J. Chem. Eng. Data **1995,** *40,* 315−320

Liquid−Liquid Equilibria of Fuel Oxygenate + Water + Hydrocarbon Mixtures. 1

Nicole Peschke

Institut fuer Thermodynamik und Reaktiontechnik, Technische Universitat Berlin, Berlin, Germany

Stanley I. Sandler*

Center for Molecular and Engineering Thermodynamics, Department of Chemical Engineering,
University of Delaware, Newark, Delaware 19716

We have measured the liquid−liquid equilibria of water + 2,2,4-trimethylpentane and water + toluene separately with the four oxygenates ethanol, 2-methoxy-2-methylpropane (methyl *tert*-butyl ether or MTBE), 2-methoxy-2-methylbutane (*tert*-amyl methyl ether or TAME), and 2-methyl-2-butanol (*tert*-amyl alcohol or TAOH) at 25 °C. Ethanol with the water + hydrocarbon systems forms a type 1 liquid−liquid phase diagram, while the other water + hydrocarbon + oxygenate systems we studied form a type 2 phase diagram. An implication of this is that the addition of ethanol to a water + hydrocarbon mixture leads to a greatly increased solubility of the hydrocarbon in water and water in the hydrocarbon, while the addition of any of the other oxygenates studied leads to no measurable increase in the hydrocarbon solubility in water, and perhaps even a decrease in the solubility. This observation may be important when assessing both the water pollution potential of possible gasoline reformulations and the sensitivity of the gasoline to water. We have found that our experimental data can be accurately correlated with either the NRTL or UNIQUAC models. Finally, the liquid−liquid UNIFAC model leads to reasonable, 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 added to reformulated 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. If the addition of the oxygenate results in a greater solubility of water in the hydrocarbon, it would decrease the likelihood of problems with automobile performance due to an aqueous phase appearing in the gasoline tank or fuel line. Conversely if the water solubility in the hydrocarbon phase is decreased, the appearance of an aqueous phase is more likely. Also, if the presence of the oxygenate increases the solubility of the hydrocarbon in the water-rich phase, then greater hydrocarbon concentration in aquifers and other bodies of water might be expected in the event of a gasoline spill.

To assess the effect of oxygenate addition on hydrocarbon + water mutual solubility, we have measured the liquid−liquid equilibrium phase diagrams of eight water + hydrocarbon + oxygenate mixtures at 25 °C. The eight systems we have studied are water + 2,2,4-trimethylpentane with separately ethanol, 2-methyl-2-butanol (*tert*-amyl alcohol or TAOH), 2-methoxy-2-methylbutane (*tert*-amyl methyl ether or TAME), and 2-methoxy-2-methylpropane (methyl *tert*-butyl ether or MTBE) and water + toluene separately with these same oxygenates. The experimental data are 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*).

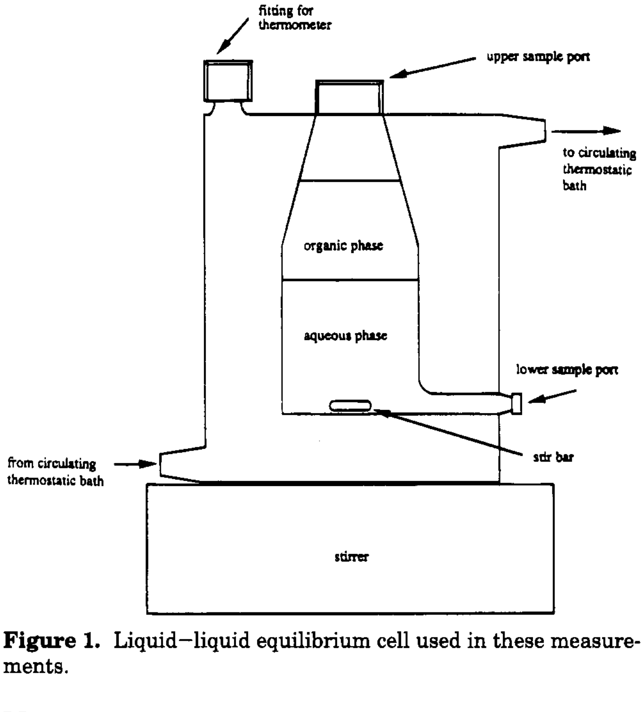


Figure 1. Liquid−liquid equilibrium cell used in these measurements.

Measurements

All measurements were carried out in specially constructed liquid−liquid equilibrium cells shown in Figure 1. The equilibrium vessel is thermostatically jacketed to maintain temperature constant to within ±0.1 K. The contents of the equilibrium cell were well-stirred with a magnetic stirrer for several hours, before allowing a 12-h period for phase separation prior to sampling. The construction of the cell allows samples to be obtained from the

---

* To whom correspondence should be addressed.

0021-9568/95/1740-0315$09.00/0

Table 1. Experimental Tie Lines and Correlation Parameters for the System Water + Ethanol + 2,2,4-Trimethylpentane at 25 °C

aqueous phase			organic phase		
x_{H_2O}	x_{EtOH}	x_{TMP}	x_{H_2O}	x_{EtOH}	x_{TMP}
1.0000	0.0000	0.0000	0.0036	0.0000	0.9964
0.9562	0.0438	0.0000	0.0046	0.0024	0.9930
0.9191	0.0809	0.0000	0.0067	0.0056	0.9877
0.8332	0.1668	0.0000	0.0076	0.0130	0.9794
0.7249	0.2748	0.0006	0.0099	0.0233	0.9667
0.5917	0.4061	0.0022	0.0105	0.0348	0.9547
0.4414	0.5467	0.0119	0.0107	0.0567	0.9326
0.3460	0.6241	0.0299	0.0121	0.0946	0.8933
0.3184	0.6461	0.0355	0.0140	0.0954	0.8906
0.2982	0.6640	0.0378	0.0140	0.0995	0.8865
0.2010	0.7030	0.0960	0.0213	0.1951	0.7837
0.1831	0.7068	0.1101	0.0217	0.2155	0.7628
0.1416	0.6957	0.1627	0.0397	0.3166	0.6437
0.1347	0.6820	0.1833	0.0397	0.3320	0.6283
0.1251	0.6718	0.2030	0.0436	0.3622	0.5942

Correlation Parameters

	NRTL		UNIQUAC	
	a_{ij}	a_{ji}	a_{ij}	a_{ji}
water + ethanol	−594.3	−732.3	−615.2	−48.6
water + TMP	2307.0	820.4	758.6	658.2
ethanol + TMP	315.1	144.7	−103.1	293.9

Table 2. Experimental Tie Lines and Correlation Parameters for the System Water + *tert*-Amyl Alcohol + 2,2,4-Trimethylpentane at 25 °C

aqueous phase			organic phase		
x_{H_2O}	x_{TAOH}	x_{TMP}	x_{H_2O}	x_{TAOH}	x_{TMP}
1.0000	0.0000	0.0000	0.0036	0.0000	0.9964
0.9909	0.0091	0.0000	0.0095	0.0934	0.8971
0.9891	0.0109	0.0000	0.0163	0.1394	0.8444
0.9881	0.0119	0.0000	0.0236	0.1810	0.7955
0.9880	0.0120	0.0000	0.0275	0.1880	0.7845
0.9866	0.0134	0.0000	0.0582	0.2707	0.6711
0.9856	0.0144	0.0000	0.0881	0.3383	0.5736
0.9854	0.0146	0.0000	0.0881	0.3530	0.5589
0.9849	0.0151	0.0000	0.1020	0.3775	0.5206
0.9841	0.0159	0.0000	0.1548	0.4444	0.4007
0.9837	0.0163	0.0000	0.1702	0.4617	0.3681
0.9836	0.0164	0.0000	0.1915	0.4748	0.3334
0.9821	0.0179	0.0000	0.3062	0.5187	0.1752
0.9819	0.0181	0.0000	0.3372	0.5197	0.1431
0.9796	0.0204	0.0000	0.4792	0.4774	0.0434
0.9793	0.0207	0.0000	0.5248	0.4541	0.0211
0.9787	0.0213	0.0000	0.5804	0.4155	0.0041
0.9254	0.0746	0.0000	0.6248	0.3752	0.0000

Correlation Parameters

	NRTL		UNIQUAC	
	a_{ij}	a_{ji}	a_{ij}	a_{ji}
water + TAOH	1356.9	−305.9	236.1	−24.6
water + TMP	1649.9	1357.0	748.5	875.5
TAOH + TMP	44.4	−311.0	130.0	40.9

Table 3. Experimental Tie Lines and Correlation Parameters for the System Water + Methyl *tert*-Butyl Ether + 2,2,4-Trimethylpentane at 25 °C

aqueous phase			organic phase		
x_{H_2O}	x_{MTBE}	x_{TMP}	x_{H_2O}	x_{MTBE}	x_{TMP}
1.0000	0.0000	0.0000	0.0036	0.0000	0.9964
0.9996	0.0004	0.0000	0.0021	0.0428	0.9551
0.9992	0.0008	0.0000	0.0028	0.0812	0.9160
0.9982	0.0018	0.0000	0.0041	0.2065	0.7893
0.9980	0.0020	0.0000	0.0055	0.2323	0.7622
0.9978	0.0022	0.0000	0.0044	0.2243	0.7713
0.9968	0.0032	0.0000	0.0056	0.3510	0.6434
0.9957	0.0043	0.0000	0.0096	0.5034	0.4870
0.9955	0.0045	0.0000	0.0120	0.5623	0.4257
0.9953	0.0047	0.0000	0.0151	0.5723	0.4126
0.9946	0.0054	0.0000	0.0179	0.6544	0.3277
0.9943	0.0057	0.0000	0.0242	0.6892	0.2866
0.9937	0.0063	0.0000	0.0273	0.8007	0.1720
0.9932	0.0068	0.0000	0.0310	0.8062	0.1628
0.9934	0.0066	0.0000	0.0381	0.8605	0.1013
0.9930	0.0070	0.0000	0.0424	0.8904	0.0671
0.9921	0.0079	0.0000	0.0574	0.9426	0.0000

Correlation Parameters

	NRTL		UNIQUAC	
	a_{ij}	a_{ji}	a_{ij}	a_{ji}
water + MTBE	1066.2	434.9	50.6	614.0
water + TMP	1302.1	1511.1	522.8	1053.8
MTBE + TMP	−11.4	−687.1	195.9	−138.3

Table 4. Experimental Tie Lines and Correlation Parameters for the System Water + *tert*-Amyl Methyl Ether + 2,2,4-Trimethylpentane at 25 °C

aqueous phase			organic phase		
x_{H_2O}	x_{TAME}	x_{TMP}	x_{H_2O}	x_{TAME}	x_{TMP}
1.0000	0.0000	0.0000	0.0036	0.0000	0.9964
0.9998	0.0002	0.0000	0.0019	0.1632	0.8349
0.9998	0.0002	0.0000	0.0023	0.2425	0.7552
0.9996	0.0004	0.0000	0.0023	0.3206	0.6771
0.9996	0.0004	0.0000	0.0018	0.3729	0.6253
0.9994	0.0006	0.0000	0.0027	0.4277	0.5696
0.9994	0.0006	0.0000	0.0026	0.4701	0.5273
0.9994	0.0006	0.0000	0.0028	0.4749	0.5223
0.9992	0.0008	0.0000	0.0030	0.5251	0.4719
0.9990	0.0010	0.0000	0.0129	0.6248	0.3623
0.9990	0.0010	0.0000	0.0189	0.7400	0.2411
0.9990	0.0010	0.0000	0.0106	0.8413	0.1481
0.9990	0.0010	0.0000	0.0140	0.9237	0.0623

Correlation Parameters

	NRTL		UNIQUAC	
	a_{ij}	a_{ji}	a_{ij}	a_{ji}
water + TAME	1331.7	670.4	69.8	813.9
water + TMP	1158.2	1411.3	671.6	1077.0
TAME + TMP	−359.4	−123.3	99.0	−112.2

upper (hydrocarbon-rich) and lower (aqueous) phases without contamination resulting from penetrating the interface.

Samples were withdrawn using a Perfectum Model MicroMate hypodermic syringe. 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. The injection port and detector temperatures were set at 250 °C, and the oven at 200 °C. The helium flow rates for both the reference and separation columns were set at 30 mL/min, and the detector signals were monitored with a Hewlett-Packard Model 3390A integrator. Calibration of the gas chromatograph was done by determining the response of the gas chromatograph/integrator system to 10 injections of each pure component evenly spaced between 0.1 and 1.0 μL. 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 be ±0.001 in mole fraction.

Water deionized with Barbstaed NANOpure equipment was used in our measurements. The 2,2,4-trimethylpentane, methyl *tert*-butyl ether, toluene, and *tert*-amyl alcohol used were obtained from the Aldrich Chemical Co. with reported mass fraction purities of 99.7+%, 99.8% (HPLC grade), 99.9% (GLC grade), and 99+%, respectively. Also, 200 proof ethanol was obtained from U.S. Industrial Chemicals Co. Each of these chemicals was used as received. *tert*-Amyl methyl ether obtained from the Aldrich Chemical Co. had a purity of only 94%. It was distilled in

Table 5. Experimental Tie Lines and Correlation Parameters for the System Water + Ethanol + Toluene at 25 °C

aqueous phase			organic phase		
x_{H_2O}	x_{EtOH}	x_{Tol}	x_{H_2O}	x_{EtOH}	x_{Tol}
1.0000	0.0000	0.0000	0.0023	0.0000	0.9977
0.9163	0.0837	0.0000	0.0192	0.0188	0.9620
0.8613	0.1385	0.0002	0.0281	0.0431	0.9288
0.7851	0.2115	0.0034	0.0454	0.0809	0.8737
0.7493	0.2441	0.0066	0.0423	0.0968	0.8609
0.6604	0.3253	0.0143	0.0426	0.1350	0.8223
0.6388	0.3406	0.0206	0.0435	0.1461	0.8104
0.4736	0.4394	0.0870	0.0845	0.2406	0.6749
0.3943	0.4672	0.1385	0.1022	0.2820	0.6158
0.2816	0.4525	0.2659	0.1857	0.3825	0.4319

Correlation Parameters

	NRTL		UNIQUAC	
	a_{ij}	a_{ji}	a_{ij}	a_{ji}
water + ethanol	923.6	−599.7	431.9	−271.9
water + toluene	2511.4	847.3	316.7	585.5
ethanol + toluene	335.8	84.9	−120.7	419.7

Table 6. Experimental Tie Lines and Correlation Parameters for the System Water + *tert*-Amyl Alcohol + Toluene at 25 °C

aqueous phase			organic phase		
x_{H_2O}	x_{TAOH}	x_{Tol}	x_{H_2O}	x_{TAOH}	x_{Tol}
1.0000	0.0000	0.0000	0.0023	0.0000	0.9977
0.9925	0.0075	0.0000	0.0195	0.0962	0.8842
0.9905	0.0095	0.0000	0.0631	0.1605	0.7764
0.9891	0.0109	0.0000	0.0768	0.2369	0.6864
0.9876	0.0124	0.0000	0.1170	0.3289	0.5541
0.9874	0.0126	0.0000	0.1212	0.3336	0.5453
0.9870	0.0130	0.0000	0.1428	0.3594	0.4978
0.9860	0.0140	0.0000	0.2030	0.4294	0.3677
0.9856	0.0144	0.0000	0.2084	0.4308	0.3608
0.9844	0.0156	0.0000	0.2975	0.4626	0.2399
0.9838	0.0162	0.0000	0.3305	0.4802	0.1893
0.9815	0.0185	0.0000	0.4644	0.4563	0.0792
0.9785	0.0215	0.0000	0.6248	0.3752	0.0000

Correlation Parameters

	NRTL		UNIQUAC	
	a_{ij}	a_{ji}	a_{ij}	a_{ji}
water + TAOH	1400.9	−343.7	155.2	42.8
water + toluene	1390.0	884.8	284.4	779.9
TAOH + toluene	−260.8	−96.4	11.0	55.6

a 100 theoretical plate column at high reflux to a purity of 99.9%, as determined by gas chromatography before use.

Table 7. Experimental Tie Lines and Correlation Parameters for the System Water + Methyl *tert*-Butyl Ether + Toluene at 25 °C

aqueous phase			organic phase		
x_{H_2O}	x_{MTBE}	x_{Tol}	x_{H_2O}	x_{MTBE}	x_{Tol}
1.0000	0.0000	0.0000	0.0023	0.0000	0.9977
0.9998	0.0002	0.0000	0.0043	0.0239	0.9717
0.9986	0.0014	0.0000	0.0102	0.2113	0.7785
0.9985	0.0015	0.0000	0.0115	0.2886	0.6999
0.9974	0.0026	0.0000	0.0137	0.3293	0.6570
0.9971	0.0029	0.0000	0.0169	0.4042	0.5789
0.9969	0.0031	0.0000	0.0170	0.4472	0.5359
0.9964	0.0036	0.0000	0.0218	0.5215	0.4568
0.9954	0.0046	0.0000	0.0251	0.5979	0.3770
0.9950	0.0050	0.0000	0.0315	0.6903	0.2782
0.9938	0.0062	0.0000	0.0373	0.7697	0.1930
0.9930	0.0070	0.0000	0.0408	0.8301	0.1291
0.9921	0.0079	0.0000	0.0574	0.9426	0.0000

Correlation Parameters

	NRTL		UNIQUAC	
	a_{ij}	a_{ji}	a_{ij}	a_{ji}
water + MTBE	1115.5	409.8	6.5	572.1
water + toluene	1295.7	1085.8	243.0	814.0
MTBE + toluene	−102.7	−344.2	173.7	−234.4

Table 8. Experimental Tie Lines and Correlation Parameters for the System Water + *tert*-Amyl Methyl Ether + Toluene at 25 °C

aqueous phase			organic phase		
x_{H_2O}	x_{TAME}	x_{Tol}	x_{H_2O}	x_{TAME}	x_{Tol}
1.0000	0.0000	0.0000	0.0023	0.0000	0.9977
0.9999	0.0001	0.0000	0.0039	0.0791	0.9169
0.9998	0.0002	0.0000	0.0084	0.1714	0.8202
0.9997	0.0003	0.0000	0.0086	0.2323	0.7590
0.9997	0.0003	0.0000	0.0089	0.2944	0.6967
0.9995	0.0005	0.0000	0.0103	0.3476	0.6421
0.9993	0.0007	0.0000	0.0132	0.4053	0.5815
0.9994	0.0006	0.0000	0.0141	0.4478	0.5382
0.9993	0.0007	0.0000	0.0150	0.4916	0.4935
0.9992	0.0008	0.0000	0.0150	0.5478	0.4372
0.9992	0.0008	0.0000	0.0176	0.5904	0.3921
0.9991	0.0009	0.0000	0.0188	0.6470	0.3342
0.9991	0.0009	0.0000	0.0232	0.7135	0.2633
0.9989	0.0011	0.0000	0.0251	0.8002	0.1746
0.9975	0.0025	0.0000	0.0255	0.8740	0.1004
0.9973	0.0027	0.0000	0.0267	0.9733	0.0000

Correlation Parameters

	NRTL		UNIQUAC	
	a_{ij}	a_{ji}	a_{ij}	a_{ji}
water + TAME	1323.9	535.6	105.7	683.2
water + toluene	1329.3	1067.2	314.8	830.2
TAME + toluene	−249.8	−294.0	−9.8	−0.3

Experimental Data

The results are presented in Tables 1−4 for water + oxygenate mixtures containing 2,2,4-trimethylpentane, and in Tables 5−8 for mixtures containing toluene. Concentrations of the organic in water below our detection limit are indicated to be 0. The data for these mixtures are also shown in the form of Gibbs triangles in Figure 2 for mixtures with 2,2,4-trimethylpentane and in Figure 3 for mixtures with toluene.

From our data we see that the oxygenated compounds we have used are totally miscible with both hydrocarbons studied here. Also, ethanol is the only oxygenate which is completely miscible with water; the other oxygenates are only slightly soluble in the water-rich phase. Consequently, the ethanol mixtures studied here exhibit type 1 liquid−liquid equilibrium behavior. The other oxygenate mixtures exhibit type 2 behavior, that is, a continuous transition from partial miscibility of the water + hydrocarbon mixture to partial miscibility of the oxygenate + hydrocarbon mixture. However, since water is much more soluble in TAOH than in TAME or MTBE, the shapes of these type 2 liquid−liquid equilibrium phase diagrams are quite different. Also, the behavior of mixtures containing toluene and those containing 2,2,4-trimethylpentane are only qualitatively different.

Whether an oxygenate forms a type 1 or type 2 liquid−liquid equilibrium system with a water + hydrocarbon mixture has important implications for both the water sensitivity of gasoline and the hydrocarbon (gasoline) solubility in water. We can see this difference, for example, by comparing the results in Tables 1 and 3. In Table 1 we see that the solubility of 2,2,4-TMP in the water-rich phase increases with increasing concentration of ethanol (type 1 phase diagram); this is also shown in Figure 4 and compared with the solubility of 2,2,4-TMP in pure water reported by Polak and Lu (*4*). From Table 3 we see that the addition of MTBE (leading to a type 2 phase diagram)

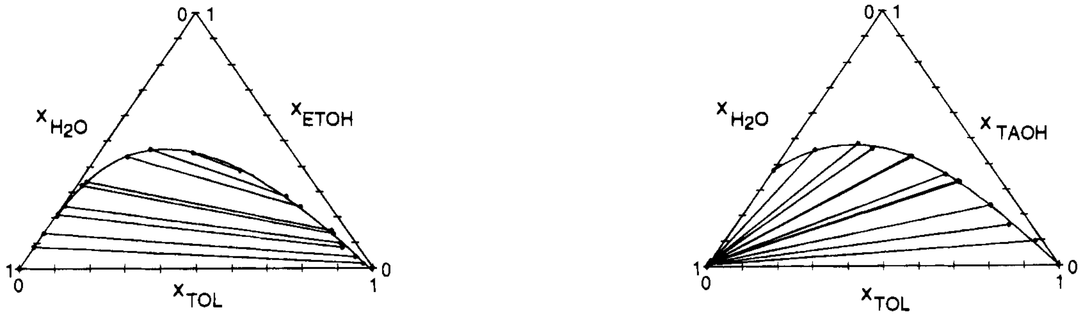
Water + Ethanol + 2,2,4-Trimethyl Pentane

Water + tert-Amyl Alcohol - 2,2,4-Trimethyl Pentane

Water + tert-Butyl Methyl Ether + 2,2,4-Trimethyl Pentane

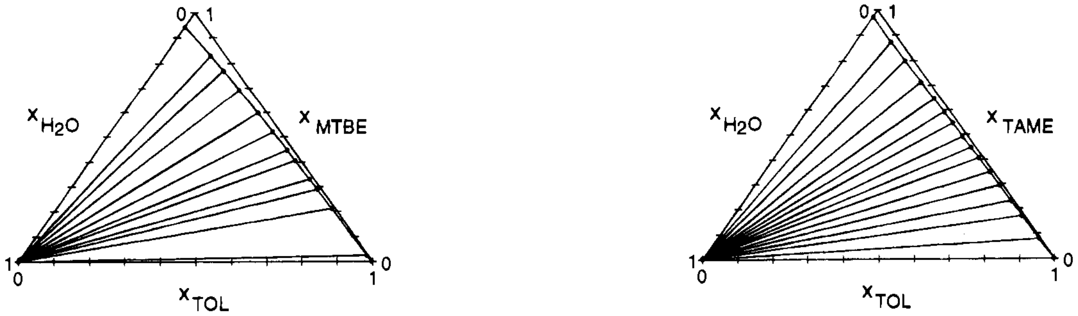
Water + tert-Amyl Methyl Ether + 2,2,4-Trimethyl Pentane

Figure 2. Experimental liquid–liquid equilibrium data for the four systems of this study containing 2,2,4-trimethylpentane.



Water + Ethanol + Toluene

Water + tert-Amyl Alcohol + Toluene



Water + tert-Butyl Methyl Ether + Toluene

Water + tert-Amyl Methyl Ether + Toluene

Figure 3. Experimental liquid–liquid equilibrium data for the four systems of this study containing toluene.

has, to the limit of our detection, no discernible effect on the 2,2,4-TMP solubility in the aqueous phase. In fact, other data (*5*) indicate that the addition of MTBE reduces the hydrocarbon solubility in water.

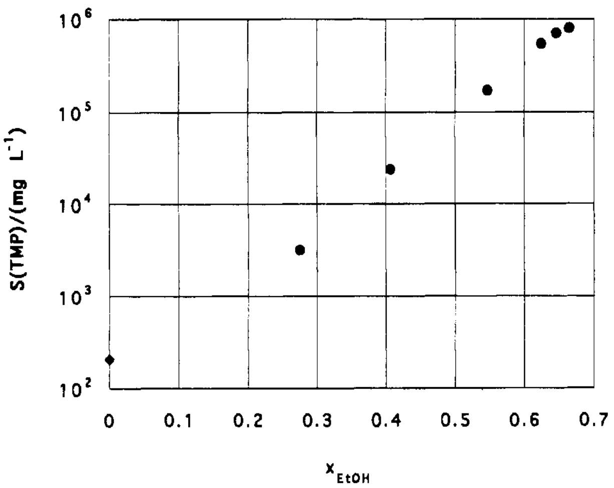


Figure 4. Solubilities of 2,2,4-trimethylpentane per liter of water in water + ethanol mixtures as a function of ethanol concentration. The filled circles indicate data measured in this work, while the solubility in pure water indicated by a filled tilted square is from Polak and Lu (*4*).

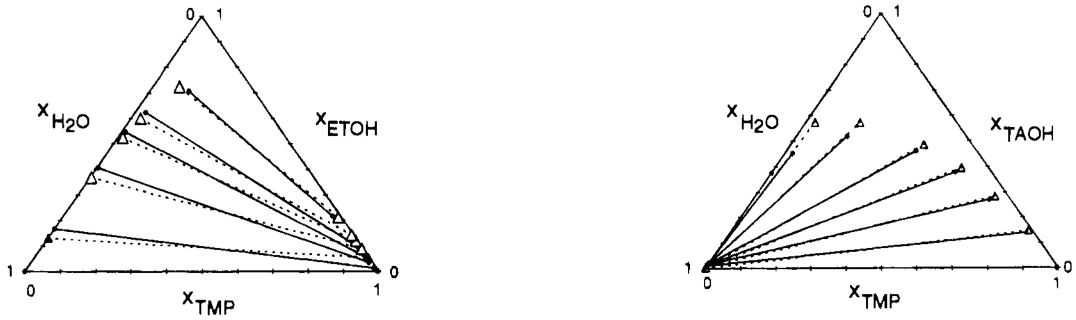
Nowakowska et al. (*6*) and Hubers et al. (*7*) have also reported liquid–liquid equilibrium binodal and tie line data for the ethanol + water + TMP system at 298.15 K, while Kretschmer and Wiebe (*8*) reported several points along the binodal curve. The binodal curves from all these investigations are in good agreement with each other and with our data. The three sets of tie line data are, however, only in qualitative agreement with each other; our more extensive data, which go closer to the plait point, are in reasonable agreement with the data of Hubers et al. Our binodal curve at 298.15 K for the system ethanol + water + toluene is in good agreement with the data of Washburn et al. (*9*); however, they do not present any tie lines. We have not found any liquid–liquid equilibrium data for the other systems we measured.

Modeling of the Experimental Data

We have correlated our data using two activity coefficient models: the NRTL (nonrandom two-liquid) model of Renon and Prausnitz (*1*) and the UNIQUAC model of Abrams and Prausnitz (*2*). The forms of these models are given in Sandler (*10*). For the NRTL model the parameter α was set to 0.2, and the parameters a_{ij} ($=T\tau_{ij}$) are given in the tables with the experimental data. In the UNIQUAC model the coordination number z was set to 10, and the parameters $a_{ij} = (u_{ji} - u_{ij})/R$ are also reported in the data tables. Note that with both models no attempt was made to use the same values of the parameters for a given binary pair when it occurred in different mixtures.

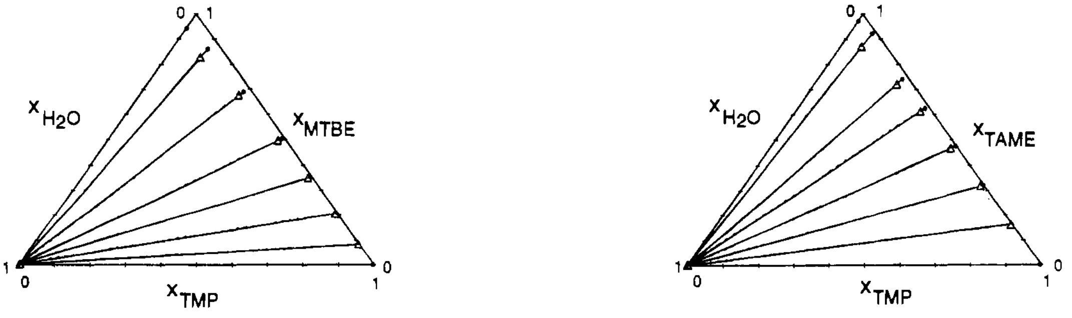
Rather than present detailed results of the correlations, we will only describe the results obtained here. These two models can fit the experimental data very well, both in the location of the binodal curve and in the slope of the tie lines. In the scale of our diagrams, there would be very little difference visible between the correlations and the experimental data. In general, the UNIQUAC fit was slightly better than that obtained with the NRTL model. Also, as might be expected, the simpler type 2 diagrams obtained for mixtures with TAME or MTBE were more accurately described than the type 1 diagrams with ethanol, or the type 2 diagrams with TAOH.

In Figure 5 we compare some of our experimental data for the water + 2,2,4-trimethylpentane system separately



Water + Ethanol +
2,2,4-Trimethyl Pentane

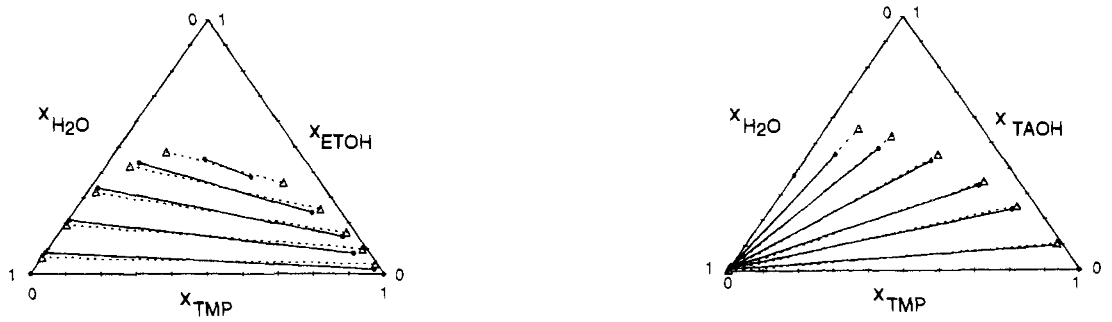
Water + tert-Amyl Alcohol -
2,2,4-Trimethyl Pentane



Water + tert-Butyl Methyl Ether +
2,2,4-Trimethyl Pentane

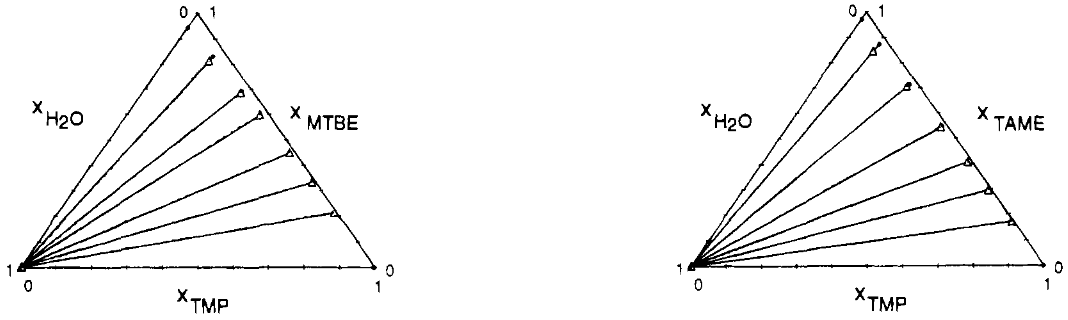
Water + tert-Amyl Methyl Ether +
2,2,4-Trimethyl Pentane

Figure 5. UNIFAC predictions for the liquid–liquid equilibrium of the four systems of this study containing 2,2,4-trimethylpentane. The dashed lines and triangles indicate the UNIFAC predictions, while the solid lines and filled circles indicate the experimental data.



Water + Ethanol + Toluene

Water + tert-Amyl Alcohol + Toluene



Water + tert-Butyl Methyl Ether + Toluene

Water + tert-Amyl Methyl Ether + Toluene

Figure 6. UNIFAC predictions for the liquid–liquid equilibrium of the four systems of this study containing toluene. The symbols and lines are as in Figure 5.

with each of the oxygenates with predictions of the liquid–liquid UNIFAC model (*3*). Similar results for the toluene-containing systems are given in Figure 6. We see that in both cases the liquid–liquid UNIFAC predictions are reasonably good with regard to the location of the binodal curve and the slope of the tie lines.

Conclusions

Liquid–liquid equilibrium data at 25 °C are reported for the water + 2,2,4-trimethylpentane and the water + toluene mixtures separately with four oxygenates: ethanol, MTBE, TAME, and TAOH. Ethanol with the water + hydrocarbon systems forms a type 1 liquid–liquid equilibrium phase diagram, while the other oxygenates form a type 2 phase diagram. An implication of this is that the addition of ethanol to a water + hydrocarbon mixture leads to a greatly increased solubility of the hydrocarbon in water and water in the hydrocarbon. In contrast the addition of any of the other oxygenates studied leads to no measurable increase in the hydrocarbon solubility in water, and perhaps even a decrease in the solubility. This observation may be important when assessing the water pollution potential of possible gasoline reformulations.

We have also found that our experimental data can be accurately correlated with either the NRTL or UNIQUAC model. Finally, the liquid–liquid UNIFAC model leads to reasonable, qualitatively correct predictions for the liquid–liquid equilibria of the systems studied here.

Acknowledgment

We would like to thank Dr. Maria Antosik for her help in designing the liquid–liquid equilibrium cells used in this work.

Literature Cited

(1) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135.
(2) Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116.
(3) Magnussen, T.; Rasmussen, P.; Fredenslund, Aa. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 331.
(4) Polak, J.; Lu, B. C.-Y. *Can. J. Chem.* **1973**, *51*, 4018.
(5) Hellinger, S.; Sandler, S. I. Submitted for publication in *J. Chem. Eng. Data*.
(6) Nowakowska, J.; Kretschmer, C. B.; Wiebe, R. *Chem. Eng. Data Ser.* **1956**, *1*, 42.
(7) Huber, J. F. K.; Meijers, C. A. M.; Hulsman, J. A. R. *J. Anal. Chem.* **1972**, *44*, 111.
(8) Kretschmer, C. B.; Wiebe, R. *Ind. Eng. Chem.* **1945**, *37*, 1130.
(9) Washburn, R. E., Beguin, A. E., Beckford, O. C. *J. Am. Chem. Soc.* **1939**, *61*, 1694.
(10) Sandler, S. I. *Chemical and Engineering Thermodynamics*, 2nd ed.; J. Wiley & Sons: New York, 1989; Chapter 7.

Received for review July 20, 1994. Accepted August 29, 1994.[⊗] This research was supported, in part, by Grant Number CTS-9123434 from the U.S. National Science Foundation to the University of Delaware.

JE9401474

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1994.