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VAPOR–LIQUID EQUILIBRIUM DATA FOR METHYL *TERT*-BUTYL ETHER–ETHANOL MIXTURES AT 90.0 AND 101.3 kPA

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ABSTRACT

Isobaric vapor–liquid equilibrium (VLE) has been measured using the modified Othmer circulation still for the 2-methoxy-2-methylpropane (MTBE)–ethanol mixtures at 90.0 and 101.3 kPa. Such oxygenate mixtures are being considered for use as octane enhancers in gasoline. The experimental data showed that at 101.3 kPa, this system has an azeotropic point at 95.02 mol% MTBE and 328.06 K. Reducing the pressure to 90.0 kPa did not result in a significant alteration of the VLE of this system. The experimental data were compared with those predicted by the ASOG, the original UNIFAC and the UNIFAC–Dortmund methods of prediction which predicted the bubble point temperature with a root-mean-square deviation (RMSD) at 90.0 kPa of: 1.66, 0.36, and 0.71 K, respectively, and with an RMSD at 101.3 kPa of: 1.97, 0.90, and 1.00 K, respectively. RMSD values of the vapor phase composition

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given by these models at 90.0 kPa were: 0.0201, 0.0046, and 0.0102, respectively, and at 101.3 kPa the RMSD values of the vapor phase composition were: 0.0222, 0.0107, and 0.0117, respectively. Moreover, the experimental data were correlated to the Wilson and the NRTL models. The parameters obtained for these models were used to calculate the bubble point temperature and the vapor phase composition. The calculated data were in a good agreement with the experimental results.

Key Words: 2-Methoxy-2-methylpropane; Ethanol; Vapor–liquid equilibrium; Data

Abbreviations: RMSD, root-mean-square-deviation; VLE, vapor–liquid equilibrium

INTRODUCTION

Separation processes to recover and purify chemical products account for substantial energy consumption in many chemical industries. Distillation is the most common separation process used in the chemical industries. Accurate and reliable vapor–liquid equilibrium (VLE) data are essential to the design of distillation columns. Moreover, the existence of a reliable thermodynamic data bank is a prerequisite for the design, modeling and simulation, optimization, and operation of any separation process.

Ether based oxygenates enhance octane and help complete combustion of blended fuels, and thus are used to reduce the carbon monoxide in the exhaust gas of cars. They have been preferred by refiners over alcohol oxygenates (e.g., ethanol) due to the lower polarity and hence better blending characteristics with gasoline. During the last ten years, thus, ether based oxygenates have been active areas of research as gasoline additives (1–3). So far, methyl *tert*-butyl ether (MTBE), produced by the reaction of methanol with isobutylene in the liquid phase over a strongly acidic ion exchange resin catalyst (3), has been the most common ether candidate due to the favorable economics and availability of the two feedstocks (1). Thus, a blend of gasoline and 7–15% MTBE has been used for high performance premium gasoline. Further, mixtures of ethers–alcohols (e.g., MTBE–alcohols) have also been considered as octane enhancers. In the literature, only recently some studies have been reported on the measurment of the VLE of MTBE–alcohols (4–9).

The objective of this study is to measure the VLE of MTBE–ethanol (1,2) mixtures at two different pressures: 90.0 and 101.3 kPa. The experimental data will be compared with those predicted by the ASOG, the original UNIFAC and the UNIFAC–Dortmund prediction methods. In addition, the experimental data will be correlated to the Wilson and the NRTL models.

EXPERIMENTAL SECTION

Chemicals

MTBE (purity: 99.93%, supplier: Aldrich) and ethanol (purity: 99.9+, supplier: Aldrich, USA) were used in this study. MTBE was used without further purification after GC failed to show any significant impurities. The ethanol was dried with 3 Å and 4 Å molecular sieves (supplier: Aldrich) before use. Purity of the chemicals was checked by measuring the refractive index and the boiling point of the pure components and comparing the measured data with those from the literature as shown in Table 1.

Procedure

The still used in this study is an 800 mL circulation still similar to that used by Subbaiah (10), Abu Al-Rub et al. (11), and Abu Al-Rub and Datta (12) which is a modification of the Othmer still. A detailed description of this still can be found in the above references.

The experiments were conducted at pressures of 90.0 and 101.13 kPa. Steady state was attained after 45 min, where the temperature was measured, using a calibrated thermometer with a resolution of ±0.01 K. Samples of liquid and condensed vapor were withdrawn and analyzed for five times using a Perkin Elmer Auto System Gas Chromatograph with a 6 feet, 1/8 in., SE-30 column.

The consistency of the analysis of GC measurements was checked by preparing known compositions of MTBE–ethanol mixtures and comparing them with those obtained by the GC analysis. The accuracy was found to be ±0.01%. The reproducibility of the VLE data of the MTBE–ethanol mixtures using the

Table 1. Refractive Indices and Boiling Points of the Pure Components

	Refractive Index at 298.15 K		Boiling Point (K) at 101.3 kPa	
Compound	Experimental	Literature (8)	Experimental	Literature (8)
MTBE	1.3664	1.3663	328.32	328.11
Ethanol	1.3593	1.3592	351.45	351.44

modified Othmer still was checked by performing up to three replicate experiments to obtain deviation of the measured data due to random error and was found to be within ±0.01%.

RESULTS AND DISCUSSION

A check on the reliability of the experimental technique, procedure, and apparatus was done in another study by Abu Al-Rub et al. (11) by performing VLE measurements for ethanol–water mixtures at 101.3 kPa. The experimental results thus obtained are compared with those reported in the literature (13) and they showed a good agreement.

Table 2. Vapor–Liquid Equilibria Data for the System MTBE–Ethanol at 90.0 kPa

T (K)	x_1	y_1
348.47	0.0000	0.0000
347.15	0.0125	0.0663
346.04	0.0250	0.1206
343.76	0.0510	0.2139
339.84	0.1052	0.3500
338.55	0.1251	0.3851
333.81	0.2235	0.5211
332.30	0.3001	0.5980
330.75	0.3605	0.6432
329.48	0.4510	0.7002
328.02	0.5222	0.7388
327.30	0.5899	0.7619
326.39	0.6512	0.8001
325.60	0.7495	0.8361
325.26	0.7941	0.8554
324.90	0.8501	0.8851
324.61	0.8900	0.9047
324.52	0.9251	0.9300
324.50	0.9367	0.9382
324.49	0.9400	0.9411
324.48	0.9501	0.9492
324.57	0.9601	0.9579
324.58	0.9910	0.9899
324.76	1.0000	1.0000

The experimental VLE data (T–x–y) for the system MTBE–ethanol at 90.0 and 101.3 kPa are presented in Tables 2 and 3, respectively. Furthermore, Fig. 1 shows the experimental VLE (x–y) of the MTBE–ethanol mixtures at 101.3 kPa along with the ones reported in the literature (4). As can be seen from Fig. 1, a good agreement between the experimental data of this study and those from the literature is obtained. Figures 2 and 3 show the (T–x–y) and (x–y) diagrams for the system MTBE–ethanol at 90.0 and 101.3 kPa respectively. These figures indicate that this system shows a minimum boiling temperature azeotrope. The experimental boiling temperature and the composition at the azeotropic points, along with those from the literature, are summarized in Table 4. In addition, these figures show that changing the pressure by about 10% did not result in any significant alteration in the VLE of the MTBE–ethanol mixtures.

Table 3. Vapor–Liquid Equilibria Data for the System MTBE–Ethanol at 101.3 kPa

T (K)	x_1	y_1
351.45	0.0000	0.0000
348.51	0.0312	0.1310
346.92	0.0518	0.1971
342.31	0.1215	0.3851
340.71	0.1500	0.4415
338.38	0.2009	0.5206
336.84	0.2515	0.5762
335.95	0.2851	0.6091
335.38	0.3002	0.6201
333.01	0.4001	0.6935
332.10	0.5187	0.7400
329.72	0.6689	0.8068
329.00	0.7500	0.8400
328.59	0.8115	0.8615
328.41	0.8445	0.8701
328.20	0.8891	0.9001
328.07	0.9225	0.9279
328.05	0.9305	0.9316
328.06	0.9367	0.9372
328.06	0.9624	0.9613
328.32	1.0000	1.0000

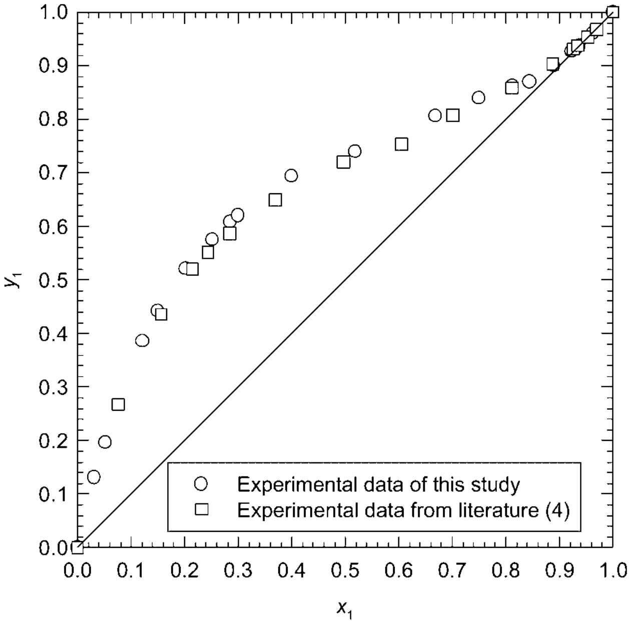

Figure 1. Isobaric x–y data of the MTBE–ethanol mixtures at 101.3 kPa.

The activity coefficients, γ_i, were calculated using the equation (14),

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^s} + \frac{(B_{ii} - V_i^L)(P - P_i^s)}{RT} + \frac{(1 - y_i)^2 P \delta_{ij}}{RT} \tag{1}$$

where γ_i is the activity coefficient of the ith component, y_i is its composition in the vapor phase, x_i is its composition in the liquid phase, P_i^s is its vapor pressure, V_i^L is its molar liquid volume, P is the total pressure, B_{ii} is the second virial coefficient, and $\delta_{ij} \equiv 2B_{ij} - B_{ii} - B_{jj}$. Equation (1) is valid at low pressures where the liquid volumes of the pure components are incompressible and the virial equation of state truncated after the second virial coefficient can adequately describe the vapor phase. The molar virial coefficients were estimated by the method of Hayden and O'Connell (15).

The vapor pressures, P_i^s were calculated using the Antoine equation

$$\log(P_i^s)\,(\mathrm{kPa}) = A + \frac{B}{C + T\,(\mathrm{K})} \tag{2}$$

using the Antoine constants (8) given in Table 5.

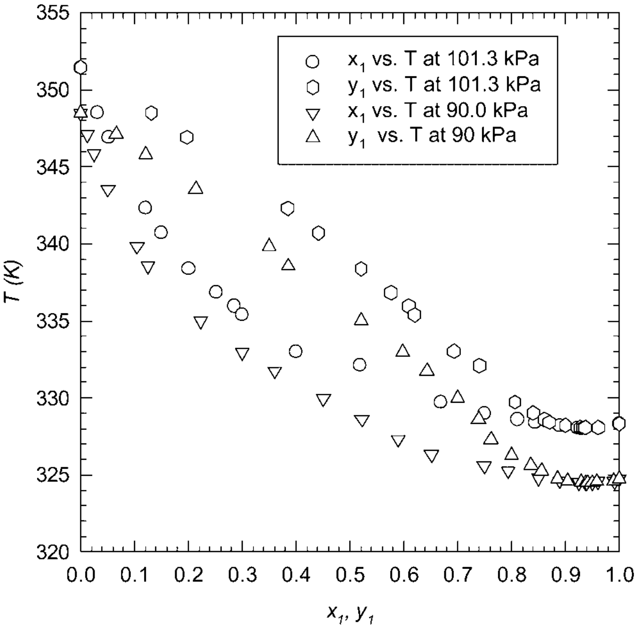

Figure 2. Isobaric T–x–y data of the MTBE–ethanol mixtures at 90.0 and 101.3 kPa.

The calculated activity coefficients can then be used to calculate the molar excess Gibbs energy G^E,

$$G^E/RT = x_1\ln(\gamma_1) + x_2\ln(\gamma_2) \tag{3}$$

Figure 4 shows the molar excess Gibbs energy of the MTBE–ethanol mixtures against the mole fraction of MTBE in the liquid phase. As can be seen from Fig. 4, this system exhibits a positive deviation from ideality ($G^E/RT > 0$).

Thermodynamic Consistency of the Experimental Data

The thermodynamic consistency of the measured VLE data of MTBE–ethanol mixtures at the two studied pressures was checked by the point to point method of Van Ness et al. (16) as modified by Fredenslund et al. (17), the infinite dilution test of Kojima et al. (18) as modified by Jackson and Wilsak (19), and the modified Integral test (20). A four parameter Legendre polynomial was used for the excess Gibbs free energy. According to Van Ness–Byer–Gibbs–Fredenslund test, the VLE data are consistent if the mean absolute deviation

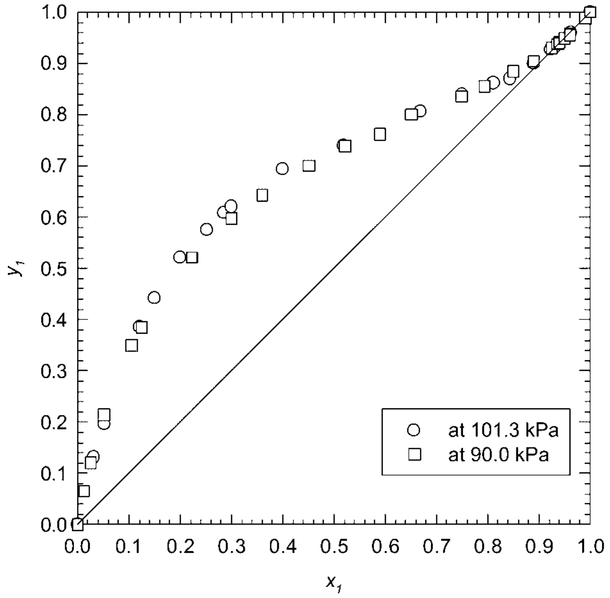

Figure 3. Isobaric x–y data of the MTBE–ethanol mixtures at 90.0 and 101.3 kPa.

between the measured and calculated vapor phase mole fraction is less than 0.01. The experimental VLE data of this study, as shown in Table 6, were found to be thermodynamically consistent according to this test.

The infinite dilution test of Kojima–Jackson–Wilsak involves the calculation of the excess Gibbs energy from the experimental data, and then the extrapolation to infinite dilution. Then, a comparison is made between these extrapolated values and those values obtained by extrapolating the ln γ_1 and ln γ_2 curves to infinite dilution, as shown in Fig. 5. According to this test, the VLE data are consistent if the values agree within 30%. The experimental data of this study, as shown in Table 6, were also found to be thermodynamically consistent according to this test.

Table 4. Antoine Coefficients

Compound	*A*	*B*	*C*
MTBE	6.07034	−1158.19	−43.200
Ethanol	7.16879	−1552.601	−50.731

Table 5. Azeotropic Composition for the System MTBE–Ethanol at 90.0 and 101.3 kPa

	Azeotropic Composition (mol% MTBE)	Azeotropic Temperature (K)
Hiaki et al., (4) at 101.3 kPa	0.9550	327.94
Arce et al., (8) at 101.3 kPa	0.9370	328.06
101.3 kPa	0.9502	328.06
90.0 kPa	0.9565	324.48

Finally, the experimental data were also found to be thermodynamically consistent according to Herington's method (20).

Prediction of the VLE of MTBE–Ethanol Mixtures

The VLE for the system MTBE–ethanol at the two studied pressures were predicted using the ASOG (21), UNIFAC (17) and UNIFAC–Dortmund (22)

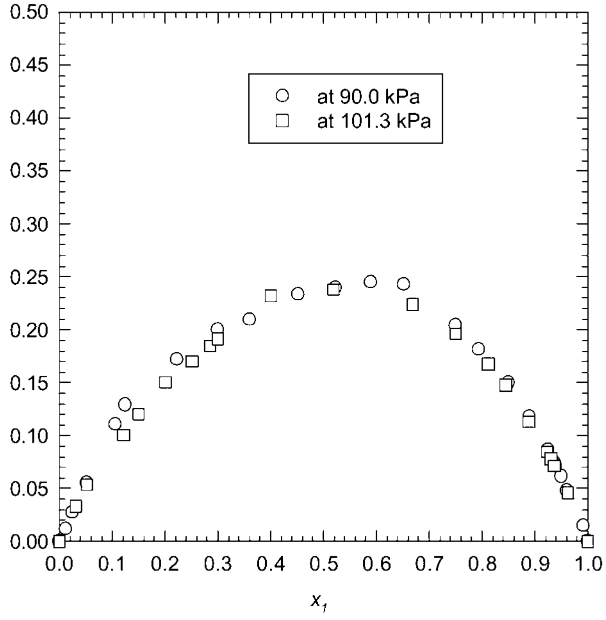

Figure 4. Excess Gibbs energy for the MTBE–ethanol mixtures.

Table 6. Thermodynamic Consistency Tests for the Experimental VLE Data

P (kPa)	Van Ness–Byer–Gibbs–Fredenslund MAD (y)	Kojima–Jackson–Wilsak Error for Dilute Component 1 (%)	Error for Dilute Component 2 (%)
90.0	0.0087	12.8	5.4
101.3	0.0088	15.4	7.5

methods of prediction. Figure 6 shows the comparison between these predictions and the experimental data at 101.3 kPa. Comparison in terms of root-mean-square deviations (RMSD) is shown in Table 7. As can be seen from Fig. 6 and Table 7, the VLE of this system can be predicted satisfactorily by either the original UNIFAC or the UNIFAC–Dortmund methods with the original UNIFAC being the best to predict both bubble point temperature and the vapor phase composition. Prediction of the bubble point temperature and the vapor phase composition using the ASOG method gave poorer agreement with the experimental data.

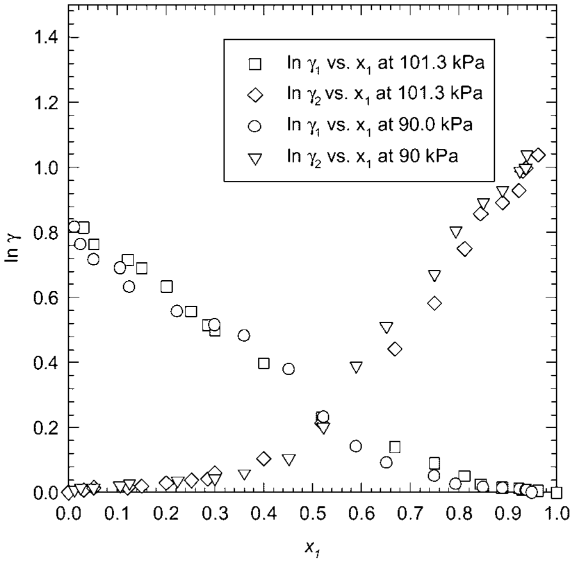

Figure 5. ln γ_1 and ln γ_2 for the MTBE–ethanol mixtures.

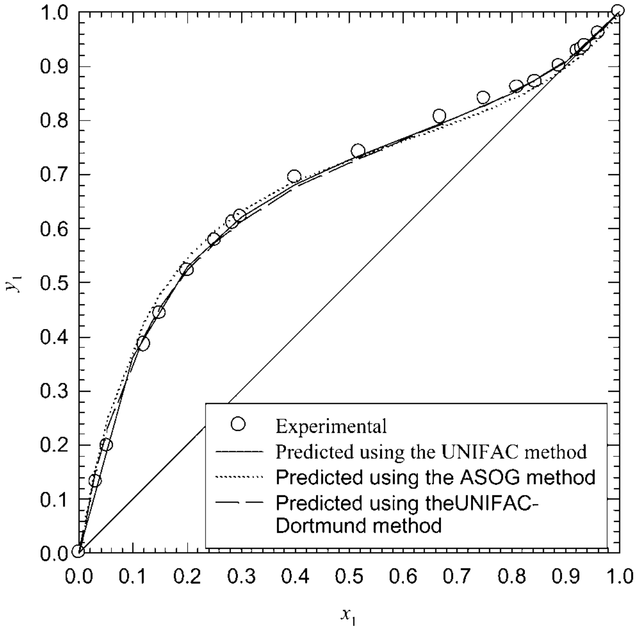

Figure 6. Comparison between experimental and predicted VLE data at 101.3 kPa.

Table 7. RMSD of Bubble Point Temperature and Vapor Phase Composition

Method	T-RMSD	y_1-RMSD
ASOG		
at 90.0 KPa	1.66	0.0201
at 101.3 kPa	1.97	0.0222
Original UNIFAC		
at 90.0 kPa	0.36	0.0046
at 101.3 kPa	0.90	0.0107
Modified UNIFAC		
at 90.0 KPa	0.71	0.0102
at 101.3 kPa	1.00	0.0117

Table 8. Correlation Parameters and Deviations between Experimental and Calculated Values for Different Models

Model	A_{12} (J/mol)	A_{21} (J/mol)	α_{12}	T-RMSD	y_1-RMSD
Wilson					
at 90.0 Kpa	−1444.2	5527.1		0.16	0.0022
at 101.3 kPa	−1423.9	5543.8		0.14	0.0021
NRTL					
at 90.0 Kpa	2590.4	794.9	0.47	0.15	0.0022
at 101.3 kPa	2610.7	774.5	0.47	0.14	0.0019

Correlation

Finally, the activity coefficients were correlated with the Wilson (23) and the NRTL (24) models. The parameters of these equations were obtained by minimizing the following objective function (OF):

$$\mathrm{OF} = \sum_{j=1}^{n} \left(\frac{\gamma_{1,j,\exp} - \gamma_{1,j,\mathrm{cal}}}{\gamma_{1,j,\exp}} \right)^2 + \left(\frac{\gamma_{2,j,\exp} - \gamma_{2,j,\mathrm{cal}}}{\gamma_{2,j,\exp}} \right)^2 \tag{4}$$

where n is the number of data points. The parameters found by minimizing the above OF, and the corresponding root-mean-square mean-deviations (RMSD) are given in Table 8. The results in Table 8 show that the Wilson and NRTL interaction parameters, found in this study, can represent adequately the VLE of the MTBE–ethanol mixtures.

CONCLUSIONS

Isobaric vapor–liquid equilibrium for the system MTBE–ethanol has been measured at 101.3 and 90.0 kPa. The experimental data showed that at 101.3 kPa, this system has an azeotropic point at 95.02 mol% MTBE and 328.06 K. Reducing the pressure to 90.0 kPa did not result in significant alteration in the azeotropic point. Three methods of prediction: the ASOG, original UNIFAC, and the UNIFAC–Dortmund methods were used to predict the VLE of the studied system. Both the original UNIFAC and the modified UNIFAC methods gave satisfactory results with the original UNIFAC being the best in the prediction. Moreover, the experimental data were correlated to the Wilson and NRTL models and the VLE data calculated using these models were in a good agreement with the experimental ones.

NOMENCLATURE

B_{ii}	the second virial coefficient
G	molar Gibbs energy
P	total system pressure (mmHg)
P_i^s	vapor pressure of ith component (mmHg)
T	temperature (K)
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase

Greek letters

φ	the overall range of boiling points of the system
γ_i	activity coefficient of the ith component

Subscript

1	MTBE
2	ethanol
ii	th component

Superscript

E	excess property
L	liquid
s	saturation

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