

Isobaric Vapor–Liquid Equilibria of Binary and Ternary Mixtures of Heavy Ethers, Isoamylenes, and Alcohols. 1. The Tertiary Amyl Methyl Ether, 2-Methyl-1-butene, and Methanol

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The vapor–liquid equilibrium of binary and ternary mixtures consisting of methanol, 2-methyl-1-butene (2M1B), and *tert*-amyl methyl ether (TAME) was determined at a constant pressure (87 kPa) with an Othmer-type equilibrium still, and activity coefficient models were evaluated. Using a nonlinear regression technique for evaluating the equilibrium models and associated interaction parameters, it was found that the Wilson, NRTL, and UNIQUAC models agreed very well with the binary experimental results. It was also found that the theoretical predictions using the multicomponent NRTL and UNIQUAC models, with binary interaction parameters evaluated from the binary data, agreed with experimental ternary results.

Introduction

The addition of ethers to gasoline to replace leaded octane enhancers and to reduce emissions of carbon monoxide and unburned hydrocarbons is well-known.¹ Interest in the use of the heavier ethers, *tert*-amyl methyl ether (TAME) and *tert*-amyl ethyl ether (TAEE), to supplement the present supply of methyl *tert*-butyl ether (MTBE) has grown steadily over the past decade.^{2,3} The availability of isoamylenes at some refineries, especially oil-from-coal plants, has also stimulated this interest.

Vapor–liquid equilibria of mixtures involving TAME have been examined by Oh and Park,⁴ Marcela et al.,⁵ and Cervenková and Boublik.⁶ These investigators examined essentially binary mixtures consisting of TAME with alcohols (C₁–C₄) and phenol. Phase equilibria involving 2-methyl-1-butene (2M1B) with methanol (MeOH) or/and TAME have not yet been published. Oh and Park⁴ used headspace gas chromatography to obtain isothermal results (323 and 333 K); Marcela et al.⁵ used a Swietoslawski ebulliometric still, and Cervenková and Boublik⁶ used a Boublik and Dvarak apparatus to obtain isobaric results.

An investigation consisting of the experimental determination of isobaric vapor–liquid equilibria of mixtures consisting of MeOH, 2M1B, and TAME and the evaluation of well-known equilibrium models to describe the equilibria was undertaken. This paper presents (1) experimental vapor–liquid equilibria results at 87 kPa for three binary mixtures (MeOH with TAME, 2M1B with TAME, and 2M1B with MeOH) and a ternary mixture (MeOH with 2M1B and TAME), (2) an evaluation of the validity of the Wilson, NRTL, and UNIQUAC models for predicting the binary equilibria, and (3) the prediction of the ternary equilibria with the NRTL and UNIQUAC multicomponent models.

Experimental Section

Apparatus and Procedure. An Othmer-type laboratory still designed by Raal and Brouchaert⁷ was used for

all experimentation. This circulating still consisted of a Cottrell pump and a bubbling chamber and was tested for reproducibility and accuracy with a well-known mixture. The still was operated at local atmospheric pressure (87 kPa). The pressure was measured with a Buchi pressure gauge with an accuracy of ± 0.5 kPa, and temperatures were recorded with a thermocouple (PT 100) with an accuracy of ± 0.01 K. The liquid samples were analyzed with a Hewlett-Packard (HP 6890) gas chromatograph with a CP-wax 52CB column using FID detection with an accuracy of 1 mol %. The experimental procedure consisted of loading the still with 80 mL of liquid followed by heating until a steady-state equilibrium condition was attained at a constant temperature. Microsamples of both phases were taken at appropriate intervals and analyzed.

Chemicals. The purities of all the chemicals used were greater than 99.8 mass %, and the chemicals were supplied by Sigma Aldrich (South Africa). The purities of all chemicals were checked with an analysis by gas chromatography and the measurement of boiling points.

Results and Discussion

Binary Mixtures. Vapor–liquid equilibria data at 87 kPa for the three binary mixtures, namely MeOH (1) with TAME (3), 2M1B (2) with TAME (3), and 2M1B (2) with MeOH (1), are listed in Tables 1–3. The errors associated with the calculated mole fractions (x and y) were estimated to be of the order of 1 mol %. The two binary mixtures involving MeOH both have a minimum boiling azeotrope, whereas the mixture consisting of 2M1B and TAME displayed characteristics close to that of an ideal mixture (see also Figures 1–3). Liquid-phase activity coefficients (γ_i) are also shown in these tables and were calculated using the following equation:

$$\gamma_i = \frac{y_i P}{x_i P_i^{\text{sat}}} \quad (1)$$

which is applicable to low-pressure equilibrium systems with an assumed ideal vapor phase. The symbols x_i and y_i

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Table 1. Experimental Binary VLE Data for MeOH (1) with TAME (3) at 87 kPa

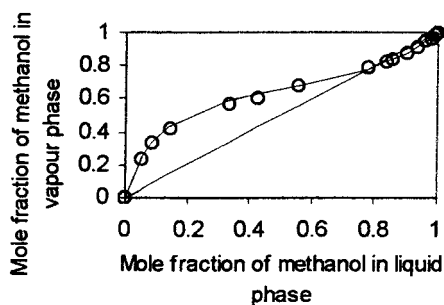
<i>T</i> /K	<i>x</i> ₁	<i>y</i> ₁	γ_1	γ_3
347.3	0.052	0.230	2.657	1.019
344.6	0.086	0.329	2.520	1.008
339.1	0.142	0.416	2.376	1.126
334.4	0.332	0.564	1.664	1.273
333.9	0.427	0.600	1.402	1.388
332.5	0.555	0.679	1.294	1.506
332.3	0.776	0.790	1.085	1.974
333.2	0.837	0.830	1.019	2.125
333.3	0.858	0.840	1.002	2.286
333.7	0.900	0.880	0.983	2.416
334.0	0.935	0.915	0.973	2.588
334.4	0.964	0.947	0.962	2.824
334.6	0.978	0.967	0.960	2.853
335.0	0.990	0.985	0.950	2.895

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

<i>T</i> /K	<i>x</i> ₂	<i>y</i> ₂	γ_2	γ_3
352.9	0.013	0.065	0.996	0.995
349.9	0.032	0.146	1.019	1.018
345.9	0.073	0.295	1.000	0.999
340.7	0.124	0.441	1.000	1.000
337.2	0.155	0.512	1.023	1.022
332.3	0.216	0.620	1.022	1.021
316.8	0.499	0.870	0.991	0.991
315.4	0.533	0.886	0.987	0.987
311.0	0.647	0.929	0.984	0.984
307.6	0.753	0.957	0.977	0.978
302.3	0.930	0.990	0.984	0.985
301.3	0.972	0.996	0.981	0.983

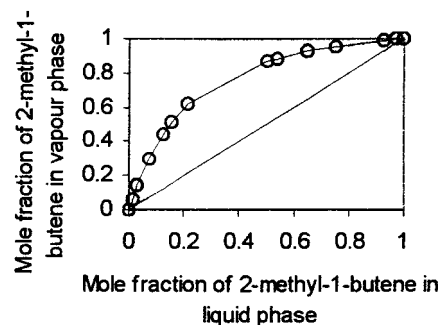
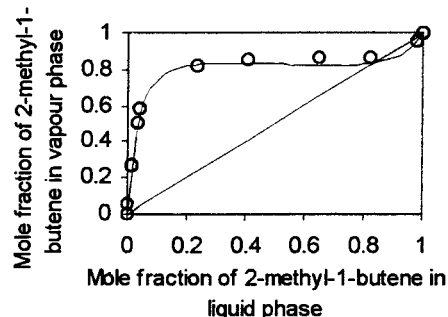
Table 3. Experimental Binary VLE Data for MeOH (1) with 2M1B (2) at 87 kPa

<i>T</i> /K	<i>x</i> ₂	<i>y</i> ₂	γ_1	γ_2
334.4	0.002	0.056	9.004	0.925
329.1	0.012	0.273	8.838	0.895
316.3	0.035	0.508	8.363	1.084
312.1	0.044	0.582	8.670	1.130
299.7	0.238	0.817	3.481	1.148
298.7	0.409	0.856	2.201	1.224
298.6	0.648	0.863	1.405	1.966
298.5	0.823	0.865	1.112	3.880
299.1	0.980	0.952	1.006	11.960

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

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 obtained from the Antoine equation given below with constants listed in Table 4⁸

$$\ln(P_i^{\text{sat}}) = A_i + \frac{B_i}{T + C_i} + D_i T + E_i \ln(T) + F_i T^{G_i} \quad (2)$$

**Figure 2.** Comparison of experimental and model results for the binary mixture of 2M1B with TAME (*x*-*y* plot): experimental data (○); UNIQUAC model (—).**Figure 3.** Comparison of experimental and model results for the binary mixture of 2M1B with MeOH (*x*-*y* plot): experimental data (○); UNIQUAC model (—).**Table 4. Antoine Equation Constants⁸**

component	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>	<i>G</i>
MeOH (1)	82.718	-6904.5	0	0	-8.8622	7.466×10^{-6}	2
2M1B (2)	97.33	-5631.8	0	0	-12.589	1.5395×10^{-2}	1
TAME (3)	62.342	-5911.7	0	0	-5.8464	1.1641×10^{-17}	6

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

binary mixture	<i>D</i>	<i>J</i>	<i>D</i> - <i>J</i>
MeOH + TAME	18.98	9.90	9.08
2M1B + TAME	40.54	26.83	13.76
2M1B + MeOH	13.94	18.59	-4.65

The results from this equation were compared with results from a truncated Antoine equation with corresponding constants published by Krähenbühl and Gmehling,⁹ and the results were found to agree.

The activity coefficients reported in Tables 1–3 were used to test the experimental results obtained for thermodynamic consistency according to the method of Herington¹⁰ (1951). According to this method, the logarithm of the activity coefficient ratio is plotted against the mole fraction of one of the components and the following terms are determined:

$$D = \frac{(K_1 - K_2)}{(K_1 + K_2)} \times 100 \quad (3)$$

$$J = \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{min}}} \times 150 \quad (4)$$

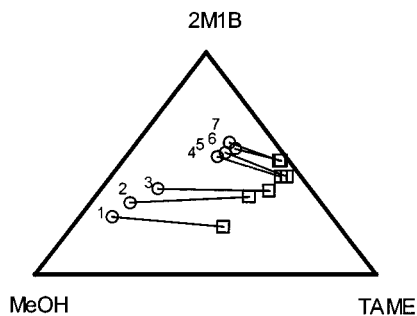
with K_1 and K_2 being the areas lying above and below the axis where the logarithmic coordinate is zero. T_{max} and T_{min} are the maximum and minimum temperatures measured. According to this method, the experimental data are

Table 6. Binary Interaction Parameters from Nonlinear Regression Analyses with Parameters Indicating Quality of the Fit

mixture and models	interaction parameters (J.mol ⁻¹)			absolute average deviation	
	A ₁₂	A ₂₁	α ₁₂	ΔTK	vapor phase mole fraction (ΔY)
MeOH + TAME					
Wilson	-2229.9	-843.0		0.860	0.008
NRTL	2219.9	1338.6	0.3	0.825	0.008
UNIQUAC	807.3	-4112.2		0.767	0.009
2M1B + TAME					
Wilson	-1696.9	1185.6		0.258	0.003
NRTL	-1637.0	2168.3	0.3	0.258	0.003
UNIQUAC	902.9	-1188.9		0.251	0.002
2M1B + MeOH					
Wilson	-4220.3	-5003.5		1.011	0.013
NRTL	3653.3	3772.2	0.3	1.147	0.018
UNIQUAC	-4503.0	279.3		0.149	0.015

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

TK	vapor-phase (mole fraction)			liquid-phase (mole fraction)		
	MeOH	2M1B	TAME	MeOH	2M1B	TAME
314.4	0.215	0.338	0.446	0.262	0.640	0.097
316.9	0.348	0.198	0.453	0.320	0.560	0.119
321.3	0.375	0.125	0.499	0.386	0.443	0.169
324.8	0.478	0.076	0.445	0.461	0.310	0.227
328.5	0.532	0.043	0.424	0.541	0.222	0.236
330.8	0.512	0.022	0.464	0.570	0.127	0.302
330.7	0.510	0.026	0.462	0.595	0.135	0.269
329.2	0.539	0.036	0.424	0.555	0.168	0.276
330.2	0.446	0.037	0.516	0.548	0.166	0.285
342.8	0.842	0.005	0.152	0.385	0.074	0.539
341.3	0.789	0.001	0.209	0.458	0.010	0.531
328.6	0.457	0.049	0.492	0.529	0.202	0.267
337.7	0.674	0.012	0.313	0.526	0.084	0.388
339.8	0.749	0.006	0.243	0.482	0.056	0.460
341.9	0.816	0.004	0.178	0.419	0.052	0.527
339.5	0.897	0.002	0.099	0.305	0.044	0.649
346.7	0.916	0.001	0.082	0.272	0.016	0.711
344.4	0.873	0.000	0.126	0.353	0.002	0.644
345.3	0.893	0.001	0.105	0.317	0.018	0.663
342.6	0.836	0.004	0.159	0.395	0.055	0.549
341.8	0.823	0.008	0.167	0.400	0.087	0.512
330.7	0.756	0.012	0.231	0.463	0.107	0.429
330.3	0.734	0.013	0.251	0.479	0.118	0.402

**Figure 4.** Experimental ternary VLE data for MeOH, 2M1B, and TAME at 87 kPa: vapor phase (○); liquid phase (□); 314.4 K (1); 316.9 K (2); 321.3 K (3); 323.5 K (4); 330.2 K (5); 330.8 K (6); 330.7 K (7).

thermodynamically consistent provided $|D - J|$ is less than a value of 10. The equilibrium results obtained in this

investigation were accordingly analyzed for thermodynamic consistency, and results are given in Table 5. The highly nonideal mixtures (involving methanol) were found to satisfy the criterion for thermodynamic consistency fairly well whereas the binary mixture with characteristics close to that of an ideal mixture deviated slightly from the criterion.

The experimental results shown above were used with a nonlinear regression technique to determine an appropriate equilibrium model and to evaluate corresponding binary interaction parameters. The well-known Wilson, NRTL, and UNIQUAC models which are documented in the literature¹¹ were considered. For the regression calculation the following objective function Q was minimized

$$Q = \sum_N \sum_i \left(\frac{\gamma_i^{\text{exp}} - \gamma_i^{\text{cal}}}{\gamma_i^{\text{exp}}} \right)^2 \quad (5)$$

where N is the total number of points (different temperatures), i is the number of components ($i = 2$), and the superscripts exp and cal indicate experimental and calculated values, respectively. The results of the regression involving the interaction parameters (according to the notation of Gmehling et al.¹¹) are shown in Table 6 with appropriate statistical parameters to indicate the quality of the fit. Figures 1–3 show a comparison between experimental and calculated results for the three mixtures with the UNIQUAC model only (x - y plot). It is clear from the results that all three models can be used to predict the binary equilibria. For the MeOH and TAME mixture, Oh and Park⁴ also found that these models were valid while Marcela et al.⁵ found that the Wilson model was significantly better than the other models. The values of the binary interaction parameters obtained in this investigation for MeOH and TAME, however, are different from that published by these authors. Equilibrium results for the binary mixtures consisting of 2M1B with TAME and 2M1B with MeOH have not been published before.

Ternary Mixtures. Vapor–liquid equilibrium results involving ternary mixtures consisting of MeOH, 2M1B, and TAME at a constant pressure of 87 kPa are shown in Table 7, and some are shown in Figure 4. Theoretical predictions

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

variables	absolute average deviation		average root mean square deviation	
	NRTL	UNIQUAC	NRTL	UNIQUAC
equilibrium temperature/K	2.90	2.37	3.46	2.77
mole fraction of 2M1B in vapor phase	0.033	0.030	0.038	0.037
mole fraction of MeOH in vapor phase	0.036	0.035	0.041	0.042

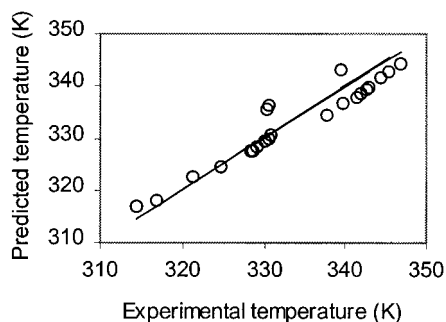


Figure 5. Comparison of experimental and model results (UNIQUAC) of the equilibrium temperature of the ternary mixture; parity plot with a 45° line (—) indicating agreement.

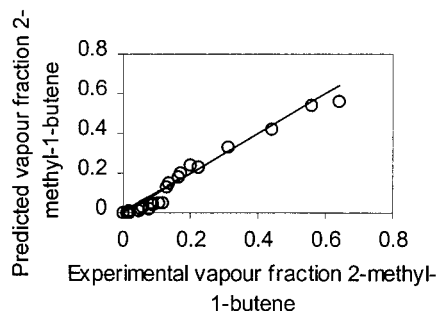


Figure 6. Comparison of experimental and model results (UNIQUAC) of the mole fraction of 2M1B in the equilibrium vapor phase of the ternary mixture; parity plot with a 45° line (—) indicating agreement.

with the Wilson, NRTL, and UNIQUAC multicomponent models, with experimentally determined binary interaction parameters (Table 6), were compared with the experimental ternary equilibrium results. It was found that only the NRTL and UNIQUAC models gave results which agree with the experimental results. Parameters indicating the quality of fit are given in Table 8, and parity plots comparing experimental and calculated results involving temperature and the mole fraction of 2-methyl-1-butene in the vapor phase using the UNIQUAC model are shown in Figures 5 and 6.

Conclusions

Vapor-liquid equilibria of binary mixtures consisting of methanol with *tert*-amyl methyl ether, 2-methyl-1-butene

with *tert*-amyl methyl ether, and 2-methyl-1-butene with methanol were determined experimentally at 87 kPa and were found to be adequately described with the Wilson, NRTL, and UNIQUAC equilibrium models. The mixtures involving methanol have low boiling azeotropes while the other mixture has nearly ideal equilibrium characteristics. Ternary equilibria at 87 kPa involving methanol, 2-methyl-1-butene, and *tert*-amyl methyl ether can be predicted with the NRTL and UNIQUAC multicomponent models with experimentally determined binary interaction parameters.

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