J. Chem. Eng. Data **2001,** *46,* 247−250

Isobaric Vapor−Liquid Equilibria of Binary and Ternary Mixtures of Heavy Ethers, Isoamylenes, and Alcohols. 2. Tertiary Amyl Ethyl Ether, 2-Methyl-1-butene, and Ethanol

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An Othmer-type still at a pressure of 87 kPa was used to determine the vapor−liquid equilibria of binary and ternary mixtures consisting of ethanol, 2-methyl-1-butene (2M1B), and *tert*-amyl ethyl ether (TAEE). A nonlinear technique was used to test different activity coefficient-based models and to evaluate the corresponding binary interaction parameters. The Wilson, NRTL, and UNIQUAC models were found to give predictions that agreed with binary experimental results, whereas only the NRTL and UNIQUAC multicomponent models were able to predict ternary equilibria with binary interaction parameters evaluated from binary data. The mixtures examined behave very much like corresponding mixtures involving tertiary amyl methyl ether (TAME), 2-methyl-1-butene (2M1B), and methanol.

Introduction

Tertiary amyl ethyl ether (TAEE), which is catalytically synthesized from isoamylenes (2-methyl-1-butene, 2M1B, and 2-methyl-2-butene, 2M2B) and ethanol (EtOH), has been identified as a suitable additive to gasoline in order to reduce pollution and to enhance octane ratings.[1] This ether is of particular interest, as ethanol can be obtained from a renewable source and the isoamylenes are readily available.

In comparison with the other well-known ethers suitable for enhancing gasoline performance (methyl *tert*-butyl ether, MTBE, ethyl *tert*-butyl ether, ETBE, *tert*-amyl methyl ether, TAME) very little information required for design purposes appears in the literature.[2,3] The reaction kinetics of the synthesis reaction of TAEE over a cation-exchange resin catalyst (Amberlyst 35) was examined in our laboratories,[4,5] and this research was extended to include the determination of vapor−liquid equilibria. This investigation also involved the determination of vapor−liquid equilibria of similar mixtures involving TAME[6] for comparison.

This paper presents (1) experimentally determined vapor−liquid equilibria at 87 kPa for three binary mixtures (EtOH with TAEE, 2M1B with TAEE, and 2M1B with EtOH) and a ternary mixture consisting of EtOH, 2M1B, and TAEE, (2) an evaluation of equilibrium models involving the Wilson, NRTL, and UNIQUAC models with experimental data, and (3) the validity of the NRTL and UNIQUAC multicomponent models for predicting the ternary equilibria.

Experimental Section

An Othmer-type laboratory still consisting of a Cottrel pump and a bubbling chamber with circulation designed by Raal and Brouchaert[7] was used. The experimental details and procedures used were identical to those used for the determination of vapor−liquid equilibria of TAME mixtures reported in another publication.[6] The purities of the chemicals used were greater than 99.8 mass %, with TAEE supplied by Phillips Petroleum (U.S.) and the other reagents by Sigma Aldrich (South Africa). The purities of all chemicals were checked with an analysis by gas chromatography and the measurement of boiling points.

Table 1. Experimental Binary VLE Data for EtOH (1) with TAEE (3) at 87 kPa

T/K	x_1	y_1	γ_1	γ_3
347.1	0.994	0.990	1.017	3.767
346.2	0.938	0.908	1.025	3.209
345.4	0.859	0.826	1.052	2.737
345.2	0.771	0.773	1.107	2.199
345.1	0.730	0.752	1.143	2.043
345.2	0.698	0.742	1.173	1.902
347.0	0.439	0.631	1.472	1.373
349.0	0.400	0.621	1.468	1.229
349.6	0.337	0.578	1.583	1.212
351.3	0.245	0.542	1.908	1.090
357.2	0.100	0.376	2.591	1.023

Table 2. Experimental Binary VLE Data for 2M1B (2) with TAEE (3) at 87 kPa

T/K	x_2	y_2	γ_2	γ_3
366.1	0.015	0.065	1.119	1.026
352.8	0.119	0.408	1.091	1.027
338.3	0.231	0.731	1.100	1.044
330.5	0.317	0.804	1.077	1.031
322.1	0.408	0.879	1.076	1.054
316.5	0.508	0.922	1.028	1.038
314.4	0.571	0.943	1.042	1.065
307.4	0.703	0.974	1.028	1.094
304.3	0.851	0.987	1.025	1.132
302.1	0.959	0.991	0.999	1.165

Results and Discussion

Binary Mixtures. Experimentally determined isobaric vapor−liquid equilibria for the three binary mixtures, EtOH (1) with TAEE (3), 2M1B (2) with TAEE (3), and 2M1B (2) with EtOH (1), are given in Tables 1−3 and Figures 1−3. The errors associated with the calculated

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10.1021/je000053w CCC: $20.00

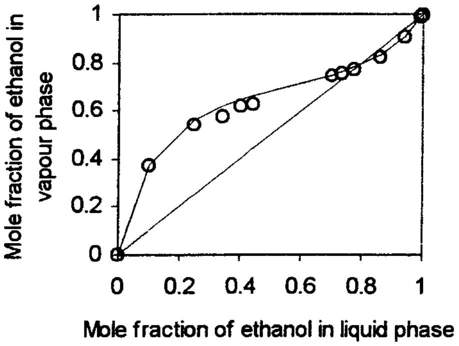

Figure 1. Comparison of experimental and model results for the binary mixture of EtOH with TAEE ($x-y$ plot): experimental data (○); UNIQUAC model (—).

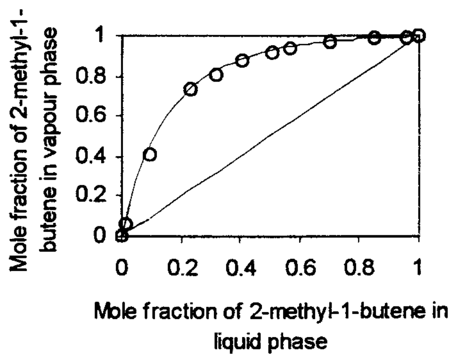

Figure 2. Comparison of experimental and model results for the binary mixture of 2M1B with TAEE ($x-y$ plot): experimental data (○); UNIQUAC model (—).

Table 3. Experimental Binary VLE Data for 2M1B (2) and EtOH (1) at 87 kPa

T/K	x_2	y_2	γ_1	γ_2
348.1	0.002	0.047	7.247	0.937
343.3	0.015	0.172	6.977	0.995
339.9	0.019	0.258	7.362	1.034
336.9	0.027	0.377	5.737	0.998
332.4	0.029	0.480	5.932	1.024
329.6	0.043	0.591	5.305	0.928
325.6	0.063	0.648	4.489	0.981
320.4	0.072	0.657	4.620	1.242
315.0	0.094	0.750	4.806	1.211
321.5	0.104	0.743	3.517	0.912
314.1	0.130	0.807	3.860	1.021
309.5	0.143	0.821	4.145	1.223
314.1	0.161	0.836	3.215	0.901
311.7	0.200	0.859	2.883	0.921
305.1	0.240	0.876	3.057	1.211
300.1	0.509	0.924	1.814	1.527
298.6	0.764	0.927	1.280	3.305
298.2	0.944	0.949	1.076	10.041

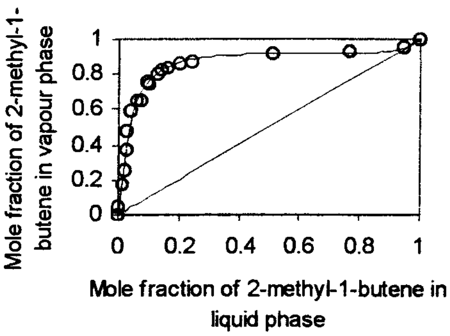

Figure 3. Comparison of experimental and model results for the binary mixture of 2M1B with EtOH ($x-y$ plot): experimental data (○); UNIQUAC model (—).

Table 4. Antoine Equation Constants[8]

component	A	B	C	D	E	F	G
EtOH	73.304	7122.3	0	0	−7.1424	2.8853×10^{-6}	2
2M1B	97.33	−5631.8	0	0	−12.589	1.5395×10^{-2}	1
TAEE	59.056	−5880.2	0	0	−5.4353	2.665×10^{-6}	2

Table 5. Consistency Test Results of Binary Vapor−Liquid Experimental Data

binary mixture	D	J	D − J
EtOH + TAEE	22.31	11.85	10.56
2M1B + TAEE	31.29	30.75	0.54
2M1B + EtOH	10.31	19.29	8.98

mole fractions (x and y) were estimated to be of the order of 1% mole fraction. Liquid-phase activity coefficients (γ_i) are also given in these tables and were calculated from the following equilibrium relationship applicable to low pressures and based on ideal vapor-phase behavior.

$$\gamma_i = \frac{y_i P}{x_i P_i^{\mathrm{sat}}} \tag{1}$$

The symbols x_i and y_i are the equilibrium mole fractions of component i in the liquid and vapor phases, respectively, P is the total pressure, and P_i^{sat} is the saturated vapor pressure of component i. The saturated vapor pressures were calculated from the following Antoine equation with constants listed in Table 4.[8]

$$\ln(P_i^{\mathrm{sat}}) = A_i + \frac{B_i}{T + C_i} + D_i T + E_i \ln(T) + F_i T^{G} \tag{2}$$

The thermodynamic consistency of the experimental results obtained was also checked according to the method of Herrington.[9] This method involves determining essentially two parameters (D and J) using areas obtained from plots of the logarithm of the activity coefficient ratio against the mole fraction of one of the components.[6,9] The criterion for thermodynamic consistency is that the modulus of the quantity ($D - J$) is less than a value of 10. The experimental results shown in Tables 1−3 were tested for thermodynamic consistency, and the results given in Table 5 show that the experimental results satisfy this criterion.

The binary mixtures consisting of EtOH with TAEE and 2M1B with EtOH have minimum boiling azeotropes (Figures 1 and 3); the mixture of 2M1B with TAEE (Figure 2) has properties close to that of an ideal mixture.

A nonlinear regression procedure was used to evaluate the validity of the Wilson, NRTL, and UNIQUAC equilibrium models in order to predict the binary equilibria. These models are well documented.[10] The regression technique consisted of the minimization of an objective function Q involving calculated (calc) and experimental (exp) activity coefficients.

$$Q = \sum_N \sum_i \left(\frac{\gamma_i^{\mathrm{exp}} - \gamma_i^{\mathrm{cal}}}{\gamma_i^{\mathrm{exp}}} \right)^2 \tag{3}$$

with N being the total number of points (different temperatures) and i the number of components ($i = 2$). The results from this calculation involving the binary interaction parameters (according to the notation of Gmehling et al.[10]) together with parameters indicating the quality of the fit are given in Table 6, and plots of the theoretical predictions using the UNIQUAC model only are shown in Figures 1−3.

Table 6. Binary Interaction Parameters from Nonlinear Regression Analysis with Parameters Indicating Quality of the Fits

	interaction parameters (J.mol$^{-1)}$			absolute average deviation	
mixture and models	A_{12}	A_{21}	α_{12}	ΔT/K	vapor phase mole fraction (ΔY)
EtOH + TAEE					
Wilson	−1718.5	−2595.7		0.491	0.011
NRTL	2768.6	877.1	0.3	0.510	0.012
UNIQUAC	641.8	−2811.9		0.521	0.012
2M1B + TAME					
Wilson	2631.4	−8724.2		0.609	0.023
NRTL	9095.8	−3948.4	0.3	1.011	0.020
UNIQUAC	−4281.8	2125.1		0.625	0.022
2M1B + EtOH					
Wilson	2606.5	−5865.7		1.748	0.016
NRTL	4292.6	2116.0	0.3	1.928	0.022
UNIQUAC	−3514.4	260.2		1.872	0.021

Table 7. Experimental VLE Data for EtOH, 2M1B, and TAME at 87 kPa

	vapor-phase (mole fraction)			liquid-phase (mole fraction)		
T/K	EtOH	2M1B	TAEE	EtOH	2M1B	TAEE
307.4	0.319	0.538	0.142	0.089	0.896	0.014
310.5	0.379	0.415	0.204	0.125	0.846	0.028
313.7	0.519	0.313	0.167	0.131	0.795	0.072
313.9	0.112	0.518	0.369	0.133	0.895	0.029
315.2	0.245	0.384	0.370	0.166	0.815	0.017
316.8	0.531	0.273	0.195	0.127	0.756	0.115
317.6	0.358	0.287	0.354	0.215	0.737	0.047
319.6	0.525	0.236	0.237	0.235	0.708	0.055
320.5	0.427	0.216	0.355	0.223	0.653	0.122
321.6	0.509	0.225	0.264	0.244	0.688	0.067
324.1	0.684	0.105	0.210	0.421	0.490	0.087
324.6	0.533	0.172	0.294	0.308	0.600	0.090
328.5	0.726	0.074	0.199	0.499	0.401	0.099
329.2	0.582	0.100	0.317	0.432	0.434	0.133
329.7	0.622	0.094	0.283	0.446	0.430	0.123
330.2	0.913	0.051	0.035	0.558	0.419	0.022
332.7	0.642	0.062	0.293	0.530	0.319	0.150
332.9	0.536	0.074	0.388	0.483	0.335	0.181
333.3	0.739	0.047	0.213	0.590	0.283	0.126
333.5	0.776	0.047	0.176	0.589	0.304	0.106
334.2	0.589	0.065	0.344	0.515	0.314	0.170
335.1	0.851	0.034	0.113	0.652	0.266	0.081
335.5	0.684	0.046	0.269	0.587	0.258	0.153
335.6	0.642	0.076	0.281	0.493	0.371	0.134
335.6	0.611	0.058	0.329	0.537	0.292	0.170
336.2	0.541	0.050	0.408	0.545	0.242	0.212
336.8	0.756	0.042	0.200	0.607	0.268	0.123
336.8	0.591	0.072	0.336	0.497	0.341	0.161
337.5	0.794	0.032	0.172	0.655	0.226	0.117
337.6	0.611	0.048	0.340	0.566	0.249	0.184
337.7	0.821	0.023	0.155	0.703	0.180	0.116
338.8	0.726	0.033	0.239	0.638	0.209	0.151
341.8	0.679	0.012	0.308	0.711	0.078	0.210
342.2	0.480	0.014	0.504	0.624	0.075	0.299
344.3	0.412	0.005	0.582	0.616	0.029	0.354

The results show that all three models are applicable with the binary interaction parameters listed. These results have not been published before.

Ternary Mixtures. Experimentel isobaric vapor−liquid equilibria for the ternary mixture consisting of EtOH, 2M1B, and TAEE are given in Table 7 and in Figure 4 (some results). Theoretical predictions of ternary equilibria using the Wilson, NRTL, and UNIQUAC models with the binary interaction parameters given in Table 6 were carried out, and it was found that the NRTL and UNIQUAC models were suitable. The quality of the fit of the calculated results with the experimental results and parity plots showing agreement are given in Table 8 and Figures 5 and 6, respectively.

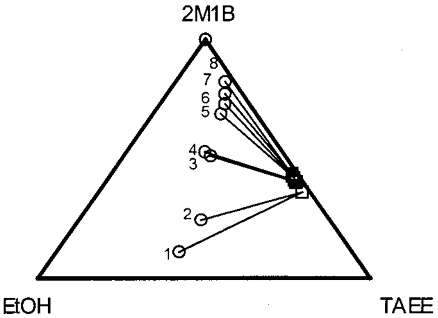

Figure 4. Experimental ternary VLE data for EtOH, 2M1B, and TAME at 87 kPa: vapor phase (○); liquid phase (□); 313.9 K (1); 315.2 K (2); 321.6 K (3); 319.6 K (4); 324 K (5); 328 K (6); 333.5 K (7); 337.7 (8).

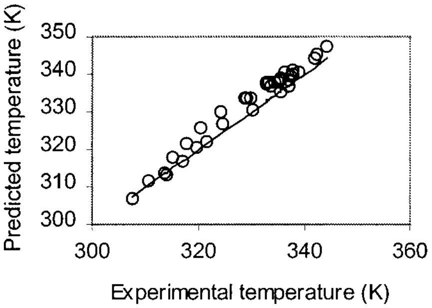

Figure 5. Comparison of experimental and model results (UNIQUAC) of the equilibrium temperature of the ternary mixture; parity plot with a 45° line (—) indicating agreement.

Conclusions

The vapor−liquid equilibria of binary mixtures involving ethanol, 2-methyl-1-butene, and *tert*-amyl ethyl ether can be predicted with the use of either the Wilson, NRTL, or UNIQUAC equilibrium models. The mixtures containing

Table 8. Parameters Indicating Quality of the Fit for a Ternary Mixture Involving Experimental Results Given in Table 7 and Models with Binary Interaction Parameters Given in Table 6

	absolute average deviation		average root mean square deviation	
variables	NRTL	UNIQUAC	NRTL	UNIQUAC
equilibrium temperature/K	2.14	2.71	2.48	3.17
mole fraction of 2M1B in vapor phase	0.046	0.020	0.054	0.028
mole fraction of MeOH in vapor phase	0.049	0.032	0.057	0.039

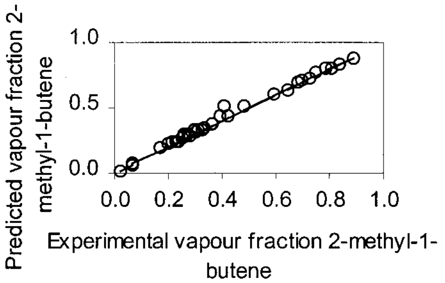

Figure 6. Comparison of experimental and model results (UNIQUAC) of the mole fraction of 2-methyl-1-butene in the equilibrium vapor phase of the ternary mixture; parity plot with a 45° line (—) indicates agreement.

ethanol are characterized by the occurrence of low boiling azeotropes whereas the other mixtures have behavior close to that of an ideal mixture. The NRTL and UNIQUAC multicomponent models are most suitable for the prediction of ternary equilibria involving ethanol, 2-methyl-1-butene, and *tert*-amyl ethyl ether. The results obtained for the *tert*-amyl ethyl ether mixtures are similar to those obtained with the *tert*-amyl methyl ether mixture[6] and have not been published before.

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Received for review February 14, 2000. Accepted November 20, 2000. The financial support for this investigation from Sastech (Sasol), South Africa, is gratefully acknowledged.

JE000053W