.567 |
| 6 | 0.190 | 0.052 | 1.692 | 0.150 | 0.024 | 2.341 | 0.026 | 0.007 | 4.596 |
| | | 343.41 K | | | 330.51 K | | | 328.56 K | |
| 1 | 0.060 | 0.350 | 3.729 | 0.372 | 0.714 | 1.846 | 0.889 | 0.893 | 1.030 |
| 2 | 0.139 | 0.242 | 1.661 | 0.081 | 0.106 | 1.860 | 0.014 | 0.058 | 6.809 |
| 3 | 0.127 | 0.075 | 1.417 | 0.071 | 0.029 | 1.563 | 0.012 | 0.009 | 3.097 |
| 4 | 0.326 | 0.215 | 1.566 | 0.233 | 0.098 | 1.567 | 0.048 | 0.027 | 2.256 |
| 5 | 0.166 | 0.074 | 1.595 | 0.112 | 0.034 | 1.773 | 0.020 | 0.008 | 2.528 |
| 6 | 0.182 | 0.046 | 2.288 | 0.132 | 0.021 | 2.493 | 0.018 | 0.005 | 4.758 |
| | | 337.29 K | | | 329.37 K | | | 328.78 K | |
| 1 | 0.115 | 0.484 | 3.257 | 0.622 | 0.792 | 1.272 | 0.948 | 0.948 | 1.018 |
| 2 | 0.129 | 0.201 | 1.795 | 0.046 | 0.083 | 2.773 | 0.005 | 0.025 | 7.578 |
| 3 | 0.111 | 0.052 | 1.394 | 0.046 | 0.022 | 1.913 | 0.006 | 0.006 | 4.097 |
| 4 | 0.315 | 0.170 | 1.578 | 0.158 | 0.069 | 1.673 | 0.019 | 0.013 | 2.723 |
| 5 | 0.156 | 0.058 | 1.669 | 0.067 | 0.023 | 2.099 | 0.012 | 0.005 | 2.611 |
| 6 | 0.173 | 0.034 | 2.292 | 0.062 | 0.011 | 2.927 | 0.010 | 0.003 | 5.091 |

**Table 3. Experimental VLE Data at 101.3 kPa for the System Diisopropyl Ether (1) + Heptane (2) + 2,2,4-Trimethyl Pentane (3) + Toluene (4) + *p*-Xylene (5)**

| $i$ | $x_i$ | $y_i$ | $\gamma_i$ | $x_i$ | $y_i$ | $\gamma_i$ | $x_i$ | $y_i$ | $\gamma_i$ |
|---|---|---|---|---|---|---|---|---|---|
| | | 364.63 K | | | 355.84 K | | | 346.68 K | |
| 1 | 0.132 | 0.283 | 1.118 | 0.460 | 0.683 | 0.980 | 0.777 | 0.890 | 0.983 |
| 2 | 0.105 | 0.091 | 0.947 | 0.065 | 0.043 | 1.081 | 0.027 | 0.017 | 1.352 |
| 3 | 0.389 | 0.351 | 1.009 | 0.228 | 0.149 | 1.047 | 0.095 | 0.051 | 1.145 |
| 4 | 0.205 | 0.189 | 1.446 | 0.130 | 0.084 | 1.503 | 0.054 | 0.029 | 1.710 |
| 5 | 0.173 | 0.098 | 2.038 | 0.117 | 0.040 | 1.912 | 0.047 | 0.013 | 2.196 |
| | | 363.44 K | | | 353.56 K | | | 344.82 K | |
| 1 | 0.211 | 0.422 | 1.075 | 0.545 | 0.748 | 0.965 | 0.841 | 0.919 | 0.991 |
| 2 | 0.091 | 0.075 | 1.045 | 0.055 | 0.118 | 1.113 | 0.020 | 0.012 | 1.307 |
| 3 | 0.322 | 0.261 | 1.038 | 0.192 | 0.067 | 1.055 | 0.066 | 0.038 | 1.305 |
| 4 | 0.184 | 0.137 | 1.356 | 0.110 | 0.032 | 1.529 | 0.038 | 0.022 | 1.969 |
| 5 | 0.162 | 0.080 | 2.099 | 0.099 | 0.035 | 1.968 | 0.034 | 0.009 | 2.263 |
| | | 361.74 K | | | 351.40 K | | | 343.91 K | |
| 1 | 0.267 | 0.491 | 1.034 | 0.622 | 0.799 | 0.961 | 0.889 | 0.945 | 0.991 |
| 2 | 0.084 | 0.067 | 1.051 | 0.046 | 0.028 | 1.145 | 0.014 | 0.009 | 1.348 |
| 3 | 0.297 | 0.231 | 1.046 | 0.160 | 0.094 | 1.079 | 0.046 | 0.026 | 1.320 |
| 4 | 0.172 | 0.120 | 1.340 | 0.091 | 0.054 | 1.603 | 0.027 | 0.015 | 1.952 |
| 5 | 0.155 | 0.071 | 2.067 | 0.082 | 0.025 | 2.015 | 0.024 | 0.006 | 2.217 |
| | | 358.89 K | | | 348.87 K | | | 342.36 K | |
| 1 | 0.380 | 0.617 | 0.985 | 0.696 | 0.844 | 0.976 | 0.965 | 0.983 | 0.995 |
| 2 | 0.073 | 0.053 | 1.056 | 0.037 | 0.023 | 1.276 | 0.005 | 0.003 | 0.995 |
| 3 | 0.251 | 0.178 | 1.037 | 0.129 | 0.073 | 1.125 | 0.015 | 0.008 | 1.311 |
| 4 | 0.156 | 0.100 | 1.350 | 0.074 | 0.042 | 1.673 | 0.008 | 0.005 | 2.323 |
| 5 | 0.140 | 0.052 | 1.857 | 0.064 | 0.018 | 2.049 | 0.007 | 0.002 | 2.698 |

by Hunsmann.[12] The still has a total volumetric capacity of about 100 cm$^3$. The charge for experimental runs was prepared by mixing known masses of oxygenate and the hydrocarbon mixture. A set of 12 compositions with an increment of about 0.1 mole fractions of oxygenate was prepared by weight for each system. Equilibrium conditions were indicated by constant boiling temperatures of the liquid and vapor phases within the equilibrium cell and their difference was within 0.02 K. The system was maintained at an equilibrium state for about 1 h before samples were taken.

The equilibrium boiling temperature was measured with a digital thermometer (Hart Scientific Model 1560/5644) with an accuracy of ±0.005 K. System pressure was regulated through a manostat pressure control. To facilitate control of a constant pressure and to give it a higher accuracy, a modified Świętosławski ebulliometer[13] was built to measure the boiling point of pure water. During an experimental run, the system was maintained at the pressure when the temperature reading on the ebulliometer was exactly 373.15 K with an uncertainty of ±0.02 K. System pressure could then be controlled at 101.3 kPa and measured with an uncertainty of ±0.1 kPa. The uncertainty of equilibrium boiling-temperature measurements was estimated to be ±0.06 K.

Equilibrium compositions of sampled liquid and condensed vapor phases were analyzed with a Perkin-Elmer Autosystem GC. A flame ionization detector was used along with a (60 m long, 0.25 mm i.d., 0.5 $\mu$m film) capillary column packed with Petrocol DH (SUPELCO, PA/USA). The GC response peaks were integrated by using Perkin-Elmer Turbochrom software. Calibration analyses using gravimetrically prepared standard solutions were carried out to convert the peak area ratio to mole fraction of the sample. The pertinent polynomial fits had a correlation coefficient $R^2$ better than 0.99. The uncertainty of equilibrium composition measurements was estimated to be ±0.001 mole fraction.

## Results and Discussion

The isobaric $T-x-y$ data together with the activity coefficients for oxygenate + hydrocarbon mixtures are presented in Tables 2−5. The oxygenates investigated were

**Table 4. Experimental VLE Data at 101.3 kPa for the System Ethanol (1) +Hexane (2) + Heptane (3) + 2,2,4-Trimethyl Pentane (4) + Toluene (5) + *p*-Xylene (6)**

| $i$ | $x_i$ | $y_i$ | $\gamma_i$ | $x_i$ | $y_i$ | $\gamma_i$ | $x_i$ | $y_i$ | $\gamma_i$ |
|---|---|---|---|---|---|---|---|---|---|
| | 355.23 K | | | 342.93 K | | | 343.34 K | | |
| 1 | 0.038 | 0.168 | 3.797 | 0.379 | 0.516 | 1.912 | 0.779 | 0.630 | 1.116 |
| 2 | 0.191 | 0.371 | 1.242 | 0.110 | 0.222 | 1.988 | 0.038 | 0.197 | 5.110 |
| 3 | 0.081 | 0.061 | 1.227 | 0.045 | 0.031 | 1.683 | 0.018 | 0.022 | 2.947 |
| 4 | 0.320 | 0.246 | 1.255 | 0.240 | 0.146 | 1.470 | 0.110 | 0.103 | 2.235 |
| 5 | 0.226 | 0.116 | 1.219 | 0.140 | 0.067 | 1.744 | 0.037 | 0.039 | 3.786 |
| 6 | 0.143 | 0.039 | 1.561 | 0.087 | 0.018 | 1.913 | 0.019 | 0.010 | 4.791 |
| | 348.51 K | | | 342.69 K | | | 344.24 K | | |
| 1 | 0.089 | 0.295 | 3.747 | 0.485 | 0.534 | 1.559 | 0.865 | 0.694 | 1.067 |
| 2 | 0.175 | 0.317 | 1.506 | 0.089 | 0.221 | 2.425 | 0.024 | 0.172 | 7.029 |
| 3 | 0.076 | 0.049 | 1.304 | 0.036 | 0.029 | 1.985 | 0.009 | 0.022 | 5.720 |
| 4 | 0.303 | 0.214 | 1.421 | 0.213 | 0.140 | 1.601 | 0.063 | 0.074 | 2.723 |
| 5 | 0.218 | 0.093 | 1.274 | 0.108 | 0.060 | 2.042 | 0.025 | 0.030 | 4.174 |
| 6 | 0.139 | 0.032 | 1.702 | 0.068 | 0.015 | 2.060 | 0.015 | 0.008 | 4.685 |
| | 345.60 K | | | 342.60 K | | | 345.57 K | | |
| 1 | 0.159 | 0.405 | 3.224 | 0.594 | 0.567 | 1.356 | 0.905 | 0.744 | 1.037 |
| 2 | 0.160 | 0.265 | 1.495 | 0.066 | 0.215 | 3.178 | 0.019 | 0.148 | 7.095 |
| 3 | 0.064 | 0.039 | 1.358 | 0.030 | 0.025 | 2.060 | 0.006 | 0.018 | 6.713 |
| 4 | 0.279 | 0.182 | 1.443 | 0.180 | 0.127 | 1.725 | 0.045 | 0.060 | 2.961 |
| 5 | 0.210 | 0.082 | 1.292 | 0.084 | 0.053 | 2.327 | 0.016 | 0.024 | 4.976 |
| 6 | 0.128 | 0.027 | 1.750 | 0.045 | 0.012 | 2.500 | 0.009 | 0.005 | 4.630 |
| | 343.95 K | | | 342.74 K | | | 347.94 K | | |
| 1 | 0.251 | 0.476 | 2.549 | 0.697 | 0.592 | 1.201 | 0.954 | 0.834 | 1.003 |
| 2 | 0.140 | 0.229 | 1.561 | 0.047 | 0.209 | 4.274 | 0.012 | 0.102 | 7.191 |
| 3 | 0.052 | 0.035 | 1.558 | 0.024 | 0.024 | 2.461 | 0.004 | 0.015 | 7.759 |
| 4 | 0.263 | 0.165 | 1.465 | 0.140 | 0.115 | 1.999 | 0.019 | 0.032 | 3.467 |
| 5 | 0.183 | 0.073 | 1.405 | 0.058 | 0.049 | 3.101 | 0.007 | 0.014 | 6.105 |
| 6 | 0.111 | 0.022 | 1.766 | 0.033 | 0.011 | 3.108 | 0.004 | 0.003 | 5.697 |

**Table 5. Experimental VLE Data at 101.3 kPa for the System Methyl Ethyl Ketone (1) + Hexane (2) + Heptane (3) + 2,2,4-Trimethyl Pentane (4) + Toluene (5) + *p*-Xylene (6)**

| $i$ | $x_i$ | $y_i$ | $\gamma_i$ | $x_i$ | $y_i$ | $\gamma_i$ | $x_i$ | $y_i$ | $\gamma_i$ |
|---|---|---|---|---|---|---|---|---|---|
| | 362.37 K | | | 351.36 K | | | 349.99 K | | |
| 1 | 0.041 | 0.128 | 2.322 | 0.313 | 0.376 | 1.238 | 0.696 | 0.645 | 0.995 |
| 2 | 0.198 | 0.364 | 1.052 | 0.156 | 0.288 | 1.418 | 0.081 | 0.177 | 1.774 |
| 3 | 0.102 | 0.089 | 1.142 | 0.070 | 0.062 | 1.632 | 0.033 | 0.047 | 2.745 |
| 4 | 0.313 | 0.235 | 0.992 | 0.226 | 0.173 | 1.407 | 0.096 | 0.091 | 1.821 |
| 5 | 0.196 | 0.140 | 1.345 | 0.145 | 0.081 | 1.511 | 0.042 | 0.027 | 1.823 |
| 6 | 0.150 | 0.045 | 1.324 | 0.090 | 0.020 | 1.471 | 0.053 | 0.012 | 1.581 |
| | 359.52 K | | | 350.39 K | | | 350.31 K | | |
| 1 | 0.087 | 0.200 | 1.849 | 0.371 | 0.413 | 1.181 | 0.762 | 0.699 | 0.975 |
| 2 | 0.191 | 0.343 | 1.103 | 0.148 | 0.274 | 1.460 | 0.065 | 0.146 | 1.803 |
| 3 | 0.093 | 0.075 | 1.115 | 0.068 | 0.061 | 1.705 | 0.024 | 0.040 | 3.179 |
| 4 | 0.308 | 0.221 | 1.030 | 0.210 | 0.168 | 1.516 | 0.083 | 0.083 | 1.902 |
| 5 | 0.189 | 0.125 | 1.364 | 0.121 | 0.066 | 1.526 | 0.026 | 0.022 | 2.374 |
| 6 | 0.131 | 0.036 | 1.343 | 0.082 | 0.018 | 1.509 | 0.041 | 0.010 | 1.683 |
| | 356.20 K | | | 349.70 K | | | 350.81 K | | |
| 1 | 0.140 | 0.254 | 1.616 | 0.461 | 0.480 | 1.127 | 0.818 | 0.757 | 0.968 |
| 2 | 0.183 | 0.328 | 1.204 | 0.131 | 0.255 | 1.571 | 0.052 | 0.121 | 1.814 |
| 3 | 0.087 | 0.070 | 1.271 | 0.063 | 0.056 | 1.729 | 0.017 | 0.029 | 3.202 |
| 4 | 0.291 | 0.207 | 1.127 | 0.181 | 0.144 | 1.541 | 0.065 | 0.067 | 1.930 |
| 5 | 0.183 | 0.113 | 1.420 | 0.092 | 0.050 | 1.557 | 0.023 | 0.020 | 2.398 |
| 6 | 0.116 | 0.029 | 1.380 | 0.072 | 0.016 | 1.569 | 0.025 | 0.006 | 1.625 |
| | 353.11 K | | | 349.45 K | | | 351.59 K | | |
| 1 | 0.223 | 0.319 | 1.396 | 0.570 | 0.544 | 1.041 | 0.889 | 0.850 | 0.976 |
| 2 | 0.172 | 0.300 | 1.281 | 0.112 | 0.229 | 1.655 | 0.029 | 0.068 | 1.853 |
| 3 | 0.074 | 0.064 | 1.506 | 0.056 | 0.054 | 1.891 | 0.008 | 0.014 | 3.204 |
| 4 | 0.259 | 0.194 | 1.304 | 0.139 | 0.121 | 1.700 | 0.052 | 0.055 | 1.933 |
| 5 | 0.172 | 0.099 | 1.467 | 0.060 | 0.038 | 1.830 | 0.011 | 0.010 | 2.441 |
| 6 | 0.100 | 0.023 | 1.425 | 0.063 | 0.014 | 1.584 | 0.012 | 0.003 | 1.643 |

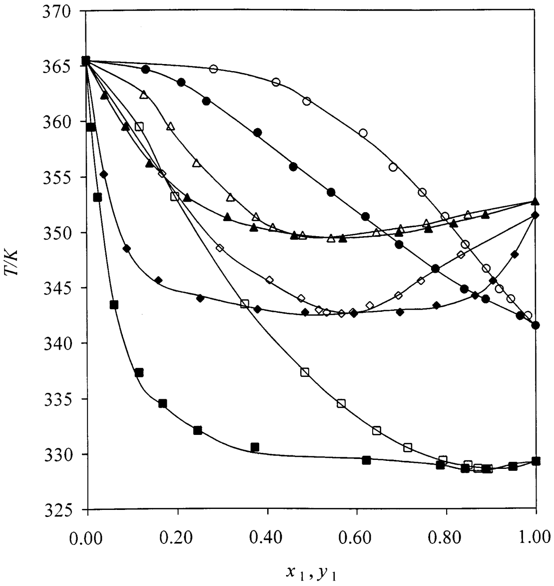

**Figure 1.** Experimental $T-x_1-y_1$ diagram for oxygenate + hydrocarbon mixtures at 101.3 kPa: □, ■, acetone; ○, ●, diisopropyl ether; ◇, ◆, ethanol; △, ▲, methyl ethyl ketone. Solid symbols represent the liquid phase, and hollow symbols represent the vapor phase.

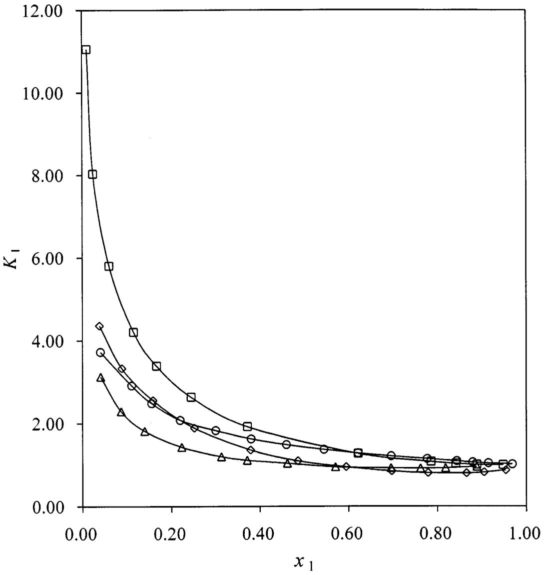

**Figure 2.** Vaporization equilibrium ratios of oxygenate as a function of liquid-phase mole fraction of oxygenate for oxygenate + hydrocarbon mixtures at 101.3 kPa: (□), acetone; (○), diisopropyl ether; (◇), ethanol; (△), methyl ethyl ketone.

those that have been tested as possible fuel additive candidates, e.g., ethanol, acetone, diisopropyl ether, and methyl ethyl ketone. The hydrocarbon mixture consists of hexane, heptane, 2,2,4-trimethyl pentane, toluene, and *p*-xylene. The activity coefficients $\gamma$ of pure liquid $i$ at temperature $T$ and pressure $P$ were calculated by taking into account the nonideality of the vapor phase with

$$\gamma_i = \phi_i P y_i / P_i^0 x_i \phi_i^s \exp[v_i^L (P - P_i^0)/RT] \qquad (1)$$

where $x$ and $y$ are the liquid and vapor mole fractions in equilibrium, $\phi$ is the vapor-phase fugacity coefficient, $P^0$ is the vapor pressure of the pure component, $v^L$ is the liquid molar volume, and superscript s stands for saturation. The vapor-phase fugacity coefficients were calculated from the Soave−Redlich−Kwong equation of state,[14] with the binary interaction parameter $k_{ij}$ set to be 0. The required pure component data such as vapor pressures, liquid molar volumes, and critical properties were directly taken from the CHEMCAD Data Bank.[15] The calculated activity coefficients are estimated to be accurate within ±0.003.

Table 6 gives the equilibrium boiling temperatures, equilibrium compositions, vaporization equilibrium ratio,

**Table 6. Equilibrium Boiling Temperatures, Vapor−Liquid Compositions, Vaporization Equilibrium Ratios, and Activity Coefficients of Oxygenate for Oxygenate (1) + Hydrocarbon Mixtures at 101.3 kPa**

| $T$/K | $x_1$ | $y_1$ | $K_1$ | $\gamma_1$ | $T$/K | $x_1$ | $y_1$ | $K_1$ | $\gamma_1$ |
|---|---|---|---|---|---|---|---|---|---|
| | | Acetone | | | | | Diisopropyl Ether | | |
| 365.49[a] | 0.000 | 0.000 | | | 365.49[a] | 0.000 | 0.000 | | |
| 359.46 | 0.011 | 0.117 | 11.05 | 4.532 | 364.63 | 0.132 | 0.283 | 2.144 | 1.118 |
| 353.16 | 0.024 | 0.196 | 8.03 | 3.900 | 363.44 | 0.211 | 0.422 | 2.000 | 1.075 |
| 343.41 | 0.060 | 0.350 | 5.81 | 3.729 | 361.74 | 0.267 | 0.491 | 1.839 | 1.034 |
| 337.29 | 0.115 | 0.484 | 4.21 | 3.257 | 358.89 | 0.380 | 0.617 | 1.622 | 0.985 |
| 334.50 | 0.167 | 0.566 | 3.39 | 2.865 | 355.84 | 0.460 | 0.683 | 1.486 | 0.980 |
| 332.05 | 0.244 | 0.644 | 2.64 | 2.410 | 353.56 | 0.545 | 0.748 | 1.374 | 0.965 |
| 330.51 | 0.372 | 0.714 | 1.92 | 1.846 | 351.40 | 0.622 | 0.799 | 1.285 | 0.961 |
| 329.37 | 0.622 | 0.792 | 1.27 | 1.272 | 348.87 | 0.696 | 0.844 | 1.211 | 0.976 |
| 328.94 | 0.786 | 0.848 | 1.08 | 1.092 | 346.68 | 0.777 | 0.890 | 1.146 | 0.983 |
| 328.63 | 0.841 | 0.870 | 1.03 | 1.058 | 344.82 | 0.841 | 0.919 | 1.093 | 0.991 |
| 328.56 | 0.889 | 0.893 | 1.01 | 1.030 | 343.91 | 0.889 | 0.945 | 1.063 | 0.991 |
| 328.78 | 0.948 | 0.948 | 1.00 | 1.018 | 342.36 | 0.965 | 0.983 | 1.018 | 0.995 |
| 329.24 | 1.000 | 1.000 | | | 341.49 | 1.000 | 1.000 | | |
| | | Ethanol | | | | | Methyl Ethyl Ketone | | |
| 365.49[a] | 0.000 | 0.000 | | | 365.49[a] | 0.000 | 0.000 | | |
| 355.23 | 0.038 | 0.168 | 4.36 | 3.797 | 362.37 | 0.041 | 0.128 | 3.13 | 2.322 |
| 348.51 | 0.089 | 0.295 | 3.33 | 3.747 | 359.52 | 0.087 | 0.200 | 2.29 | 1.849 |
| 345.60 | 0.159 | 0.405 | 2.56 | 3.224 | 356.20 | 0.140 | 0.254 | 1.82 | 1.616 |
| 343.95 | 0.251 | 0.476 | 1.89 | 2.549 | 353.11 | 0.223 | 0.319 | 1.43 | 1.396 |
| 342.93 | 0.379 | 0.516 | 1.36 | 1.913 | 351.36 | 0.313 | 0.376 | 1.20 | 1.238 |
| 342.69 | 0.485 | 0.534 | 1.10 | 1.559 | 350.39 | 0.371 | 0.413 | 1.11 | 1.181 |
| 342.60 | 0.594 | 0.567 | 0.95 | 1.356 | 349.70 | 0.461 | 0.480 | 1.04 | 1.127 |
| 342.74 | 0.697 | 0.592 | 0.85 | 1.201 | 349.45 | 0.570 | 0.544 | 0.95 | 1.041 |
| 343.34 | 0.779 | 0.630 | 0.81 | 1.116 | 349.99 | 0.696 | 0.645 | 0.93 | 0.995 |
| 344.24 | 0.865 | 0.694 | 0.80 | 1.067 | 350.31 | 0.762 | 0.699 | 0.92 | 0.975 |
| 345.57 | 0.905 | 0.744 | 0.82 | 1.037 | 350.81 | 0.818 | 0.757 | 0.93 | 0.968 |
| 347.94 | 0.954 | 0.834 | 0.87 | 1.003 | 351.59 | 0.889 | 0.850 | 0.96 | 0.976 |
| 351.48 | 1.000 | 1.000 | | | 352.75 | 1.000 | 1.000 | | |

[a] Equilibrium boiling temperature of the base fuel at 101.3 kPa.

**Table 7. Results in Correlation of Boiling Temperatures and Vapor-Phase Compositions of Oxygenate for Oxygenate + Hydrocarbon Mixtures**

| system | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $a_4$ | $a_5$ | $\sigma$ |
|---|---|---|---|---|---|---|---|
| | | | Wisniak−Tamir, eq 3 for boiling temperature | | | | |
| acetone | −74.46 | 76.07 | 2.51 | −49.09 | −208.98 | 227.37 | 0.58 |
| diisopropyl ether | 5.66 | −11.92 | 8.68 | −25.85 | −6.22 | 34.55 | 0.19 |
| ethanol | −64.13 | 28.07 | −30.43 | −12.63 | −120.36 | 100.76 | 0.20 |
| methyl ethyl ketone | −38.10 | 18.42 | −15.31 | 22.20 | 7.42 | −23.81 | 0.13 |
| | | | Redlich−Kister, eq 4 for vapor-phase composition of oxygenate | | | | |
| acetone | 1.09 | −1.60 | −0.11 | 0.65 | 2.60 | −3.29 | 0.014 |
| diisopropyl ether | 0.86 | −0.47 | 0.33 | −0.46 | −0.28 | 0.74 | 0.003 |
| ethanol | 0.17 | −1.69 | 0.20 | −0.09 | 0.14 | −2.47 | 0.010 |
| methyl ethyl ketone | 0.01 | −0.71 | −0.14 | 0.01 | 1.28 | −0.94 | 0.004 |

and activity coefficients of oxygenate in the hydrocarbon mixture. The vaporization equilibrium ratio of oxygenate is defined by the equation

$$K_1 = y_1/x_1 \tag{2}$$

where $x_1$ and $y_1$ are the equilibrium liquid-phase and vapor-phase mole fractions of the oxygenate, respectively. Figure 1 graphically represents the experimental $T-x_1-y_1$ data for each of the systems. It can be seen that the systems of acetone, ethanol, and methyl ethyl ketone show a minimum boiling temperature. However, no such result was found for the system of diisopropyl ether. This kind of behavior seems to be characteristic for oxygenate + hydrocarbon.[16−19] The vaporization equilibrium ratio of oxygenate was plotted as a function of oxygenate mole fraction in Figure 2. The values of $K_1$ at $x_1 < 0.3$ follow the order acetone > ethanol > diisopropyl ether > methyl ethyl ketone. However, the values of $K_1$ at $0.3 < x_1 < 0.6$ are varied according to the order acetone > diisopropyl ether > ethanol > methyl ethyl ketone. No significant difference in the values of $K_1$ after $x_1 = 0.6$ was observed among all of the systems.

The compositions where the minimum boiling temperatures occurred have been obtained, in all cases, by determining the $x_1$ values that make the function $(x_1 - y_1) = f(x_1)$ zero. The minimum boiling temperatures were then computed from a cubic polynomial equation, $T = f(x_1)$, whose coefficients were obtained by fitting the experimental results around the minimum boiling temperature, using the $x_1$ values previously determined. The minimum boiling temperatures and the corresponding compositions for the oxygenate + hydrocarbon mixtures are $T = 328.78$ K and $x_1 = 0.948$ for actone, $T = 342.53$ K and $x_1 = 0.553$ for ethanol, $T = 349.56$ K and $x_1 = 0.500$ for methyl ethyl ketone.

The boiling temperature of the system was correlated with its liquid-phase concentration of oxygenate in mole fraction by the equation proposed by Wisniak and Tamir[20]

$$T = x_1T_1 + (1 - x_1)T_2 + x_1(1 - x_1)\sum_{k=0}^{5} a_k(2x_1 - 1)^k \tag{3}$$

where $T_1$ is the boiling temperature of oxygenate, $T_2$ is the equilibrium boiling temperature of the base fuel, and $a_k$ are the coefficients. The vapor-phase mole fraction of the mixture was also fitted with its liquid-phase mole fraction by a Redlich−Kister equation[21]

$$y_1 - x_1 = x_1(1 - x_1)\sum_{k=0}^{5} a_k(2x_1 - 1)^k \qquad (4)$$

The values of coefficients $a_k$ of eqs 3 and 4 were determined by a multiple regression analysis based on the least-squares method. In all the cases, 6 parameters were required for eqs 3 and 4 to fit the $T-x_1-y_1$ data adequately. The correlated constants of the respective functions along with the standard deviations between the experimental and fitted values are summarized in Table 7. The standard deviation ($\sigma$) is defined by

$$\sigma = [\sum_{i=1}^{m} (Y_i^{\mathrm{exp}} - Y_i^{\mathrm{calc}})^2/(m - 6)]^{1/2} \qquad (5)$$

where $m$ is the number of experimental points and the superscripts "exp" and "calc" indicate experimental and calculated values, respectively. The largest standard deviations occurred for the acetone system with 0.58 K for the boiling temperature and 0.014 for the vapor-phase composition.

## Literature Cited

(1) Aucejo, A.; Loras, S.; Muñoz, R.; Reich, R.; Segura, H. Isobaric Vapor-Liquid Equilibrium in the Systems 2-Methylpentane + Methyl 1,1-Dimethylethyl Ether + Ethyl 1,1-Dimethylethyl Ether, and + Methyl 1,1-Dimethylpropyl Ether. *J. Chem. Eng. Data* **1998**, *43*, 973−977.

(2) Orge, B.; Rodríguez, A.; Canosa, J. M.; Marino, G.; Iglesias, M.; Tojo, J. Variation of Densities, Refractive Indices, and Speeds of Sound with Temperature of Methanol or Ethanol with *n*-Hexane, *n*-Heptane, and *n*-Octane. *J. Chem. Eng. Data* **1999**, *44*, 1041−1047.

(3) Segura, H.; Reich, R.; Galindo, G.; Wisniak, J. Phase Equilibria in the Systems Ethyl 1,1-Dimethyl Ethyl Ether + Methylcyclohexane, 2,2,4-Trimethylpentane + Methylcyclohexane, and Ethyl 1,1-Dimethylethyl Ether + 2,2,4-Trimethylpentane + Methylcyclohexane at 94.00 kPa. *J. Chem. Eng. Data* **1999**, *44*, 912−917.

(4) Loras, S.; Aucejo, A.; Muñoz, R.; Torre, J. Isobaric Vapor-Liquid Equilibrium for Binary and Ternary Mixtures of 2-methyl-2-propanol + Methyl 1,1-Dimethylpropyl ether + 2,2,4-trimethylpentane. *Fluid Phase Equilib.* **2000**, *175*, 125−138.

(5) Muñoz, R.; Burguet, M. C.; Martínez-Soria, V.; de Araújo, R. N. Densities, Refractive Indices, and Derived Excess Properties of *tert*-Butyl Alcohol, Methyl *tert*-Butyl Ether and 2-Methylpentane Binary and Ternary Systems at 303.15 K. *Fluid Phase Equilib.* **2000**, *167*, 99−111.

(6) Segura, H.; Wisniak, J.; Galindo, G.; Reich, R. Phase Equilibria in the Systems 1-Hexene + 2,2,4-Trimethylpentane and 1-Hexene + Ethyl 1,1-Dimethylethyl Ether + 2,2,4-Trimethylpentane at 94.0 kPa. *J. Chem. Eng. Data* **2001**, *46*, 511−515.

(7) Riddick, A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Physical Properties and Method of Purification*, 4th ed.; Wiley-Interscience: New York, 1986.

(8) Aralaguppi, M. I.; Jadar, C. V.; Aminabhavi, T. M. Density, Viscosity, Refractive Index, and Speed of Sound in Binary Mixtures of Acrylonitrile With Methanol, Ethanol, Propan-1-ol, Butan-1-ol, Pentan-1-ol, Hexan-1-ol, Heptan-1-ol, and Butan-2-ol. *J. Chem. Eng. Data* **1999**, *44*, 216−221.

(9) *TRC−Thermodynamic Tables-Nonhydrocarbons*. Thermodynamics Research Center. The Texas A & M University System: College Station, TX, 1963, extant 1996.

(10) Montón, J. B.; Toree, J.; Burguet, M. C.; Muñoz, R.; Loras, S. Isobaric Vapor-Liquid Equilibrium in the Systems 2,3-Dimethylpentane + Methyl 1,1-Dimethylethyl Ether, + Didiisopropyl Ether and + Methyl 1,1-Dimethylpropyl Ether. *J. Chem. Eng. Data* **1999**, *44*, 1158−1162.

(11) *SUPELCO catalog, Chromatography Products for Analysis and Purification*, 514, Bellefonte, PA, 2000.

(12) Hunsmann, W. Vapor-Liquid Equilibria of Formic Acid/Acetic Acid and of Tetrachloromethane/Perchloroethylene-Mixtures. *Chemie-Ing.-Tech.* **1967**, *39*, 1142−1145

(13) Hála, E.; Pick, J.; Fried, V.; Vilím, O. *Vapor-Liquid Equilibrium*, 2nd ed., Pergamon Press: New York, 1967; p 257.

(14) Soave, G. Equilibrium Constants from a Modified Redlich-Kwong Equation of State. *Chem. Eng. Sci.* **1972**, *27*, 1197−1203.

(15) *CHEMCAD Software, Version 5.1*; Chemstations, Inc.: Houston, TX, 2001.

(16) Świątek, B. E.; Malanoski, S. K. Vapor-Liquid Equilibrium in *m*-Xylene + Cyclohexanol at 19.9 and 94.93 kPa. *J. Chem. Eng. Data* **2002**, *47*, 478−471.

(17) Segura, H.; Wisniak, J.; Galindo, G.; Reich, R. Phase Equilibria in the Systems 1-Hexene + Benzene and 1-Hexene + Ethyl 1,1-Dimethylethyl Ether + Benzene at 94.0 kPa. *J. Chem. Eng. Data* **2001**, *46*, 506−510.

(18) Hiaki, T.; Takahashi, K.; Tsuji, T.; Hongo, M.; Kojima, K. Vapor-Liquid Equilibria of 1-Propanol or 2-Propanol with 2,2,4-Trimethylpentane at 101.3 kPa. *J. Chem. Eng. Data* **1994**, *39*, 602−604.

(19) Ohta, T.; Koyabu, J.; Nagata, I. Vapor-Liquid Equilibria for the Ternary Ethanol-2-Butanone-Benzene System at 298.15 K. *Fluid Phase Equilib.* **1981**, *7*, 65−73.

(20) Wisniak, J.; Tamir, A. Correlation of the Boiling Point of Mixtures. *Chem. Eng. Sci.* **1976**, *31*, 631−635.

(21) Redlich, O.; Kister, A. T. Thermodynamics of Nonelectrolyte Solutions. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

Received for review October 2, 2003. Accepted May 1, 2004. The authors wish to extend their deep gratitude for the support by the National Science Council of Republic of China under Grant NSC 90-2214-E-126-001.

JE030232O