J. Chem. Eng. Data **2001,** *46,* 557−561

Liquid−Liquid Equilibrium for *tert*-Amyl Ethyl Ether + Methanol + Water

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Liquid−liquid equilibrium data for *tert*-amyl ethyl ether + methanol + water were measured experimentally at (298.15, 308.15, and 318.15) K, and correlated with the NRTL and UNIQUAC equations. The correlation was made to each temperature and for the three temperatures simultaneously. The best results were found with the UNIQUAC and NRTL ($\alpha = 0.1$), respectively. Data prediction was carried out using the UNIFAC method, but results were not quantitative.

1. Introduction

In the last two decades, methyl *tert*-butyl ether (MTBE) has been the antiknock additive most used in gasoline. The demand has increased so much that it is becoming scarce. Moreover, today the crisis of groundwater sources pollution with MTBE in the U.S. is pushing research centers to look for other compounds to substitute the MTBE. The use of *tert*-amyl ethyl ether (TAEE) as an antiknock additive for reformated gasoline has been suggested in the recent literature. There are a few papers published with the kinetics of the production reaction,[1] physical properties,[2] and vapor−liquid equilibrium data[3] but none on liquid−liquid equilibria (LLE). Thus it is important to calculate the number of necessary stages in the design of the extraction equipment.

We report the experimental tie lines of the system TAEE + methanol + water at 298.15 K, 308.15 K, and 318.15 K. The experimental data are correlated using the UNIQUAC and NRTL equations, and the energetic parameters of these models at each temperature and those obtained with the simultaneous correlation of the three different temperature data points are reported. The LLE data have also been predicted with the UNIFAC method, and they are compared with the experimental data at each temperature.

2. Experimental Section

Materials. TAEE was supplied by the Yarsintez Research Institute (Yaroslav, Russia) with a nominal purity of 99.8 mass %. Methanol (Gradient grade) was supplied by Merck with a nominal purity of 99.8 mass %. Those purities were verified with gas chromatography, and the chemicals were used without further purification. The water content was 0.04 and 0.05 mass %, respectively. Water was purified with a Milli-Q Plus system. In Table 1 the experimental and published values[4] of density and refractive index are listed.

Table 1. Densities (ρ) and Refractive Indices (n_D) of the Pure Components at 298.15 K and Atmospheric Pressure

	ρ/kg·m^{-3}		n_D	
component	exptl	lit.[4]	exptl	lit.[4]
water	997.04	997.04	1.332 50	1.332 50
methanol	786.63	786.64	1.326 40	1.326 52
TAEE	760.50	not found	1.388 57	not found

Apparatus. All weighing was carried out in a Mettler Toledo AT 261 balance precise to within ±0.0001 g. Water content was measured with a Metrohm 737 KF coulometer. Densities were measured with an Anton Paar DMA 60/602 densimeter precise to within $\pm 10^{-2}$ kg·m^{-3}. Refractive indices were measured to an accuracy of $\pm 4 \times 10^{-5}$ in an Atago RX-5000 refractometer. A Hetoterm thermostat was used to maintain the temperature at (298.15 ± 0.02) K. Phase analysis was carried out by gas chromatography using a Hewlett-Packard 6890 Series chromatograph equipped with a thermal conductivity detector and a HP-FFAP capillary column (25 m × 0.2 mm × 0.3 μm). The injection volume was 1 μL with a split ratio of 150:1. The injector, detector, and column temperatures were held at 413.15 K, 433.15 K, and 358.15 K, respectively. The carrier gas was helium, with a flow rate of 0.7 mL/min in the column.

Procedure. The experimental procedure could be divided into two steps. First, the solubility curves were obtained using the cloud-point method.[5] The solubility curves were used to carry out the calibration of the gas chromatograph using the internal standard method. The standards used were water for the aqueous phase and TAEE for the organic phase. The greatest errors in mole fraction composition during calibration were ±0.007 in the aqueous phase and ±0.008 in the organic phase, and were found in the methanol-rich zone. After, the conjugate phases were obtained preparing mixtures whose composition lay in the immiscible region. The mixtures were vigorously stirred for at least 1.5 h in jacketed cells with septum outlets, thereafter leaving them to stand for at least 5 h (the time necessary to attain equilibrium was established in preliminary experiments). The temperature was controlled using water from a thermostat (Selecta Ultraterm 6000383), and the water temperature was measured with a thermometer Heraeus Quat 100 precise to within ±0.01 K. Finally a sample of each phase was withdrawn and injected onto the gas chromatograph. The technique is explained in more depth elsewhere.[6] The compositions of the tie-line ends are listed in Table 2.

3. Correlation

The correlation of the experimental data was made with the NRTL[7] and the UNIQUAC [8] equations, as they are two of the most used in the literature. The value of the nonrandomness parameter of the NRTL equation, α, was

10.1021/je0003344 CCC: $20.00

Table 2. Experimental Tie Lines of the System TAEE (x_1) + Methanol (x_2) + Water ($1 - x_1 - x_2$) with Compositions in Mole Fraction

organic phase		aqueous phase	
x_1	x_2	x_1	x_2
	$T = 298.15$ K		
0.9631	0.0000	0.0002	0.0000
0.9575	0.0140	0.0002	0.0377
0.9519	0.0202	0.0005	0.0600
0.9062	0.0603	0.0005	0.1551
0.8832	0.0844	0.0009	0.2554
0.8307	0.1262	0.0032	0.2958
0.8013	0.1500	0.0049	0.3158
0.7273	0.2057	0.0110	0.3858
0.6480	0.2661	0.0187	0.4415
0.4285	0.4155	0.0597	0.5065
	$T = 308.15$ K		
0.9839	0.0000	0.0002	0.0000
0.9723	0.0117	0.0001	0.0312
0.9425	0.0375	0.0001	0.1047
0.9243	0.0593	0.0008	0.1683
0.8548	0.1153	0.0011	0.2724
0.8115	0.1488	0.0038	0.3300
0.7451	0.1992	0.0069	0.3826
0.6740	0.2515	0.0081	0.4250
0.5758	0.3210	0.0300	0.4715
	$T = 318.15$		
0.9872	0.0000	0.0002	0.0000
0.9709	0.0152	0.0001	0.0377
0.9570	0.0330	0.0002	0.1045
0.9256	0.0593	0.0002	0.2013
0.8758	0.1004	0.0009	0.2635
0.8341	0.1322	0.0024	0.3209
0.8083	0.1501	0.0080	0.3396
0.7323	0.2073	0.0078	0.3875
0.6832	0.2453	0.0123	0.4171
0.6021	0.2983	0.0217	0.4537
0.5661	0.3228	0.0300	0.4817

Table 3. LLE Data Correlation: Root-Mean-Square Deviations (rmsd in %) for Each Model and Each Temperature, Defining or Not the Solute Distribution Ratio at Infinite Dilution, β_∞

	rmsd					
parameter	298.15 K		308.15 K		318.15 K	
	UNIQUAC					
β_∞		0.33		0.35		0.32
$\Delta\beta$ (%)	12.90	8.53	5.62	3.38	12.64	10.02
F (%)	0.4371	0.4829	0.3249	0.2628	0.4419	0.4785
	NRTL ($\alpha = 0.1$)					
β_∞		0.58		0.51		0.64
$\Delta\beta$ (%)	23.65	10.59	9.03	4.96	14.26	3.72
F (%)	0.5930	0.5593	0.3600	0.2992	0.3767	0.3164

Structural Parameters for the UNIQUAC Equation

	TAEE[9]	methanol[9]	water[10]
r	5.4166	1.4311	0.92
q	4.712	1.432	1.40

Table 4. LLE Data Correlation: Binary Interaction Parameters for NRTL ($\alpha = 0.1$) and UNIQUAC for Each Temperature with the Optimal Value of the Solute Distribution Ratio at Infinite Dilution, β_∞

		NRTL ($\alpha = 0.1$)		UNIQUAC	
T	components	Δg_{ij}	Δg_{ji}	Δu_{ij}	Δu_{ji}
K	$i-j$	$\text{J}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$
298.15	1−2	−6919.83	10 927.1	4232.91	−1268.72
	1−3	1200.87	34 504.8	4927.87	4330.43
	2−3	−13743.0	22 164.3	1857.10	−2966.52
308.15	1−2	−7515.77	11 804.2	3215.77	−1525.29
	1−3	1865.91	33 565.3	5808.99	5441.10
	2−3	−14082.3	22 189.2	4269.41	−5124.42
318.15	1−2	−9995.09	17 604.1	3054.40	−1627.63
	1−3	2585.57	35 054.3	6436.87	5742.56
	2−3	−15993.6	26 737.8	8470.30	−6200.41

previously assigned to 0.1, 0.2, and 0.3. The structural parameters for UNIQUAC, r and q, were taken from the literature.[9,10]

The binary interaction parameters for both NRTL and UNIQUAC equations were obtained using a computer program described by Sϕrensen,[11] who uses two objective functions. First, F_a, does not require any previous guess for parameters, and after convergence those parameters are used in the second function to fit the experimental concentrations, F_b.

$$F_a = \sum_k \sum_i \sum_j [(a_{ijk}^{\text{I}} - a_{ijk}^{\text{II}})/(a_{ijk}^{\text{I}} + a_{ijk}^{\text{II}})]^2 + Q\sum_n P_n^2 \quad (1)$$

$$F_b = \sum_k \min \sum_i \sum_j (x_{ijk} - \hat{x}_{ijk})^2 + Q\sum_n P_n^2 + \left[\ln\left(\frac{\hat{\gamma}_{s\infty}{}^{\text{I}}}{\hat{\gamma}_{s\infty}{}^{\text{II}}}\beta_\infty\right)\right]^2 \quad (2)$$

where a is the activity, P_n the parameter value, and Q a constant; x is the composition in mole fraction, $\hat{\gamma}$ the calculated activity coefficient, and β the solute distribution ratio between the organic and the aqueous phases ($x_2{}^{\text{TAEE}}/x_2{}^{\text{water}}$). min refers to the minimum obtained by the Nelder−Mead method. The subscripts and superscripts are i for the components (1, 2, 3), j for the phases (I, II), k for the tie lines (1, 2, ..., M), and n for the parameters (1, 2, ...). The symbol $\wedge$ refers to calculated magnitudes, s to the solute (methanol), and ∞ to infinite dilution.

The second terms of both eqs 1 and 2 are penalty terms designed to reduce risks of multiple solutions associated with high parameter values. In the F_b objective function (eq 2) the third term ensures that the binary interaction parameters give a solute distribution ratio at infinite dilution, β_∞, which approximates a value previously defined by the user.

The quality of the correlation is measured by the residual function F and by the mean error of the solute distribution ratio, $\Delta\beta$:

$$F = 100\left[\sum_k \min \sum_i \sum_j \frac{(x_{ijk} - \hat{x}_{ijk})^2}{6M}\right]^{0.5} \quad (3)$$

$$\Delta\beta = 100\left[\sum_k \frac{((\beta_k - \hat{\beta}_k)/\beta_k)^2}{M}\right]^{0.5} \quad (4)$$

Several different kinds of correlations were made. First, the experimental data were fitted at each temperature with both NRTL and UNIQUAC equations, at each temperature and without defining a value for the solute distribution ratio at infinite dilution,β_∞, and also using the optimal value for this parameter. In the latter case, the optimal β_∞ was found by trial and error with $\Delta\beta$ as the optimality criterion. Table 3 lists the root-mean-square deviations found with both models, NRTL ($\alpha = 0.1$) and UNIQUAC, obtained for each temperature defining the solute distribution ratio at infinite dilution, β_∞, or not. When the solute distribution ratio at infinite dilution, β_∞, is defined, the residual $\Delta\beta$ decreases extensively, and the residual F slightly increases. As the residual $\Delta\beta$ shows the fitness of the LLE data at low solute concentrations, and due to the importance of this region, the correlation defining β_∞ is

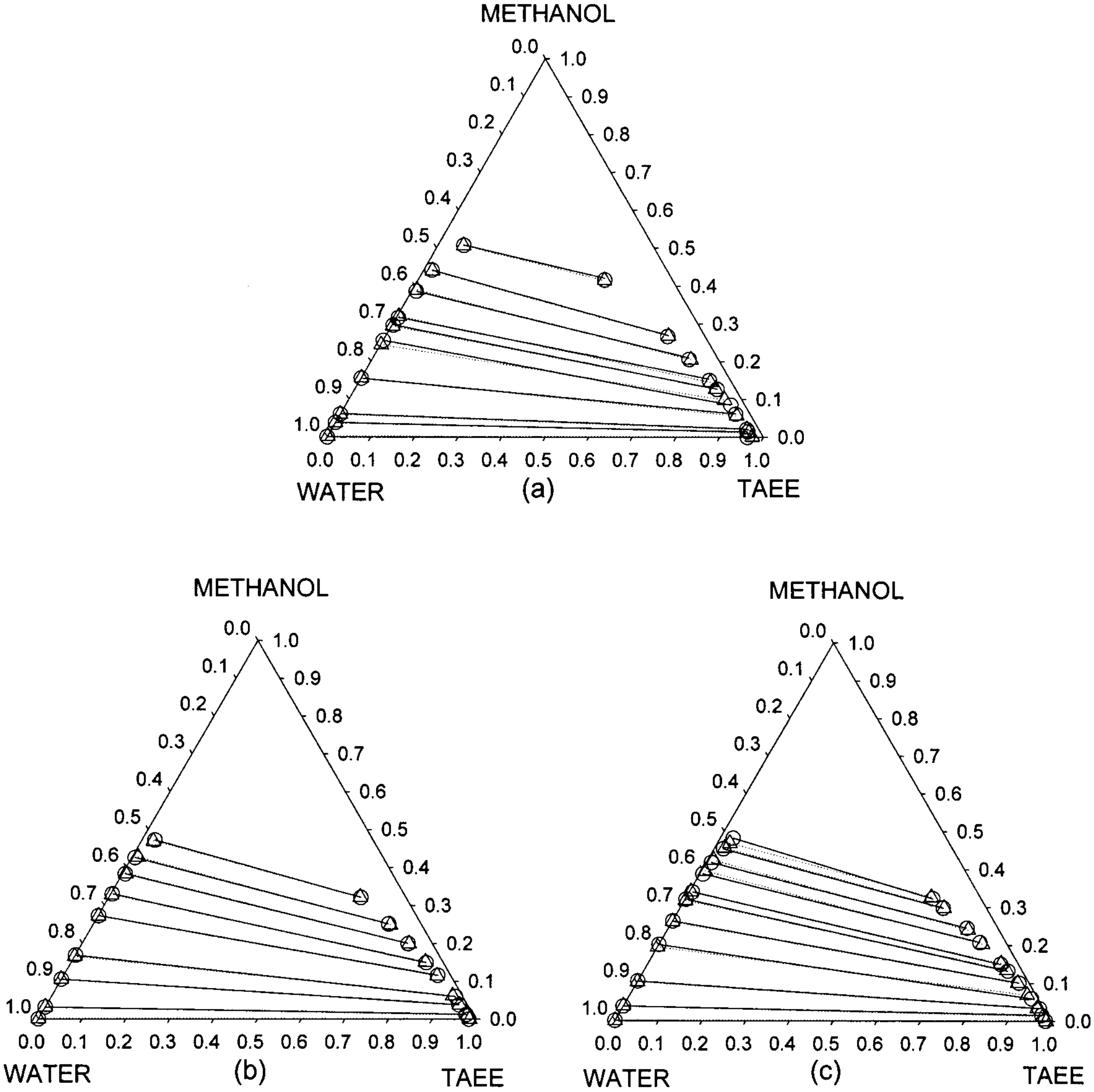

Figure 1. Experimental tie lines (O) and the corresponding UNIQUAC correlation (Δ) using the optimal value of the solute distribution ratio at infinite dilution at (a) 298.15 K, (b) 308.15 K, and (c) 318.15 K.

Table 5. Simultaneous Correlation of the Data of the Three Temperatures: Binary Interaction Parameters and Root-Mean-Square Deviations (rmsd) of the Models

model	pair i−j	Δu_{ij}/J·mol^{-1}	Δu_{ji}/J·mol^{-1}	parameter	rmsd (%) 298.15 K	rmsd (%) 308.15 K	rmsd (%) 318.15 K
UNIQUAC	1−2	4819.96	−1057.62				
	1−3	6629.33	2858.60	$\Delta\beta$	17.04	13.16	13.03
	2−3	−3276.05	6899.12	F	0.8067	0.3144	0.7514
model	**pair i−j**	**Δg_{ij}/J·mol^{-1}**	**Δg_{ji}/J·mol^{-1}**	**parameter**	**rmsd (%) 298.15 K**	**rmsd (%) 308.15 K**	**rmsd (%) 318.15 K**
NRTL	1−2	−8143.06	13 201.8				
(α = 0.1)	1−3	1550.73	34 552.2	$\Delta\beta$	16.30	9.82	7.68
	2−3	−14679.2	22 957.4	F	0.7497	0.3353	0.6344

usually preferred. This behavior can be seen from our data in Table 3; that is why we decided to fix β_∞ for the correlation. Table 4 lists the NRTL (α optimized at 0.1) and UNIQUAC parameters obtained at each temperature when the optimal value of the solute distribution ratio at infinite dilution, β_∞, is defined. Figure 1 shows a comparison of experimental tie lines and those calculated with UNIQUAC defining β_∞, for each temperature.

Since the correlations are correct only at each temperature and looking for a set of parameters valid in the range of the three temperatures, we have also made the simultaneous correlation of the data of the three temperatures. Table 5 lists the results (binary parameters and residuals) obtained with this correlation for both models, NRTL (α = 0.1) and UNIQUAC.

4. Prediction

The LLE data were predicted with the UNIFAC method.[12] The interaction and structural parameters were taken from Magnussen et al.,[13] and the values obtained for the residual

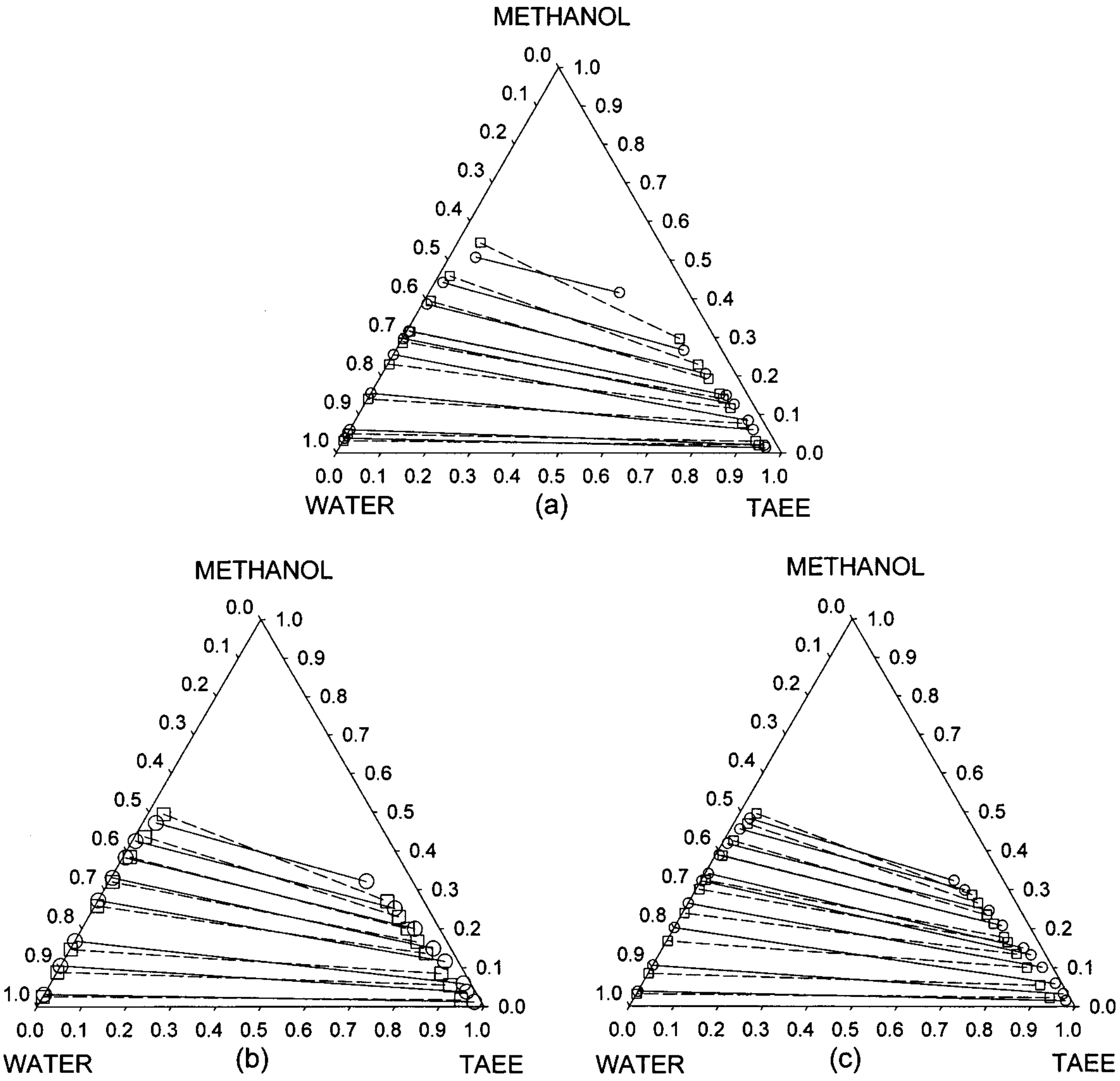

Figure 2. Experimental tie lines (○) and data predicted (□) using the UNIFAC method at (a) 298.15 K, (b) 308.15 K, and (c) 318.15 K.

F were 3.8% at 298.15 K, 2.6% at 308.15 K, and 3.1% at 318.15 K. The comparison of the predicted and the experimental data at each temperature is shown in the Figure 2.

5. Conclusions

Liquid−liquid equilibrium data of the system TAEE + methanol + water were determined experimentally at 298.15, 308.15, and 318.15 K. The temperature has practically no effect on the size of the immiscibility region for the working temperatures.

The LLE data were correlated using the NRTL and UNIQUAC activity models. The best correlation was found by fixing an optimal β_∞ value; in this way a slightly larger value of the residual F than that from the correlation without defining β_∞ was found, but the value of the residual $\Delta\beta$ is much smaller (see Table 3). The same behavior is frequently found in the open literature. The correlation with the UNIQUAC equation gives the best results, but also the NRTL equation with a value of the nonrandomness parameter optimized in $\alpha = 0.1$ fits the experimental data satisfactorily.

The simultaneous correlation of the data at the three temperatures gives common parameters in the range of the temperature considered, increasing in this way their application. As was expected, the residuals were higher than when the individual correlation at each temperature was made.

The LLE data predicted with the UNIFAC method give high values of the residual F, and as we can see in Figure 2, the results could not be considered quantitative and should only be used in preliminary studies.

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Received for review October 11, 2000. Accepted January 4, 2001. The authors are grateful to the Ministerio de Ciencia y Tecnología of Spain for financial support (Project PPQ2000-0969).

JE0003344