# Liquid−Liquid Equilibria of Fuel Oxygenate + Water + Hydrocarbon Mixtures. 3. Effect of Temperature

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We have measured the ternary liquid−liquid equilibria of water + ethanol mixtures with, separately, 2,2,4-trimethylpentane and toluene at 5 and 40 °C, water + *tert*-amyl alcohol (TAOH) mixtures with, separately, toluene and hexane at 5 and 40 °C, and of water + TAOH + pentane mixtures at 5 °C. The ethanol-containing systems exhibit type 1 liquid−liquid phase behavior, and the TAOH-containing systems exhibit type 2 behavior. These data, together with the data we have previously reported at 25 °C, provide information on how the liquid−liquid equilibria of these systems change as a function of temperature. While the addition of ethanol is found to increase the solubility of hydrocarbons in the aqueous phase, the concentration of the hydrocarbon in the water-rich phase decreases with increasing temperature. With the exception of the hydrocarbon in the water-rich phase, our experimental data could be correlated quite well with either the UNIQUAC or NRTL models. For most of the systems considered here the predictions of the phase behavior with the liquid−liquid UNIFAC group-contribution model are only qualitatively correct. However, the liquid−liquid UNIFAC model erroneously predicts type 2 phase behavior to occur for the water + ethanol + 2,2,4-trimethylpentane system at 5 °C.

## Introduction

As a result of the Clean Air Act, oxygenated compounds such as ethers and alcohols are being considered and/or mandated for addition to gasolines because of their expected air pollution-reducing capabilities. As an extension of our previous work on the effect of oxygenate addition on the hydrocarbon−water mutual solubility, we consider here the effect of temperature on the ternary liquid−liquid equilibrium phase behavior of five water + hydrocarbon + oxygenate mixtures. We report the results of measurements at 5 and 40 °C, which complement our previous measurements at 25 °C (Peschke and Sandler, 1995; Hellinger and Sandler, 1995). The experimental data obtained were correlated with the NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) models and compared with the predictions of the UNIFAC liquid−liquid equilibrium model (Magnussen et al., 1981).

## Measurements

All measurements were carried out in liquid−liquid equilibrium cells described earlier (Peschke and Sandler, 1995) following the experimental protocol described therein except for the changes noted below. The equilibrium vessels were thermostatically jacketed to maintain the temperature constant at the desired temperatures to within ±0.1 K. Samples of the aqueous and hydrocarbon phases were withdrawn using a Perfectum Model MicroMate hypodermic syringe and immediately analyzed using a Hewlett-Packard Model 5730 gas chromatograph with a thermal conductivity detector and a Poropak Q column of 6 ft length and $^1/_8$ inch diameter using the conditions described earlier (Peschke and Sandler, 1995). Calibration of the gas chromatograph was done by determining the response of the gas chromatograph and integrator system to injections of the pure substances from 0.1 to 0.8 μL in

**Table 1. Measured Mole Fractions of the Water (1) + Ethanol (2) + TMP (3) System at 5 °C and Values of the Model Correlation Parameters**

| organic phase | | | aqueous phase | | |
|---|---|---|---|---|---|
| $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| 0.001 | 0.000 | 0.999 | 1.000 | 0.000 | 0.000 |
| 0.006 | 0.008 | 0.986 | 0.949 | 0.051 | 0.000 |
| 0.006 | 0.012 | 0.982 | 0.917 | 0.083 | 0.000 |
| 0.006 | 0.015 | 0.979 | 0.870 | 0.130 | 0.000 |
| 0.007 | 0.018 | 0.975 | 0.825 | 0.175 | 0.000 |
| 0.007 | 0.021 | 0.972 | 0.781 | 0.219 | 0.000 |
| 0.009 | 0.024 | 0.967 | 0.738 | 0.261 | 0.001 |
| 0.009 | 0.029 | 0.962 | 0.699 | 0.300 | 0.001 |
| 0.009 | 0.033 | 0.957 | 0.659 | 0.339 | 0.002 |
| 0.009 | 0.039 | 0.952 | 0.617 | 0.380 | 0.004 |
| 0.009 | 0.040 | 0.951 | 0.593 | 0.403 | 0.005 |
| 0.009 | 0.042 | 0.949 | 0.558 | 0.437 | 0.005 |
| 0.009 | 0.046 | 0.945 | 0.532 | 0.461 | 0.007 |
| 0.009 | 0.049 | 0.942 | 0.510 | 0.481 | 0.008 |
| 0.010 | 0.054 | 0.937 | 0.484 | 0.506 | 0.010 |
| 0.010 | 0.054 | 0.936 | 0.454 | 0.533 | 0.013 |
| 0.010 | 0.062 | 0.928 | 0.427 | 0.557 | 0.016 |
| 0.010 | 0.073 | 0.917 | 0.399 | 0.582 | 0.019 |
| 0.010 | 0.081 | 0.909 | 0.376 | 0.601 | 0.023 |
| 0.010 | 0.089 | 0.901 | 0.342 | 0.629 | 0.029 |
| 0.010 | 0.101 | 0.889 | 0.305 | 0.656 | 0.038 |
| 0.010 | 0.120 | 0.870 | 0.278 | 0.676 | 0.047 |
| 0.011 | 0.146 | 0.842 | 0.250 | 0.692 | 0.059 |
| 0.015 | 0.184 | 0.801 | 0.190 | 0.717 | 0.093 |
| 0.018 | 0.238 | 0.744 | 0.151 | 0.719 | 0.130 |
| 0.023 | 0.302 | 0.675 | 0.107 | 0.694 | 0.199 |
| 0.040 | 0.431 | 0.528 | 0.074 | 0.639 | 0.287 |

| | UNIQUAC (Δ = 0.0177) | | NRTL (Δ = 0.0411) | |
|---|---|---|---|---|
| $i,j$ | $a_{ij}$ | $a_{ji}$ | $a_{ij}$ | $a_{ji}$ |
| water−ethanol | −373.89 | −3.27 | −470.04 | −739.72 |
| water−TMP | 1280.48 | 559.82 | 2323.09 | 684.06 |
| ethanol−TMP | −115.35 | 333.86 | 278.43 | 150.80 |

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**Table 2. Measured Mole Fractions of the Water (1) + Ethanol (2) + TMP (3) System at 40 °C and Values of the Model Parameters**

| organic phase | | | aqueous phase | | |
|---|---|---|---|---|---|
| $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| 0.003 | 0.000 | 0.997 | 1.000 | 0.000 | 0.000 |
| 0.006 | 0.013 | 0.980 | 0.945 | 0.055 | 0.000 |
| 0.006 | 0.022 | 0.972 | 0.896 | 0.104 | 0.000 |
| 0.006 | 0.030 | 0.964 | 0.827 | 0.173 | 0.000 |
| 0.006 | 0.036 | 0.958 | 0.773 | 0.226 | 0.001 |
| 0.006 | 0.042 | 0.952 | 0.719 | 0.279 | 0.002 |
| 0.007 | 0.064 | 0.929 | 0.626 | 0.369 | 0.005 |
| 0.008 | 0.072 | 0.920 | 0.543 | 0.448 | 0.009 |
| 0.009 | 0.085 | 0.907 | 0.506 | 0.481 | 0.014 |
| 0.009 | 0.093 | 0.898 | 0.461 | 0.519 | 0.020 |
| 0.009 | 0.103 | 0.888 | 0.420 | 0.555 | 0.025 |
| 0.020 | 0.197 | 0.783 | 0.323 | 0.622 | 0.054 |
| 0.026 | 0.253 | 0.721 | 0.269 | 0.649 | 0.081 |
| 0.036 | 0.317 | 0.647 | 0.209 | 0.659 | 0.132 |
| 0.059 | 0.396 | 0.545 | 0.158 | 0.639 | 0.204 |

| | UNIQUAC ($\Delta = 0.0110$) | | NRTL ($\Delta = 0.0176$) | |
|---|---|---|---|---|
| $i,j$ | $a_{ij}$ | $a_{ji}$ | $a_{ij}$ | $a_{ji}$ |
| water–ethanol | −322.77 | 8.49 | −79.64 | −705.92 |
| water–TMP | 1166.73 | 686.81 | 2349.11 | 839.36 |
| ethanol–TMP | −131.50 | 338.74 | 397.11 | 73.84 |

**Table 3. Measured Mole Fractions of the Water (1) + Ethanol (2) + Toluene (3) System at 5 °C and Values of the Model Parameters**

| organic phase | | | aqueous phase | | |
|---|---|---|---|---|---|
| $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| 0.002 | 0.000 | 0.998 | 1.000 | 0.000 | 0.000 |
| 0.005 | 0.011 | 0.984 | 0.950 | 0.050 | 0.000 |
| 0.006 | 0.023 | 0.972 | 0.913 | 0.087 | 0.000 |
| 0.006 | 0.042 | 0.952 | 0.865 | 0.134 | 0.000 |
| 0.009 | 0.065 | 0.926 | 0.815 | 0.181 | 0.004 |
| 0.010 | 0.086 | 0.903 | 0.772 | 0.224 | 0.004 |
| 0.012 | 0.095 | 0.893 | 0.746 | 0.248 | 0.006 |
| 0.014 | 0.107 | 0.879 | 0.721 | 0.270 | 0.009 |
| 0.015 | 0.117 | 0.868 | 0.697 | 0.291 | 0.012 |
| 0.017 | 0.126 | 0.857 | 0.671 | 0.312 | 0.016 |
| 0.019 | 0.137 | 0.844 | 0.645 | 0.334 | 0.021 |
| 0.020 | 0.150 | 0.830 | 0.622 | 0.352 | 0.026 |
| 0.025 | 0.170 | 0.805 | 0.569 | 0.395 | 0.037 |
| 0.026 | 0.178 | 0.796 | 0.542 | 0.413 | 0.045 |
| 0.031 | 0.202 | 0.767 | 0.502 | 0.435 | 0.063 |
| 0.037 | 0.230 | 0.733 | 0.462 | 0.456 | 0.082 |
| 0.046 | 0.256 | 0.698 | 0.424 | 0.474 | 0.102 |
| 0.056 | 0.270 | 0.674 | 0.384 | 0.487 | 0.129 |
| 0.093 | 0.325 | 0.582 | 0.316 | 0.493 | 0.191 |
| 0.105 | 0.345 | 0.550 | 0.286 | 0.494 | 0.220 |

| | UNIQUAC ($\Delta = 0.0028$) | | NRTL ($\Delta = 0.0041$) | |
|---|---|---|---|---|
| $i,j$ | $a_{ij}$ | $a_{ji}$ | $a_{ij}$ | $a_{ji}$ |
| water–ethanol | 271.44 | −165.48 | 262.96 | −215.65 |
| water–toluene | 426.17 | 1959.04 | 3446.71 | 1206.51 |
| ethanol–toluene | −123.17 | 295.49 | 274.71 | 106.43 |

**Table 4. Measured Mole Fractions of the Water (1) + Ethanol (2) + Toluene (3) System at 40 °C and Values of the Model Parameters**

| organic phase | | | aqueous phase | | |
|---|---|---|---|---|---|
| $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| 0.006 | 0.000 | 0.994 | 1.000 | 0.000 | 0.000 |
| 0.007 | 0.028 | 0.966 | 0.944 | 0.056 | 0.000 |
| 0.014 | 0.075 | 0.911 | 0.891 | 0.109 | 0.001 |
| 0.021 | 0.130 | 0.849 | 0.817 | 0.179 | 0.004 |
| 0.034 | 0.186 | 0.780 | 0.743 | 0.245 | 0.012 |
| 0.056 | 0.234 | 0.710 | 0.657 | 0.311 | 0.033 |
| 0.078 | 0.266 | 0.656 | 0.576 | 0.371 | 0.053 |
| 0.125 | 0.299 | 0.576 | 0.497 | 0.400 | 0.104 |
| 0.149 | 0.322 | 0.529 | 0.471 | 0.412 | 0.117 |
| 0.187 | 0.338 | 0.476 | 0.434 | 0.416 | 0.151 |

| | UNIQUAC ($\Delta = 0.0071$) | | NRTL ($\Delta = 0.0052$) | |
|---|---|---|---|---|
| $i,j$ | $a_{ij}$ | $a_{ji}$ | $a_{ij}$ | $a_{ji}$ |
| water–ethanol | 241.45 | −100.05 | 640.43 | −399.26 |
| water–toluene | 165.90 | 1903.57 | 2308.30 | 1012.76 |
| ethanol–toluene | −161.58 | 366.75 | −47.81 | 336.27 |

**Table 5. Measured Mole Fractions of the Water (1) + TAOH (2) + Toluene (3) System at 5 °C and Values of the Model Parameters**

| organic phase | | | aqueous phase | | |
|---|---|---|---|---|---|
| $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| 0.002 | 0.000 | 0.998 | 1.000 | 0.000 | 0.000 |
| 0.004 | 0.014 | 0.982 | 0.995 | 0.005 | 0.000 |
| 0.010 | 0.061 | 0.929 | 0.988 | 0.012 | 0.000 |
| 0.027 | 0.153 | 0.821 | 0.985 | 0.015 | 0.000 |
| 0.058 | 0.257 | 0.685 | 0.982 | 0.018 | 0.000 |
| 0.125 | 0.367 | 0.507 | 0.980 | 0.020 | 0.000 |
| 0.192 | 0.436 | 0.372 | 0.980 | 0.020 | 0.000 |
| 0.261 | 0.457 | 0.282 | 0.977 | 0.023 | 0.000 |
| 0.336 | 0.466 | 0.198 | 0.976 | 0.024 | 0.000 |
| 0.384 | 0.465 | 0.150 | 0.975 | 0.025 | 0.000 |
| 0.429 | 0.458 | 0.112 | 0.975 | 0.025 | 0.000 |
| 0.464 | 0.449 | 0.087 | 0.974 | 0.026 | 0.000 |
| 0.485 | 0.442 | 0.073 | 0.974 | 0.026 | 0.000 |
| 0.514 | 0.430 | 0.056 | 0.973 | 0.027 | 0.000 |
| 0.537 | 0.419 | 0.044 | 0.972 | 0.028 | 0.000 |
| 0.558 | 0.408 | 0.034 | 0.972 | 0.028 | 0.000 |
| 0.584 | 0.392 | 0.023 | 0.971 | 0.029 | 0.000 |
| 0.610 | 0.376 | 0.014 | 0.971 | 0.029 | 0.000 |
| 0.623 | 0.366 | 0.011 | 0.970 | 0.030 | 0.000 |
| 0.680 | 0.320 | 0.000 | 0.968 | 0.032 | 0.000 |

| | UNIQUAC ($\Delta = 0.0009$) | | NRTL ($\Delta = 0.0119$) | |
|---|---|---|---|---|
| $i,j$ | $a_{ij}$ | $a_{ji}$ | $a_{ij}$ | $a_{ji}$ |
| water–TAOH | 79.41 | 121.66 | 1289.44 | −348.80 |
| water–toluene | 512.93 | 1043.51 | 1222.97 | 1416.64 |
| TAOH–toluene | −129.09 | 267.24 | −639.14 | 101.27 |

steps of 0.1 μL. Each calibration was repeated, on the average, five times. The response factor method based on the linear relation between injection size and peak area was then used for sample analysis. However, at very low sample concentrations, calibration was done using the internal standard method with mixtures whose composition was close to that of the samples we were measuring. The amount of each calibration injection was determined gravimetrically using a Mettler AE 160 balance. With these procedures, the detection limit of our equipment was found to be approximately 0.001 mole fraction.

Measurements were made using 0.8 μL samples with a 1 μL syringe, in triplicate, immediately after withdrawl from the equilibrium cell. We estimate the accuracy of our composition measurements to be ±0.002 mole fraction. Once a week, a standard solution was used to check the calibration. Water deionized with Barbstaed NANOpure equipment was used in our measurements. All the chemicals used but ethanol were obtained from the Aldrich Chemical Co. with purities (by weight) of pentane of 99+%, hexane of 99+%, 2,2,4-trimethylpentane of 99.7%, toluene of 99.9+%, and TAOH of 99+%. Ethanol was obtained from the Quantum Chemical Co. at a purity of 99.4+%. All chemicals were used as received.

## Experimental Data

The experimental measurements were made at both at 5 and 40 °C, and the data are presented in the tables as follows. Tables 1 and 2 contain the measured data for the water + ethanol + 2,2,4-trimethylpentane system, Tables 3 and 4 contain the data for the water + ethanol + toluene system, Tables 5 and 6 contain the measured data for the

**Table 6. Measured Mole Fractions of the Water (1) + TAOH (2) + Toluene (3) System at 40 °C and Values of the Model Parameters**

| organic phase | | | aqueous phase | | |
|---|---|---|---|---|---|
| $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| 0.006 | 0.000 | 0.994 | 1.000 | 0.000 | 0.000 |
| 0.018 | 0.123 | 0.859 | 0.995 | 0.005 | 0.000 |
| 0.028 | 0.148 | 0.824 | 0.994 | 0.006 | 0.000 |
| 0.038 | 0.197 | 0.765 | 0.994 | 0.006 | 0.000 |
| 0.059 | 0.255 | 0.686 | 0.993 | 0.007 | 0.000 |
| 0.125 | 0.379 | 0.496 | 0.992 | 0.008 | 0.000 |
| 0.167 | 0.425 | 0.408 | 0.991 | 0.009 | 0.000 |
| 0.218 | 0.461 | 0.321 | 0.990 | 0.010 | 0.000 |
| 0.259 | 0.482 | 0.259 | 0.990 | 0.010 | 0.000 |
| 0.286 | 0.493 | 0.221 | 0.989 | 0.011 | 0.000 |
| 0.357 | 0.503 | 0.140 | 0.988 | 0.012 | 0.000 |
| 0.399 | 0.499 | 0.102 | 0.987 | 0.013 | 0.000 |
| 0.460 | 0.486 | 0.054 | 0.987 | 0.013 | 0.000 |
| 0.494 | 0.473 | 0.033 | 0.986 | 0.014 | 0.000 |
| 0.532 | 0.454 | 0.015 | 0.985 | 0.015 | 0.000 |
| 0.585 | 0.415 | 0.000 | 0.984 | 0.016 | 0.000 |

| | UNIQUAC ($\Delta$ = 0.0005) | | NRTL ($\Delta$ = 0.0013) | |
|---|---|---|---|---|
| i,j | $a_{ij}$ | $a_{ji}$ | $a_{ij}$ | $a_{ji}$ |
| water–TAOH | 166.36 | 90.73 | 1647.27 | −405.74 |
| water–toluene | 572.64 | 813.25 | 2242.71 | 1297.14 |
| TAOH–toluene | 0.019 | 27.53 | 2185.39 | −1369.87 |

**Table 7. Measured Mole Fractions of the Water (1) + TAOH (2) + Hexane (3) System at 5 °C and Values of the Model Parameters**

| organic phase | | | aqueous phase | | |
|---|---|---|---|---|---|
| $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| 0.001 | 0.000 | 0.999 | 1.000 | 0.000 | 0.000 |
| 0.004 | 0.018 | 0.978 | 0.991 | 0.009 | 0.000 |
| 0.005 | 0.048 | 0.947 | 0.987 | 0.013 | 0.000 |
| 0.012 | 0.126 | 0.861 | 0.984 | 0.016 | 0.000 |
| 0.026 | 0.204 | 0.770 | 0.983 | 0.017 | 0.000 |
| 0.051 | 0.303 | 0.646 | 0.980 | 0.020 | 0.000 |
| 0.079 | 0.356 | 0.565 | 0.979 | 0.021 | 0.000 |
| 0.105 | 0.403 | 0.492 | 0.979 | 0.021 | 0.000 |
| 0.146 | 0.441 | 0.413 | 0.979 | 0.021 | 0.000 |
| 0.172 | 0.470 | 0.357 | 0.979 | 0.021 | 0.000 |
| 0.230 | 0.494 | 0.275 | 0.979 | 0.021 | 0.000 |
| 0.265 | 0.503 | 0.233 | 0.979 | 0.021 | 0.000 |
| 0.293 | 0.505 | 0.203 | 0.978 | 0.022 | 0.000 |
| 0.383 | 0.488 | 0.130 | 0.977 | 0.023 | 0.000 |
| 0.433 | 0.467 | 0.100 | 0.975 | 0.025 | 0.000 |
| 0.456 | 0.460 | 0.085 | 0.974 | 0.026 | 0.000 |
| 0.498 | 0.440 | 0.062 | 0.974 | 0.026 | 0.000 |
| 0.533 | 0.415 | 0.052 | 0.973 | 0.027 | 0.000 |
| 0.680 | 0.320 | 0.000 | 0.968 | 0.032 | 0.000 |

| | UNIQUAC ($\Delta$ = 0.0058) | | NRTL ($\Delta$ = 0.0080) | |
|---|---|---|---|---|
| i,j | $a_{ij}$ | $a_{ji}$ | $a_{ij}$ | $a_{ji}$ |
| water–TAOH | 123.24 | 64.89 | 1359.95 | −386.31 |
| water–hexane | 653.37 | 1633.51 | 1720.72 | 1607.53 |
| TAOH–hexane | 104.37 | −19.67 | 3369.76 | −1131.62 |

water + TAOH + toluene system, and Tables 7 and 8 contain data for the water + TAOH + hexane system. In all cases the first table in each set contains the data at 5 °C and the second table at 40 °C. Table 9 contains the measured data for the water + TAOH + pentane system at 5 °C, the only temperature we could study with our equipment for this system because of the high vapor pressure of pentane. Concentrations in the tables indicated to be zero are below our detection limit.

**Table 8. Measured Mole Fractions of the Water (1) + TAOH (2) + Hexane (3) System at 40 °C and Values of the Model Parameters**

| organic phase | | | aqueous phase | | |
|---|---|---|---|---|---|
| $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| 0.003 | 0.000 | 0.997 | 1.000 | 0.000 | 0.000 |
| 0.012 | 0.112 | 0.876 | 0.994 | 0.006 | 0.000 |
| 0.032 | 0.242 | 0.726 | 0.992 | 0.008 | 0.000 |
| 0.083 | 0.363 | 0.555 | 0.990 | 0.010 | 0.000 |
| 0.171 | 0.471 | 0.359 | 0.989 | 0.011 | 0.000 |
| 0.235 | 0.508 | 0.257 | 0.988 | 0.012 | 0.000 |
| 0.491 | 0.465 | 0.044 | 0.986 | 0.014 | 0.000 |
| 0.585 | 0.415 | 0.000 | 0.984 | 0.016 | 0.000 |

| | UNIQUAC ($\Delta$ = 0.0005) | | NRTL ($\Delta$ = 0.0017) | |
|---|---|---|---|---|
| i,j | $a_{ij}$ | $a_{ji}$ | $a_{ij}$ | $a_{ji}$ |
| water–TAOH | 179.45 | 69.06 | 1523.70 | −372.08 |
| water–hexane | 1884.23 | 5884.32 | 1536.20 | 2848.16 |
| TAOH–hexane | 44.99 | 38.62 | 4580.72 | −1552.34 |

**Table 9. Measured Mole Fractions of the Water (1) + Ethanol (2) + Pentane (3) System at 5 °C and Values of the Model Parameters**

| organic phase | | | aqueous phase | | |
|---|---|---|---|---|---|
| $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| 0.001 | 0.000 | 0.999 | 1.000 | 0.000 | 0.000 |
| 0.006 | 0.065 | 0.928 | 0.987 | 0.013 | 0.000 |
| 0.033 | 0.231 | 0.736 | 0.982 | 0.018 | 0.000 |
| 0.071 | 0.329 | 0.600 | 0.982 | 0.018 | 0.000 |
| 0.131 | 0.415 | 0.455 | 0.978 | 0.022 | 0.000 |
| 0.136 | 0.423 | 0.442 | 0.978 | 0.022 | 0.000 |
| 0.205 | 0.470 | 0.324 | 0.977 | 0.023 | 0.000 |
| 0.277 | 0.491 | 0.231 | 0.976 | 0.024 | 0.000 |
| 0.375 | 0.487 | 0.138 | 0.975 | 0.025 | 0.000 |
| 0.390 | 0.482 | 0.128 | 0.975 | 0.025 | 0.000 |
| 0.438 | 0.472 | 0.089 | 0.974 | 0.026 | 0.000 |
| 0.510 | 0.444 | 0.046 | 0.973 | 0.027 | 0.000 |
| 0.569 | 0.411 | 0.019 | 0.972 | 0.028 | 0.000 |
| 0.680 | 0.320 | 0.000 | 0.968 | 0.032 | 0.000 |

| | UNIQUAC ($\Delta$ = 0.0011) | | NRTL ($\Delta$ = 0.0124) | |
|---|---|---|---|---|
| i,j | $a_{ij}$ | $a_{ji}$ | $a_{ij}$ | $a_{ji}$ |
| water–TAOH | 93.44 | 105.92 | 1208.89 | −313.22 |
| water–pentane | 989.57 | 1678.82 | 708.75 | 1419.08 |
| TAOH–pentane | 24.53 | 62.37 | −1504.80 | −194.74 |

The measured liquid–liquid phase behavior for the systems studied are shown as Gibbs triangles in Figures 1–3. From the data in the tables and figures, we see that for the systems containing ethanol, type 1 liquid–liquid equilibrium behavior is found and that increasing the concentration of this oxygenate resulted in increasing water solubility in the organic phase and increasing hydrocarbon solubility in the aqueous phase. Also, for both ethanol-containing mixtures, the liquid–liquid two-phase region decreased with increasing temperature. In contrast, the liquid–liquid two-phase region increases with increasing temperature in the type 2 TAOH-containing systems as a result of the decreasing solubility of TAOH in water with increasing temperature. Also there is less temperature dependence of the effect of TAOH addition on the hydrocarbon–water mutual solubility than is the case with ethanol.

## Modeling of the Experimental Data

We have correlated our data with the NRTL (nonrandom two-liquid) model of Renon and Prausnitz (1968) and the UNIQUAC model of Abrams and Prausnitz (1975). Using six adjustable parameters (two parameters for each pair of components and keeping the value of $\alpha$ of the NRTL model equal to 0.20) at each temperature, these two models can fit the general features of the experimental data very well, both in the location of the binodal curve and in the slope of the tie lines. The type 2 phase behavior of the TAOH-containing systems is more accurately fit that the type 1 ethanol-containing systems. The fit of the UNI-

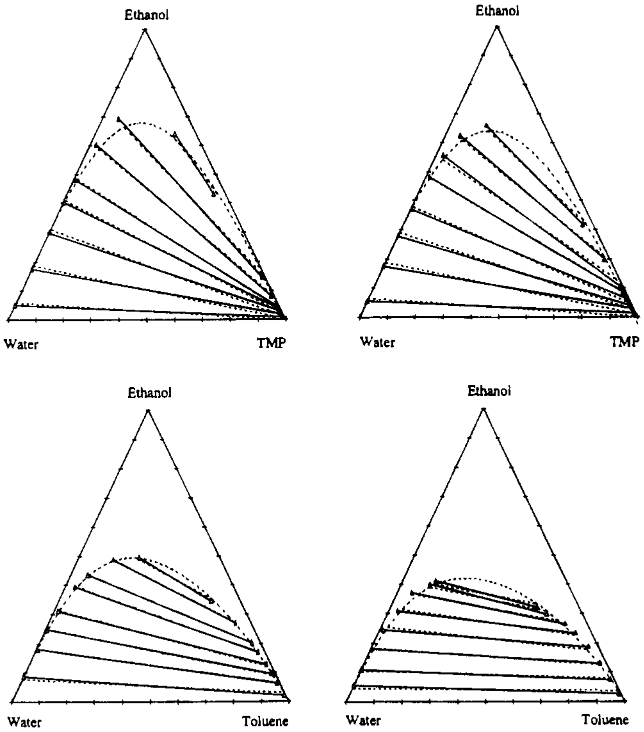

**Figure 1.** Liquid–liquid equilibrium data for the system ethanol + water + 2,2,4-trimethylpentane at 5 and 40 °C, respectively, and for the system ethanol + water + toluene at 5 and 40 °C (only some of the tie lines are shown). The triangular points are the experimental data, and the solid lines are the measured tie lines. The dashed straight lines are the tie lines resulting from the UNIQUAC correlation of each isotherm separately, and the curved, dashed line is the binodal curve calculated from that model.

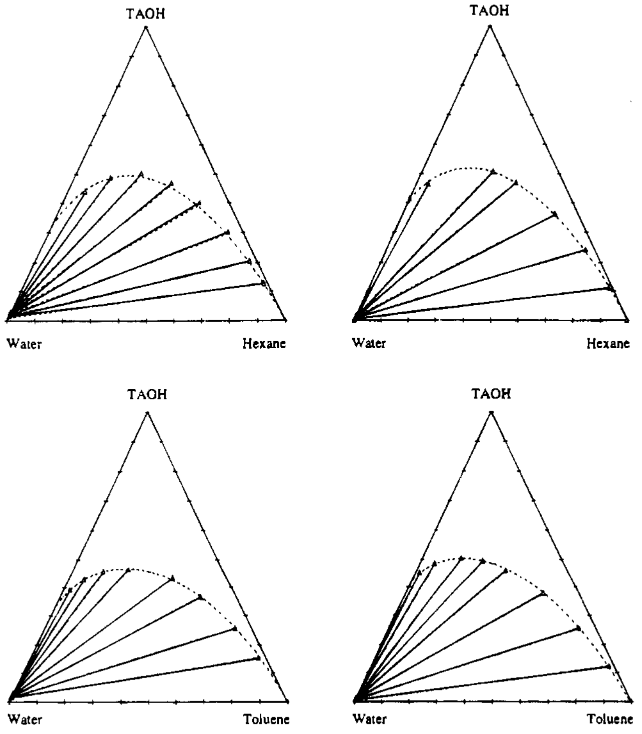

**Figure 2.** Liquid–liquid equilibrium data for the system TAOH + water + hexane at 5 and 40 °C, respectively, and for the system TAOH + water + toluene at 5 and 40 °C (only some of the tie lines are shown). Legend as in Figure 1.

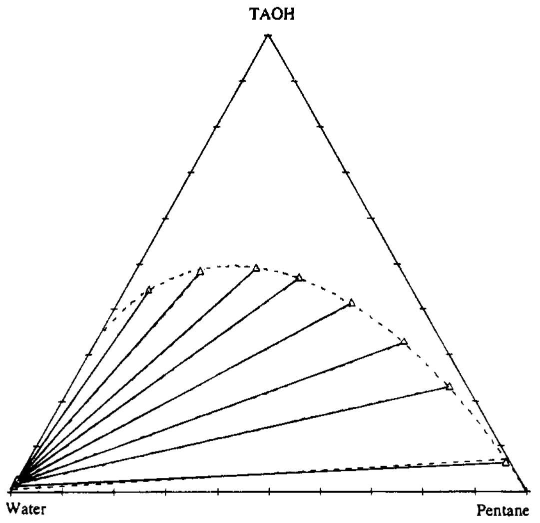

**Figure 3.** Liquid–liquid equilibrium data for the system TAOH + water + pentane at 5 °C (only some of the measured tie lines are shown). Legend as in Figure 1.

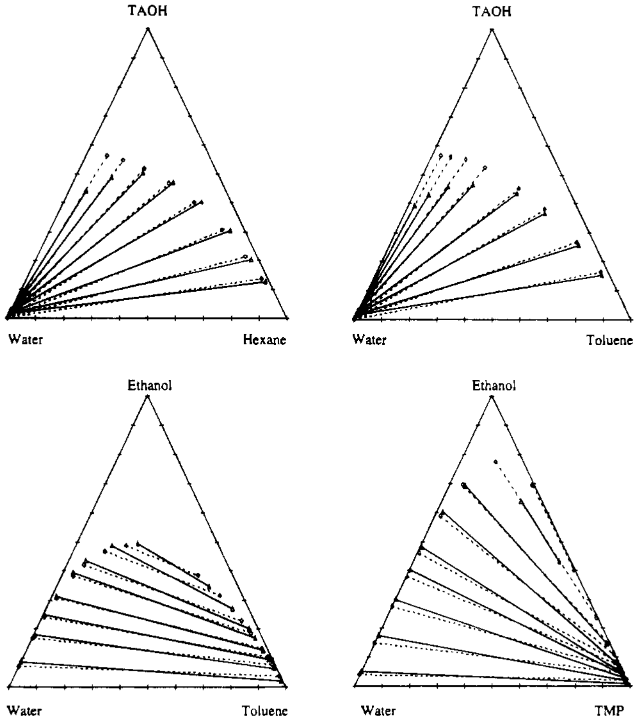

**Figure 4.** Measured liquid–liquid equilibrium data and UNIFAC predictions for the systems TAOH + water + hexane, TAOH + water + toluene, ethanol + water + toluene, and ethanol + water + 2,2,4-trimethylpentane, all at 5 °C. The triangular points are the experimental data, and the solid lines are the tie lines connecting these points. The dashed straight lines ending in diamonds are the predicted tie lines resulting from the UNIFAC liquid–liquid equilibrium model.

QUAC model was slightly better than that obtained with the NRTL model; the UNIQUAC correlations have been included in Figures 1–3. The model correlation parameters are included in Tables 1–9, as is the following measure of the accuracy of the correlations:

$$\Delta = \sum_i \sum_j \sum_k [x_{ijk}^{\text{exp}} - x_{ijk}^{\text{calc}}]^2 \qquad (1)$$

where $x$ is the mole fraction, and the subscripts $i, j$, and $k$ designate the component, phase, and tie line, respectively. As can be seen from the tables, the correlation obtained with the UNIQUAC model is more accurate for the systems studied than that obtained with the NRTL model.

In Figure 4 we compare our experimental data for two ethanol-containing mixtures and two TAOH-containing mixtures at 5 °C with the predictions of liquid–liquid UNIFAC model (Magnussen et al., 1981). Similar results were obtained for the other mixture studied and at 40 °C. We see that the liquid–liquid UNIFAC predictions are generally qualitatively correct with regard to the location of the binodal curve and the slope of the tie lines but not quantitatively accurate. However, as seen in the last of the diagrams in Figure 4, the liquid–liquid UNIFAC model erroneously predicts type 2 phase behavior to occur for the water + ethanol + 2,2,4-trimethylpentane system at 5 °C as a result of incorrectly predicting that ethanol and 2,2,4-trimethylpentane should be only partially miscible.

## Conclusions

Liquid–liquid equilibrium data at 5 and at 40 °C are reported for two water + hydrocarbon + ethanol mixtures and for two water + hydrocarbon + TAOH mixtures and at 5 °C for the water + pentane + TAOH mixture. The ethanol-containing mixtures exhibit type 1 liquid–liquid phase behavior with the two-phase region decreasing with increasing temperature, while the TAOH-containing mixtures exhibit type 2 liquid–liquid phase behavior with the two-phase region increasing with increasing temperature. The data we have measured can be reasonably well correlated with either the NRTL and UNIQUAC models, though the latter is slightly more accurate. However, the liquid–liquid UNIFAC model leads to only qualitatively correct predictions for the liquid–liquid equilibria of the systems studied here.

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