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Liquid–Liquid Equilibria of Fuel Oxygenate + Water + Hydrocarbon Mixtures. 2

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The liquid–liquid equilibria of water + *n*-decane, water + *n*-hexadecane, and water + methylcyclohexane have been measured separately with the two oxygenates 2-methoxy-2-methylbutane (tertiary amyl methyl ether or TAME) and 2-methyl-2-butanol (tertiary amyl alcohol or TAOH) at 25 °C. All of these systems exhibit type 2 liquid–liqud phase diagrams, though the shapes of the diagrams for the TAME and TAOH systems are quite different because of the much higher solubility of water in TAOH than TAME. One of the observations from our experimental data is that the addition of either TAME or TAOH to a hydrocarbon + water mixture results in an increased water solubility in the hydrocarbon phase and a decreased hydrocarbon solubility in the aqueous phase. This observation may be important when both the water pollution potential of possible gasoline reformulations and the sensitivity of the gasoline to water are assessed. We have found that the general features of the liquid–liquid phase diagrams can be accurately correlated with either the NRTL or UNIQUAC model, though some of the high dilution concentrations are incorrectly described. Finally, the liquid–liquid UNIFAC model leads to qualitatively correct predictions for the liquid–liquid equilibria of the systems studied.

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. However, the addition of an oxygenate to gasoline also may affect the mutual hydrocarbon–water solubility, resulting in either greater or less likelihood of an aqueous phase appearing in the gasoline tank or fuel line or of greater hydrocarbon concentration in aquifers and other bodies of water as a result of a spill.

To assess the effect of oxygenate addition on hydrocarbon–water mutual solubility, we have measured the liquid–liquid equilibrium phase diagrams of six water + hydrocarbon + oxygenate mixtures at 25 °C. The six systems we have studied are water + decane, water + hexadecane, and water + methylcyclohexane separately with the two oxygenates 2-methoxy-2-methylbutane (tertiary amyl methyl ether or TAME) and 2-methyl-2-butanol (tertiary amyl alcohol or TAOH). The experimental data were correlated with the NRTL (*1*) and UNIQUAC (*2*) models, and the results of our measurements are compared with the predictions of the UNIFAC liquid–liquid equilibrium model (*3*).

Measurements

All measurements were carried out in liquid–liquid equilibrium cells described earlier (*4*), largely with the experimental protocol described therein except for changes as noted below. The equilibrium vessels were thermostatically jacketed to maintain temperature constant to within ±0.1 K. Samples of the aqueous and hydrocarbon phases were withdrawn using a Perfectum Model MicroMate hypodermic syringe, and analysis was done using a Hewlett-Packard Model 5730 gas chromatograph with a thermal conductivity detector and a Poropak Q column of 6 ft length and $^1/_8$ in. diameter using the conditions described earlier. Calibration of the gas chromatograph was done by determining the response of the gas chromatograph and integrator system to injections starting at 0.5 μL and increasing in 6–10 steps of this amount. For accuracy, the amount of each injection was determined gravimetrically using a Mettler H 80 balance, and 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. We estimate the accuracy of our measurements to generally be ±0.002 in mole fraction and ±2% for the dilute solutions.

In the measurements here, to more accurately determine the small concentrations of water in the hydrocarbon-rich phase, Karl Fischer titration (*5*) was used. We used a Metrohm Model 633 automatic Karl Fischer titrator, with a Model 645 Multi-Dosimat and Model 522 exchange unit, with Karl Fischer titrant obtained from Aldrich. Since the properties of the titrant change with time, calibration was repeatedly done using a gravimetrically prepared solution of 5 wt % water in anhydrous acetic acid (from Aldrich) to obtain a linear relation between the milligrams of water reacted per milliliter of titrant. In the analysis of our solutions, 12 mL of methanol (Aldrich, 99.9%) was first placed in the titration vessel and titrated to the end point, and then 1 mL of sample was injected and titrated. If the water content of the sample was high, the analysis of the sample was repeated with a smaller sample size. Every sample was analyzed three times, and the amount of

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Table 1. Measured Mole Fractions of the System Water (1) + TAME (2) + Hexadecane (3) at 25 °C[a]

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.75×10^{-3}	0.000	0.999	1.000	0	2.94×10^{-09}
1.03×10^{-3}	0.105	0.894	1.000	8.34×10^{-05}	2.23×10^{-09}
1.40×10^{-3}	0.163	0.836	1.000	9.08×10^{-05}	*[b]
1.71×10^{-3}	0.223	0.776	0.999	4.66×10^{-04}	*[b]
2.32×10^{-3}	0.316	0.682	0.999	6.64×10^{-04}	*[b]
2.60×10^{-3}	0.344	0.653	0.999	7.23×10^{-04}	*[b]
3.25×10^{-3}	0.494	0.503	0.999	1.07×10^{-03}	*[b]
4.54×10^{-3}	0.647	0.349	0.999	1.35×10^{-03}	*[b]
4.80×10^{-3}	0.653	0.342	0.999	1.37×10^{-03}	*[b]
4.82×10^{-3}	0.671	0.324	0.999	1.43×10^{-03}	*[b]
4.99×10^{-3}	0.671	0.324	0.999	1.41×10^{-03}	*[b]
5.20×10^{-3}	0.676	0.319	0.999	1.42×10^{-03}	*[b]
5.52×10^{-3}	0.685	0.310	0.999	1.44×10^{-03}	*[b]
1.22×10^{-2}	0.834	0.154	0.998	1.75×10^{-03}	*[b]
1.32×10^{-2}	0.843	0.144	0.998	1.77×10^{-03}	*[b]
1.59×10^{-2}	0.862	0.122	0.998	1.81×10^{-03}	*[b]
1.83×10^{-2}	0.885	0.096	0.998	1.86×10^{-03}	*[b]
2.50×10^{-2}	0.939	0.036	0.998	1.77×10^{-03}	*[b]
3.91×10^{-2}	0.961	0.000	0.998	2.00×10^{-03}	0

[a] NRTL correlation parameters: water–TAME, $a_{ij} = 1566.5$, $a_{ji} = 493.2$; water–hexadecane, $a_{ij} = 2710.4$, $a_{ji} = 2258.7$; TAME–hexadecane, $a_{ij} = 6020.6$, $a_{ji} = -221.4$. UNIQUAC correlation parameters: water–TAME, $a_{ij} = 36.8$, $a_{ji} = 725.1$; water–hexadecane, $a_{ij} = 364.2$, $a_{ji} = 4624.7$; TAME–hexadecane, $a_{ji} = -436.1$, $a_{ji} = -201.8$. [b] * indicates trace, below our limit of quantitative detection.

Table 2. Measured Mole Fractions of the System Water (1) + TAME (2) + Decane (3) at 25 °C[a]

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.54×10^{-3}	0.000	0.999	1.000	0	6.27×10^{-09}
4.44×10^{-3}	0.148	0.848	1.000	1.96×10^{-04}	4.24×10^{-09}
6.67×10^{-3}	0.196	0.797	1.000	4.46×10^{-04}	3.03×10^{-09}
7.57×10^{-3}	0.239	0.754	0.999	5.07×10^{-04}	2.80×10^{-09}
9.84×10^{-3}	0.333	0.657	0.999	6.96×10^{-04}	*[b]
1.06×10^{-2}	0.366	0.624	0.999	7.63×10^{-04}	*[b]
1.13×10^{-2}	0.396	0.593	0.999	8.27×10^{-04}	*[b]
1.15×10^{-2}	0.412	0.577	0.999	8.63×10^{-04}	*[b]
1.02×10^{-2}	0.428	0.562	0.999	9.49×10^{-04}	*[b]
1.07×10^{-2}	0.472	0.517	0.999	9.88×10^{-04}	*[b]
1.19×10^{-2}	0.511	0.477	0.999	1.06×10^{-03}	*[b]
1.41×10^{-2}	0.562	0.424	0.999	1.17×10^{-03}	*[b]
1.70×10^{-2}	0.677	0.306	0.999	1.40×10^{-03}	*[b]
2.25×10^{-2}	0.770	0.208	0.998	1.59×10^{-03}	*[b]
2.22×10^{-2}	0.791	0.186	0.998	1.61×10^{-03}	*[b]
2.80×10^{-2}	0.814	0.158	0.998	1.57×10^{-03}	*[b]
3.07×10^{-2}	0.857	0.112	0.998	1.66×10^{-03}	*[b]
3.52×10^{-2}	0.902	0.063	0.998	1.67×10^{-03}	*[b]
3.81×10^{-2}	0.962	0.000	0.998	1.98×10^{-03}	0

[a] NRTL correlation parameters: water–TAME, $a_{ij} = 1568.88$, $a_{ji} = 486.3$; water–decane, $a_{ij} = 2318.56$, $a_{ji} = 1244.7$; TAME–decane, $a_{ji} = 2192.82$, $a_{ji} = -757.7$. UNIQUAC correlation parameters: water–TAME, $a_{ij} = 87.6$, $a_{ji} = 664.0$; water–decane; $a_{ij} = 1504.5$, $a_{ji} = 981.6$; TAME–decane, $a_{ij} = -151.9$, $a_{ji} = 178.2$. [b] * indicates trace, below our limit of quantitative detection.

Table 3. Measured Mole Fractions of the System Water (1) + TAME (2) + Methylcyclohexane (3) at 25 °C[a]

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
1.92×10^{-3}	0.000	0.998	1.000	0.000	2.33×10^{-06}
2.64×10^{-3}	0.054	0.943	1.000	0.14×10^{-3}	2.20×10^{-06}
3.11×10^{-3}	0.091	0.904	1.000	0.23×10^{-3}	2.14×10^{-06}
3.71×10^{-3}	0.132	0.864	1.000	0.31×10^{-3}	2.05×10^{-06}
4.59×10^{-3}	0.237	0.759	0.999	0.53×10^{-3}	1.91×10^{-06}
4.92×10^{-3}	0.243	0.752	0.999	0.53×10^{-3}	1.68×10^{-06}
8.33×10^{-3}	0.340	0.651	0.999	0.70×10^{-3}	1.60×10^{-06}
9.06×10^{-3}	0.383	0.608	0.999	0.78×10^{-3}	1.60×10^{-06}
1.14×10^{-2}	0.454	0.535	0.999	0.82×10^{-3}	1.50×10^{-06}
0.99×10^{-2}	0.470	0.520	0.999	0.92×10^{-3}	1.44×10^{-06}
1.18×10^{-2}	0.516	0.472	0.999	1.00×10^{-3}	1.32×10^{-06}
1.34×10^{-2}	0.545	0.442	0.999	1.09×10^{-3}	1.19×10^{-06}
1.38×10^{-2}	0.580	0.407	0.999	1.09×10^{-3}	1.10×10^{-06}
1.71×10^{-2}	0.614	0.369	0.999	1.17×10^{-3}	1.07×10^{-06}
1.82×10^{-2}	0.656	0.325	0.999	1.39×10^{-3}	6.02×10^{-07}
2.02×10^{-2}	0.679	0.300	0.999	1.37×10^{-3}	6.05×10^{-07}
2.22×10^{-2}	0.716	0.262	0.999	1.36×10^{-3}	7.82×10^{-07}
2.57×10^{-2}	0.752	0.222	0.999	1.48×10^{-3}	8.33×10^{-07}
2.99×10^{-2}	0.812	0.158	0.998	1.53×10^{-3}	1.08×10^{-07}
3.24×10^{-2}	0.826	0.142	0.998	1.60×10^{-3}	9.86×10^{-08}
3.68×10^{-2}	0.909	0.054	0.998	1.82×10^{-3}	5.70×10^{-08}
4.02×10^{-2}	0.960	0.000	0.998	2.12×10^{-3}	0

[a] NRTL correlation parameters: water–TAME, $a_{ij} = 1511.1$, $a_{ji} = 472.6$; water–methylcyclohexane, $a_{ij} = 2078.1$, $a_{ji} = 1410.9$; TAME–methylcyclohexane, $a_{ij} = 684.4$, $a_{ji} = -451.2$. UNIQUAC correlation parameters: water–TAME, $a_{ji} = 109.6$, $a_{ji} = 638.1$; water–methylcyclohexane, $a_{ij} = 378.6$, $a_{ji} = 1081.0$; TAME–methylcyclohexane, $a_{ij} = 405.9$, $a_{ji} = -167.9$.

Table 4. Measured Mole Fractions of the System Water (1) + TAOH (2) + Hexadecane (3) at 25 °C[a]

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.74×10^{-3}	0.000	0.999	1.000	0.000	2.98×10^{-09}
4.32×10^{-3}	0.022	0.974	0.999	1.20×10^{-3}	2.70×10^{-09}
7.18×10^{-3}	0.068	0.925	0.998	2.11×10^{-3}	2.62×10^{-09}
0.029	0.192	0.780	0.997	3.01×10^{-3}	2.47×10^{-09}
0.044	0.296	0.660	0.996	3.83×10^{-3}	2.38×10^{-09}
0.059	0.330	0.611	0.996	4.05×10^{-3}	2.27×10^{-09}
0.068	0.359	0.573	0.996	4.44×10^{-3}	2.23×10^{-09}
0.081	0.375	0.544	0.996	4.48×10^{-3}	*[b]
0.115	0.471	0.414	0.996	4.23×10^{-3}	*[b]
0.159	0.498	0.343	0.995	5.16×10^{-3}	*[b]
0.195	0.509	0.296	0.995	5.23×10^{-3}	*[b]
0.212	0.516	0.272	0.995	5.33×10^{-3}	*[b]
0.357	0.509	0.134	0.994	6.18×10^{-3}	*[b]
0.422	0.501	0.077	0.994	5.90×10^{-3}	*[b]
0.454	0.477	0.068	0.995	4.72×10^{-3}	*[b]
0.492	0.456	0.052	0.995	5.49×10^{-3}	*[b]
0.600	0.400	0.000	0.992	8.32×10^{-3}	0

[a] NRTL correlation parameters: water–TAOH, $a_{ij} = 1446.8$, $a_{ji} = -360.3$; water–hexadecane; $a_{ij} = 1469.9$, $a_{ji} = 1100.5$; TAOH–hexadecane, $a_{ij} = 4069.5$, $a_{ji} = -1548.6$. UNIQUAC correlation parameters: water–TAOH, $a_{ij} = 330.5$, $a_{ji} = -53.4$; water–hexadecane, $a_{ij} = 848.5$, $a_{ji} = 18724$; TAOH–hexadecane, a_{ij} -174.6, $a_{ji} = 357.5$. [b] * indicates trace, below our limit of quantitative detection.

sample injected was determined gravimetrically by weighing the syringe before and after each injection. The accuracy of the Karl Fischer titration results is probably of the order of 3%.

Water deionized with Barbstaed NANOpure equipment was used in our measurements. All of the chemicals used were obtained from Aldrich Chemical Co. with the purities of *n*-decane at 99+%, *n*-hexadecane at 99%, methylcyclohexane at 99%, TAME at 94%, and TAOH at 99+%. With the exception of TAME, all chemicals were used as received. The TAME was first distilled at high reflux on a 100-theoretical plate column and then stored over type 4A molecular sieves. Its purity was then found to be 99.7% by gas chromatographic analysis with both flame ionization and thermal conductivity detectors.

Experimental Data

The experimental data are presented in Tables 1–3 for water–hydrocarbon mixtures containing TAME and in Tables 4–6 for mixtures containing TAOH. Concentrations in the tables indicated to be zero are below our detection limit. The data for these mixtures are also shown in the

Table 5. Measured Mole Fractions of the System Water (1) + TAOH (2) + Decane (3) at 25 °C[a]

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.52×10^{-3}	0.000	0.999	1.000	0.000	6.13×10^{-09}
4.00×10^{-3}	0.025	0.971	0.998	1.63×10^{-3}	5.99×10^{-09}
7.37×10^{-3}	0.053	0.940	0.998	2.19×10^{-3}	5.78×10^{-09}
0.018	0.138	0.845	0.997	3.45×10^{-3}	5.23×10^{-09}
0.019	0.155	0.825	0.996	4.21×10^{-3}	4.87×10^{-09}
0.037	0.229	0.733	0.995	4.63×10^{-3}	3.54×10^{-09}
0.046	0.264	0.690	0.995	4.75×10^{-3}	2.84×10^{-09}
0.058	0.302	0.640	0.995	4.91×10^{-3}	2.12×10^{-09}
0.093	0.374	0.533	0.995	5.23×10^{-3}	*[b]
0.113	0.404	0.484	0.994	5.57×10^{-3}	*[b]
0.132	0.415	0.453	0.994	5.76×10^{-3}	*[b]
0.175	0.464	0.360	0.994	6.20×10^{-3}	*[b]
0.201	0.484	0.315	0.994	6.24×10^{-3}	*[b]
0.238	0.493	0.269	0.994	6.42×10^{-3}	*[b]
0.300	0.505	0.195	0.993	6.57×10^{-3}	*[b]
0.402	0.480	0.117	0.993	6.62×10^{-3}	*[b]
0.445	0.468	0.087	0.993	6.59×10^{-3}	*[b]
0.464	0.469	0.067	0.993	6.93×10^{-3}	*[b]
0.534	0.426	0.040	0.993	7.32×10^{-3}	*[b]
0.585	0.395	0.020	0.993	7.48×10^{-3}	*[b]
0.619	0.381	0.000	0.992	8.30×10^{-3}	0

[a] NRTL correlation parameters: water−TAOH, $a_{ij} = 1524.3$, $a_{ji} = -418.4$; water−decane, $a_{ij} = 1788.6$, $a_{ji} = 1007.4$; TAOH−decane, $a_{ij} = 3568.2$, $a_{ji} = -1500.5$. UNIQUAC correlation parameters: water−TAOH, $a_{ij} = 317.4$, $a_{ji} = -65.2$; water−decane, $a_{ij} = 8145.3$, $a_{ji} = 4952.4$; TAOH−decane, $a_{ji} = -69.0$, $a_{ji} = 1625$. [b] * indicates trace, below our limit of quantitative detection.

Table 6. Measured Mole Fractions of the System Water (1) + TAOH (2) + Methylcyclohexane (3) at 25 °C[a]

organic phase			aqueous phase		
x_1	x_2	x_3	x_1	x_2	x_3
0.82×10^{-3}	0.000	0.999	1.000	0.000	2.62×10^{-06}
6.22×10^{-3}	0.023	0.971	0.999	1.09×10^{-3}	2.32×10^{-06}
0.013	0.093	0.893	0.997	2.80×10^{-3}	2.10×10^{-06}
0.033	0.168	0.799	0.997	3.40×10^{-3}	1.99×10^{-06}
0.063	0.264	0.673	0.996	4.11×10^{-3}	1.65×10^{-06}
0.073	0.283	0.644	0.996	4.25×10^{-3}	1.42×10^{-06}
0.099	0.328	0.573	0.995	4.77×10^{-3}	9.99×10^{-07}
0.106	0.342	0.552	0.995	4.72×10^{-3}	9.59×10^{-07}
0.134	0.381	0.485	0.995	5.23×10^{-3}	8.60×10^{-07}
0.170	0.403	0.427	0.994	5.56×10^{-3}	8.13×10^{-07}
0.209	0.442	0.349	0.994	6.14×10^{-3}	7.33×10^{-07}
0.227	0.441	0.333	0.994	6.08×10^{-3}	7.43×10^{-07}
0.252	0.448	0.300	0.994	6.18×10^{-3}	7.21×10^{-07}
0.309	0.472	0.219	0.993	6.52×10^{-3}	6.86×10^{-07}
0.366	0.474	0.160	0.993	6.56×10^{-3}	6.41×10^{-07}
0.420	0.471	0.109	0.993	6.67×10^{-3}	5.88×10^{-07}
0.438	0.473	0.090	0.993	6.95×10^{-3}	5.45×10^{-07}
0.491	0.454	0.056	0.993	7.24×10^{-3}	2.31×10^{-07}
0.582	0.400	0.018	0.992	7.79×10^{-3}	6.41×10^{-08}
0.624	0.376	0.000	0.992	8.27×10^{-3}	0

[a] NRTL correlation parameters: water−TAOH, $a_{ij} = 1678.3$, $a_{ji} = -460.8$; water−methylcyclohexane, $a_{ij} = 2013.7$, $a_{ji} = 1432.7$; TAOH−methylcyclohexane, $a_{ij} = 3271.8$, $a_{ji} = -1653.9$. UNIQUAC correlation parameters: water−TAOH, $a_{ij} = 252.9$, $a_{ji} = -5.46$; water−methylcyclohexane, $a_{ij} = 673.2$, $a_{ji} = 1342.7$; TAOH−methylcyclohexane, $a_{ij} = -240.9$, $a_{ji} = -116.1$.

form of Gibbs triangles in Figure 1 for mixtures with TAME and in Figure 2 for mixtures with TAOH. From the data in the tables we see that for the type 2 liquid−liquid equilibria found here, increasing concentration of either of the oxygenates studied here results in increasing water solubility in the organic phase and decreasing hydrocarbon solubility in the aqueous phase. Therefore, the addition of these oxygenates will not increase the likelihood of the formation of an aqueous phase in gasoline tanks or the hydrocarbon solubility in water.

The averages of our measured values for the solubility of water in MCH and of MCH in water of 0.87×10^{-3} and 2.48×10^{-6}, respectively, are in reasonable agreement with the values of 0.79×10^{-3} and 2.57×10^{-6} reported by McAuliffe (*5*). Also, our average measured values for the water solubility in decane and hexadecane of 0.53×10^{-3} and 0.745×10^{-3}, respectively, are close to the values of 0.568×10^{-3} and 0.678×10^{-3} reported by Schatzberg (*6*).

Modeling of the Experimental Data

We have correlated our data with the NRTL (nonrandom two-liquid) model of Renon and Prausnitz (*1*) and with the UNIQUAC model of Abrams and Prausnitz (*2*). The excess Gibbs free energy of mixing g^E of the NRTL model is

$$\frac{g^E}{RT} = \sum_{i=1}^{3} x_i \frac{\sum_{j=1}^{3} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{3} G_{li} x_l}$$

$$\text{with } \tau_{ji} = \frac{\lambda_{ji} - \lambda_{ij}}{RT} = \frac{\alpha_{ji}}{T} \text{ and } G_{ji} = \exp(-\alpha\tau_{ji}) \qquad (1)$$

where R is the gas constant, T is the absolute temperature, we have set α equal to 0.2, and a_{ij} and a_{ji} are the two adjustable parameters in the model for each binary pair that we find from correlation. The excess Gibbs free energy of the UNIQUAC model is

$$\frac{g^g}{RT} = \sum_{i=1}^{3} x_i \ln\frac{\varphi_i}{\phi_i} + 5\sum_{i=11}^{3} x_i q_i \ln\frac{\theta_i}{\varphi_i} - \sum_{i=1}^{3} x_i q_i \ln(\sum_{i=1}^{3} q_j \tau_{ij}) \qquad (2)$$

$$\text{with } \tau_{ji} = \exp\left(-\frac{u_{ji} - u_{ij}}{RT}\right) = \exp\left(-\frac{a_{ji}}{T}\right)$$

Here θ_i and φ_i are the volume fraction and area fraction of species i, respectively, calculated as described in ref 3, and a_{ij} and a_{ji} are the two adjustable parameters in the model for each binary pair.

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. Indeed, to the scale of Figures 1 and 2, there is very little difference visible between the correlations and the experimental data. In general, the UNIQUAC fit was slightly better than that obtained with the NRTL model. However, the correlation does not produce accurate values for solubility of the hydrocarbon in the aqueous phase as a function of oxygenate concentration.

In Figure 1 we also compare some of our experimental data for the TAME-containing mixtures with the liquid−liquid UNIFAC model (*4*). Similar results for the TAOH-containing systems are given in Figure 2. We see that in both cases the liquid−liquid UNIFAC predictions are qualitatively correct with regard to the location of the binodal curve and the slope of the tie lines, though not quantitatively accurate. Also, the predictions of the hydrocarbon and oxygenate solubility in the aqueous phase are less accurate than the correlations discussed earlier.

Conclusions

Liquid−liquid equilibrium data at 25 °C are reported for three water + hydrocarbon mixtures separately with the oxygenates TAME and TAOH. All of these mixtures form type 2 liquid−liquid phase diagrams. As a result of

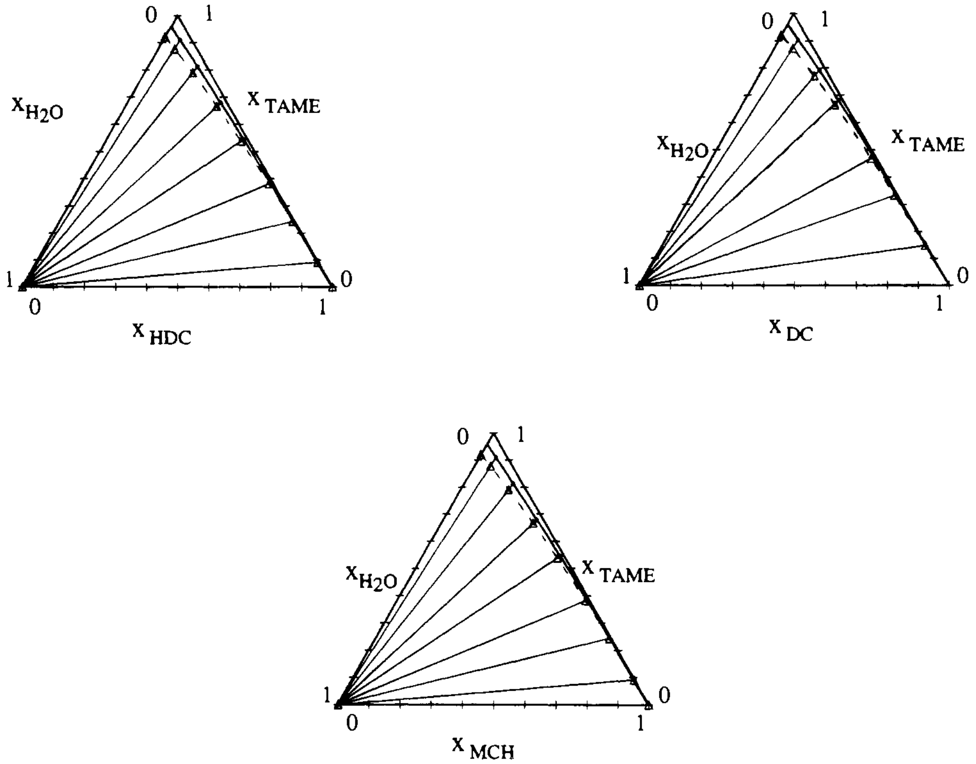

Figure 1. Selected tie lines from our experimental data and UNIFAC predictions for the three systems of this study containing TAME. The dashed lines and triangles are the UNIFAC predictions, while the solid lines are the experimental data.

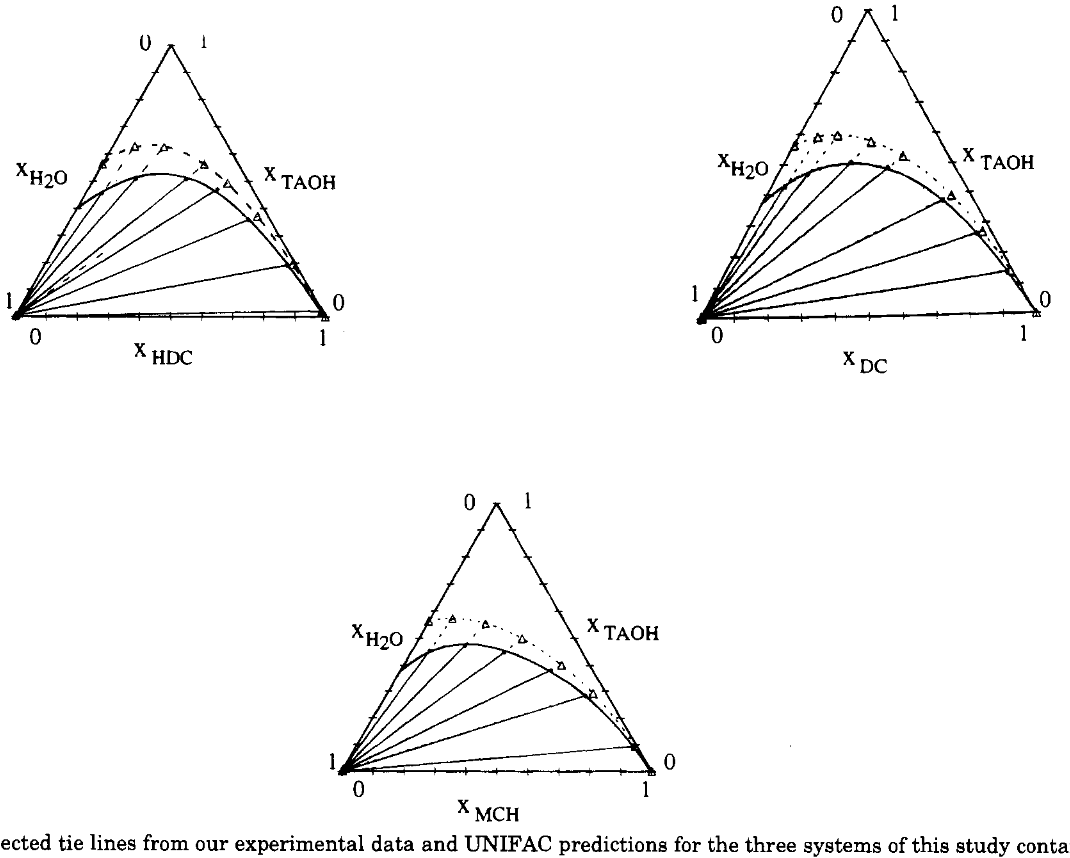

Figure 2. Selected tie lines from our experimental data and UNIFAC predictions for the three systems of this study containing TAOH. The dashed lines and triangles are the UNIFAC predictions, while the solid lines are the experimental data.

the phase diagrams produced, the addition of either TAME or TAOH to a water + hydrocarbon mixture leads to a greatly increased solubility of water in the hydrocarbon phase and a decrease in hydrocarbon solubility in the water phase. The general features of the phase diagrams we have measured can be correlated with the NRTL and UNIQUAC models. However, these correlations are not of high accuracy for the very dilute hydrocarbon and oxygenate concentrations in the aqueous phase. Finally, the liquid–liquid UNIFAC model leads to reasonable, qualitatively correct predictions for the liquid–liquid equilibria of the systems studied here.

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