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# Vapor–Liquid Equilibria and Interfacial Tensions of the System Ethanol + 2-Methoxy-2-methylbutane

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**ABSTRACT:** Isobaric vapor–liquid equilibrium (VLE) data have been measured for the binary system ethanol + 2-methoxy-2-methylbutane at (50, 75, and 94 kPa) and over the temperature range (334 to 356) K. Equilibrium determinations were performed in a VLE still with circulation of both phases. The dependence of interfacial tensions of this mixture on concentration was also determined at atmospheric pressure and 303.15 K, using the maximum differential bubble pressure technique. According to experimental results, the mixture exhibits a positive deviation and a minimum boiling point azeotrope for which the mole fraction impoverishes in ethanol as pressure (or temperature) increases. In addition, the determined interfacial tensions exhibit a negative deviation from the linear behavior. The VLE data of the binary mixture satisfy the Fredenlund's consistency test and were well-correlated by the Wohl, nonrandom two-liquid (NRTL), Wilson, and universal quasichemical (UNIQUAC) equations for all of the measured isobars. Interfacial tensions, in turn, were satisfactorily correlated using the Redlich–Kister equation.

## INTRODUCTION

Oxygenated gasolines have been incorporated in commercial fuels from the past decade, to reduce carbon monoxide emissions, and for reducing ozone depletion in zones where air pollution levels exceed the allowed limits.[1] Oxygenated gasoline approximately contains 2.7 wt % of oxygen and emit 15 % less unburned hydrocarbons than traditional gasoline mixtures. The purpose of oxygenate blending it to add oxygen-bearing solvents to fuels, and alcohols (e.g., methanol, ethanol, butanol) as well as ether oxygenates (such as 2-methoxy-2-methylpropane or MTBE, 2-ethoxy-2-methyl-propane or ETBE, 2,2′-oxybis-[propane] or DIPE, and 2-methoxy-2-methylbutane or TAME) have been demonstrated to be reliable and economical alternatives for the purpose. MTBE and ethanol were first introduced as oxygenates showing an adequate performance as motor fuels with high octane number. However, due to high solubility of MTBE in water it presents significant hazard in case of accidental release to environment, thus forcing to evaluate its substitution by other less harmful ethers. Some well-known alternatives for replacing MTBE are ETBE, DIPE, or TAME. Particularly, TAME shows an attractive potential over DIPE and ETBE since, compared to MTBE, it exhibits comparable thermophysical properties however showing clear benefits as: (a) a lower environmental impact,[2] (b) effective gasoline antiknocking, and (c) it may be produced from commercially available feedstocks.[3] Unfortunately, environmental studies[4] and thermophysical key properties of TAME as co-oxygenate (specifically vapor liquid equilibrium and interfacial tension data) are scarce when compared to other more traditional ether oxygenates.[2]

Previous works reporting vapor–liquid equilibrium (VLE) data of ethanol + TAME cover atmospheric conditions[5] and isothermal conditions ranging from (323.15 to 333.15) K.[6,8] In addition, azeotropic coordinates have also been characterized.[5–8] According to these works, ethanol + TAME exhibits a positive deviation from ideal behavior, and its azeotrope impoverishes in ethanol as pressure (or temperature) increases. In contrast to the experimental VLE characterization—and to the best of our knowledge—no interfacial tension data (IFT) data have been previously reported.

As part as our ongoing research concerning the experimental characterization of TAME mixtures,[9,10] this work is devoted to report new and accurate experimental data for the isobaric phase equilibrium at (50, 75, and 94) kPa and atmospheric interfacial tension at 303.15 K for the case of ethanol + TAME.

## EXPERIMENTAL SECTION

**Purity of Materials.** Ethanol was purchased from Merck, and it was used without further purification. TAME was purchased from Aldrich, and then was purified to 99.7+ mass fraction by rectification in a 1 m height and 30 mm diameter Normschliffgerätebau adiabatic distillation column (packed with 3 × 3 mm stainless steel spirals), working at a 1:100 reflux ratio. The properties and purity of the pure components, as determined by gas chromatography (GC), are reported in Table 1.

The mass densities ($\rho$) and refractive indexes ($n_D$) of pure liquids were measured at 298.15 K using an Anton Paar DMA 5000 densimeter (Austria) and a multiscale automatic refractometer RFM 81 (Bellingham + Stanley, England), respectively. During the operation of these equipments, the temperature was controlled to within ± 0.01 K by means of a thermostatic bath. The uncertainties in density and refractive index measurements are $5 \cdot 10^{-6}$ $g \cdot cm^{-3}$ and $\pm 10^{-5}$, respectively.

The interfacial tensions ($\sigma$) of the pure fluids were measured at 303.15 K using a maximum differential bubble pressure tensiometer, model PC500-LV (Sensadyne, USA). The uncertainties in interfacial tension measurements are $\pm$ 0.1 $mN \cdot m^{-1}$. The temperature of the sample in the vessel is measured by means of a Pt 100 probe and maintained constant to within ± 0.01 K using a thermostatic bath (Julabo, Germany). The experimental values

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**Table 1. Gas Chromatography (GC) Purities (Mass Fraction), Refractive Index ($n_D$) at Na D line, Densities ($\rho$), Normal Boiling Points ($T_b$), and Interfacial Tensions ($\sigma$) of Pure Components**

| component (purity/mass fraction) | $n_D$ at $T$/K = 298.15 | | $\rho$ /g·cm$^{-3}$ at $T$/K = 298.15 | | $T_b$/K at $p$/kPa = 101.33 | | $\sigma$/mN·m$^{-1}$ at $T$/K = 303.15 | |
|---|---|---|---|---|---|---|---|---|
| | exp. | lit.[a] | exp. | lit.[a] | exp. | lit.[a] | exp. | lit.[a] |
| ethanol (0.999) | 1.36068 | 1.35940 | 0.78505 | 0.78589 | 351.45 | 351.44 | 21.70 | 21.68 |
| TAME (0.997) | 1.38712 | 1.38590 | 0.76580 | 0.76587 | 359.52 | 359.51 | 22.00 | 22.01 |

[a] Daubert and Danner.[11]

**Table 2. Experimental VLE Data for Ethanol (1) + TAME (2) at $P$ = 50.00 kPa[a]**

| | | | | | $-B_{ij}$/cm$^3$·mol$^{-1}$ | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | 11 | 22 | 12 |
| 337.44 | 0.000 | 0.000 | | 1.000 | | 1631 | |
| 334.86 | 0.042 | 0.132 | 3.154 | 0.990 | 1210 | 1660 | 769 |
| 333.02 | 0.081 | 0.216 | 2.894 | 0.994 | 1242 | 1683 | 779 |
| 331.78 | 0.118 | 0.276 | 2.668 | 1.000 | 1265 | 1700 | 786 |
| 330.68 | 0.171 | 0.330 | 2.318 | 1.024 | 1286 | 1715 | 792 |
| 329.88 | 0.215 | 0.361 | 2.087 | 1.062 | 1301 | 1725 | 797 |
| 329.41 | 0.260 | 0.394 | 1.917 | 1.088 | 1310 | 1732 | 799 |
| 328.99 | 0.324 | 0.425 | 1.692 | 1.148 | 1319 | 1738 | 802 |
| 328.80 | 0.376 | 0.449 | 1.557 | 1.198 | 1322 | 1740 | 803 |
| 328.72 | 0.422 | 0.470 | 1.455 | 1.250 | 1324 | 1741 | 803 |
| 328.66 | 0.471 | 0.492 | 1.364 | 1.315 | 1325 | 1742 | 804 |
| 328.66 | 0.528 | 0.517 | 1.278 | 1.402 | 1325 | 1742 | 804 |
| 328.70 | 0.578 | 0.539 | 1.217 | 1.492 | 1324 | 1742 | 804 |
| 328.87 | 0.631 | 0.566 | 1.159 | 1.600 | 1321 | 1739 | 803 |
| 329.10 | 0.681 | 0.595 | 1.118 | 1.711 | 1316 | 1736 | 801 |
| 329.39 | 0.729 | 0.622 | 1.077 | 1.866 | 1311 | 1732 | 800 |
| 329.83 | 0.780 | 0.659 | 1.044 | 2.040 | 1302 | 1726 | 797 |
| 330.43 | 0.829 | 0.704 | 1.022 | 2.234 | 1291 | 1718 | 794 |
| 331.25 | 0.881 | 0.762 | 1.003 | 2.501 | 1275 | 1707 | 789 |
| 332.42 | 0.933 | 0.845 | 0.996 | 2.776 | 1253 | 1691 | 782 |
| 334.57 | 1.000 | 1.000 | 1.000 | | 1215 | | |

[a] $T$ is equilibrium temperature; $x_i$ and $y_i$ are mole fractions in liquid and vapor phase of component $i$, respectively. $\gamma_i$ are the activity coefficients of component $i$, and $B_{ij}$ are the molar virial coefficients.

of physical properties and boiling points of the pure fluids are reported in Table 1 and compared with those given in the literature.[11]

**Apparatus and Procedure.** *Vapor–Liquid Equilibrium Cell.* An all-glass VLE apparatus model 601, manufactured by Fischer Labor and Verfahrenstechnik (Germany), was used in the equilibrium determinations. In this circulation-method apparatus, the mixture is heated to its boiling point by a 250 W immersion heater. The vapor–liquid mixture flows through an extended contact line (Cottrell pump) that guarantees an intense phase exchange and then enters to a separation chamber whose construction prevents an entrainment of liquid particles into the vapor phase. The separated gas and liquid phases are condensed and returned to a mixing chamber, where they are stirred by a magnetic stirrer, and returned again to the immersion heater. The temperature in the VLE still was determined with a Systemteknik S1224 digital temperature meter and a Pt 100 probe, which was calibrated against the experimental fusion and boiling points of distilled water. The reliability of such a calibration procedure was successfully checked using the experimental boiling temperature data of the pure fluids used in this work. The accuracy is estimated as ± 0.02 K. The total pressure of the system is controlled by a vacuum pump capable of work under vacuum up to 0.25 kPa. The pressure is measured with a Fischer pressure transducer calibrated against an absolute mercury-in-glass manometer (22 mm diameter precision tubing with cathetometer reading); the overall accuracy is estimated as ± 0.03 kPa.

On average the system reaches equilibrium conditions after (2 to 3) h operation. The 1.0 $\mu$L samples taken by syringe after the system had achieved equilibrium and were analyzed by gas chromatography on a Varian 3400 apparatus provided with a thermal conductivity detector and a Thermo Separation Products model SP4400 electronic integrator. The column was 3 m long and 0.3 cm in diameter, packed with SE-30. Column, injector, and detector temperatures were (353.15, 403.15, and 493.15) K, respectively. Good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak area ratio to the mass composition of the sample. The pertinent polynomial fit of the calibration data had a correlation coefficient $R^2$ better than 0.99. At least three analyses were made of each sample. The maximum standard deviation of these analyses was 0.03 in area percentage. Concentration measurements were accurate to better than ± 0.001 in mole fraction.

*Interfacial Tension Measurements.* A maximum differential bubble pressure tensiometer model PC500-LV manufactured by Sensadyne Inc. (USA), was used in interfacial tension measurements. In this equipment, two probes of different orifice radii ($r_1, r_2$) are immersed in a vessel that contains the liquid sample to be measured. Then an inert gas (e.g., nitrogen) is blown through the probes, and the differential pressure ($\Delta P$) between them is recorded. According to Laplace's equation, $\Delta P$, $r_1$, and $r_2$ are related to the interfacial tension, $\sigma$, as:

$$\Delta P = P_1 - P_2 = 2\sigma(r_1^{-1} - r_2^{-1}) \qquad (1)$$

where $P_i$ is the pressure exerted by the gas flow in the probe of radius $r_i$. The gas flow is controlled by a sensor unit connected to a personal computer through an interface board (PCI-DAS08, Measurement Computing, USA). Besides a constant volume flow controller, this sensor unit contains a differential pressure transducer, a temperature transducer, and pressure regulator. The temperature of the sample in the vessel is measured by means of a Pt 100 probe and maintained constant to within ± 0.01 K using a thermostatic bath (Julabo, Germany).

The experimental procedure for determining interfacial tension is as follows. The mixture to be analyzed is prepared by adding appropriate volumes of each pure fluid, then the concentration of the sample is measured by GC. The sample is then placed into the vessel and heated to the experimental

Table 3. Experimental VLE Data for Ethanol (1) + TAME (2) at $P$ = 75.00 kPa[a]

| | | | | | $-B_{ij}$/cm$^3$·mol$^{-1}$ | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | 11 | 22 | 12 |
| 349.59 | 0.000 | 0.000 | | 1.000 | | 1487 | |
| 346.63 | 0.041 | 0.133 | 3.029 | 0.991 | 1028 | 1519 | 708 |
| 344.48 | 0.079 | 0.223 | 2.812 | 0.992 | 1058 | 1543 | 719 |
| 343.01 | 0.117 | 0.281 | 2.545 | 1.004 | 1079 | 1560 | 726 |
| 341.63 | 0.167 | 0.341 | 2.287 | 1.020 | 1100 | 1576 | 733 |
| 340.64 | 0.210 | 0.380 | 2.097 | 1.048 | 1115 | 1588 | 738 |
| 340.06 | 0.259 | 0.410 | 1.882 | 1.084 | 1124 | 1595 | 741 |
| 339.44 | 0.322 | 0.446 | 1.685 | 1.137 | 1133 | 1602 | 744 |
| 339.16 | 0.373 | 0.472 | 1.560 | 1.183 | 1138 | 1606 | 746 |
| 338.99 | 0.419 | 0.493 | 1.460 | 1.234 | 1141 | 1608 | 747 |
| 338.89 | 0.469 | 0.514 | 1.366 | 1.297 | 1142 | 1609 | 747 |
| 338.84 | 0.525 | 0.540 | 1.282 | 1.377 | 1143 | 1610 | 747 |
| 338.83 | 0.576 | 0.564 | 1.219 | 1.465 | 1143 | 1610 | 747 |
| 338.89 | 0.629 | 0.590 | 1.164 | 1.574 | 1142 | 1609 | 747 |
| 339.01 | 0.679 | 0.616 | 1.119 | 1.700 | 1140 | 1608 | 746 |
| 339.10 | 0.728 | 0.646 | 1.090 | 1.844 | 1139 | 1607 | 746 |
| 339.48 | 0.778 | 0.680 | 1.057 | 2.018 | 1133 | 1602 | 744 |
| 340.12 | 0.829 | 0.726 | 1.029 | 2.208 | 1123 | 1594 | 741 |
| 340.65 | 0.879 | 0.780 | 1.020 | 2.464 | 1115 | 1588 | 738 |
| 341.74 | 0.932 | 0.855 | 1.007 | 2.784 | 1098 | 1575 | 732 |
| 344.02 | 1.000 | 1.000 | 1.000 | | 1064 | | |

[a] $T$ is the equilibrium temperature; $x_i$ and $y_i$ are mole fractions in liquid and vapor phase of component $i$, respectively. $\gamma_i$ are the activity coefficients of component $i$, and $B_{ij}$ are the molar virial coefficients.

Table 4. Experimental VLE Data for Ethanol (1) + TAME (2) at $P$ = 94.00 kPa[a]

| | | | | | $-B_{ij}$/cm$^3$·mol$^{-1}$ | | |
|---|---|---|---|---|---|---|---|
| $T$/K | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | 11 | 22 | 12 |
| 356.84 | 0.000 | 0.000 | | 1.000 | | 1413 | |
| 353.67 | 0.039 | 0.132 | 2.954 | 0.991 | 940 | 1445 | 676 |
| 351.30 | 0.078 | 0.222 | 2.707 | 0.996 | 968 | 1469 | 686 |
| 349.73 | 0.114 | 0.279 | 2.477 | 1.008 | 988 | 1486 | 694 |
| 348.13 | 0.166 | 0.342 | 2.210 | 1.028 | 1008 | 1503 | 701 |
| 346.99 | 0.210 | 0.384 | 2.047 | 1.054 | 1024 | 1515 | 707 |
| 346.32 | 0.257 | 0.419 | 1.874 | 1.079 | 1033 | 1523 | 710 |
| 345.64 | 0.319 | 0.456 | 1.682 | 1.130 | 1042 | 1530 | 713 |
| 345.25 | 0.370 | 0.484 | 1.563 | 1.173 | 1047 | 1535 | 715 |
| 345.05 | 0.416 | 0.505 | 1.460 | 1.224 | 1050 | 1537 | 716 |
| 344.89 | 0.467 | 0.527 | 1.369 | 1.286 | 1052 | 1539 | 717 |
| 344.81 | 0.523 | 0.553 | 1.284 | 1.364 | 1054 | 1540 | 717 |
| 344.78 | 0.577 | 0.578 | 1.217 | 1.456 | 1054 | 1540 | 717 |
| 344.81 | 0.630 | 0.604 | 1.163 | 1.560 | 1054 | 1540 | 717 |
| 344.85 | 0.678 | 0.629 | 1.123 | 1.680 | 1053 | 1539 | 717 |
| 345.00 | 0.729 | 0.660 | 1.088 | 1.824 | 1051 | 1538 | 716 |
| 345.33 | 0.779 | 0.696 | 1.057 | 1.987 | 1046 | 1534 | 715 |
| 345.79 | 0.830 | 0.738 | 1.034 | 2.192 | 1040 | 1529 | 712 |
| 346.37 | 0.880 | 0.791 | 1.020 | 2.431 | 1032 | 1522 | 709 |
| 347.35 | 0.931 | 0.860 | 1.008 | 2.754 | 1019 | 1511 | 705 |
| 349.56 | 1.000 | 1.000 | 1.000 | | 990 | | |

[a] $T$ is the equilibrium temperature; $x_i$ and $y_i$ are mole fractions in liquid and vapor phase of component $i$, respectively. $\gamma_i$ are the activity coefficients of component $i$, and $B_{ij}$ are the molar virial coefficients.

temperature. Thereafter, an inert gas flows through the probes, and the sensor unit translates the voltage signal ($\Delta v$) to a $\Delta P$ signal. The relation between $\Delta v - \Delta P$ is obtained by calibrating the sensor unit using two reference fluids of well-known interfacial tensions (e.g., water and ethanol, respectively). Finally, the interfacial tension is calculated according to eq 1. Additional details concerning to the maximum bubble pressure technique have been extensively described by Adamson and Gast[12] and Rusanov and Prokhorov.[13]

## RESULTS AND DISCUSSION

**Vapor–Liquid Equilibrium.** The equilibrium temperature $T$ and liquid-phase of component $i$, $x_i$, and vapor-phase of component $i$, $y_i$, mole fraction measurements at $P$ = (50, 75, and 94) kPa are reported in Tables 2 to 4 and Figures 1 to 4, together with the activity coefficients ($\gamma_i$) that were calculated from the following equation:[14]

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^{\mathrm{L}})(P - P_i^0)}{RT} + y_j^2 \frac{\delta_{ij} P}{RT} \qquad (2)$$

where $P$ is the total pressure and $P_i^0$ is the pure component vapor pressure. $R$ is the universal gas constant. $V_i^{\mathrm{L}}$ is the liquid molar volume of component $i$, $B_{ii}$ and $B_{jj}$ are the second virial coefficients of the pure gases, $B_{ij}$ is the cross second virial coefficient, and the mixing rule of second virial coefficients ($\delta_{ij}$) is given by

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \qquad (3)$$

According to eq 2, the standard state for calculating activity coefficients is the pure component at the pressure and temperature of the solution. Equation 2 is valid from low to moderate pressures, where the virial equation of state truncated after the second term is adequate for describing the vapor phase of the pure components and their mixtures and, additionally, the liquid molar volumes of pure components are incompressible over the pressure range under consideration. Liquid molar volumes were estimated from the correlation proposed by Rackett.[15] Critical properties were taken from Daubert and Danner.[11] The molar virial coefficients $B_{ii}$, $B_{jj}$, and $B_{ij}$ were estimated by the method of Hayden and O'Connell[16] using the molecular and solvation parameters $\eta$ suggested by Prausnitz et al.[17] for the case of ethanol. For the case of TAME, molecular parameters and physical properties were also taken from ref 11 while the solvation parameter was estimated by smoothing experimental data of second virial coefficients reported in ref 11, thus yielding the value $\eta$ = 0.105. $B_{ii}$, $B_{jj}$, and $B_{ij}$ values are reported in Tables 2 to 4.

The vapor pressures of the pure components have been previously reported as a function of temperature.[9,18] These experimental data have been measured using the same equipment as that for obtaining the VLE data. The temperature dependence of the vapor pressure $P_i^0$ was correlated using the Antoine equation:

$$\log(P_i^0/\mathrm{kPa}) = A_i - \frac{B_i}{(T/\mathrm{K}) + C_i} \qquad (4)$$

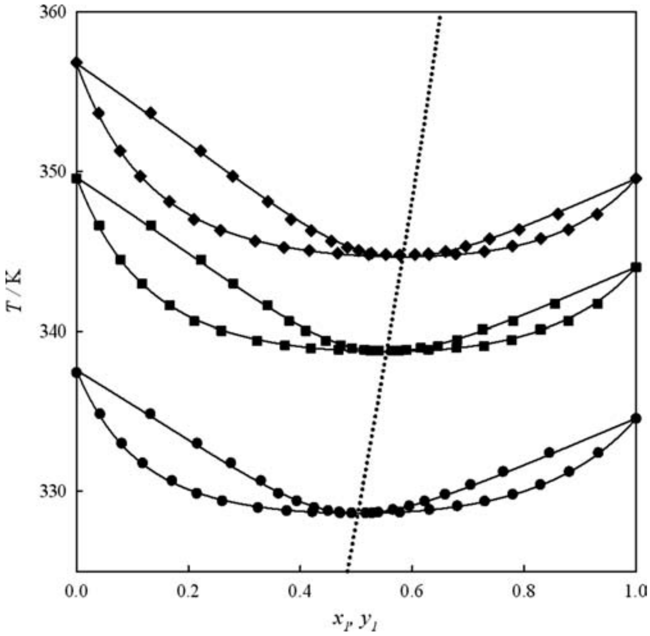

**Figure 1.** Isobaric phase diagram for the system ethanol (1) + TAME (2). Experimental data at ●, 50.00 kPa; ■, 75.00 kPa; ♦, 94.00 kPa; —, predicted from the two-parameter Legendre polynomial used in consistency analysis; - - -, azeotropic line.

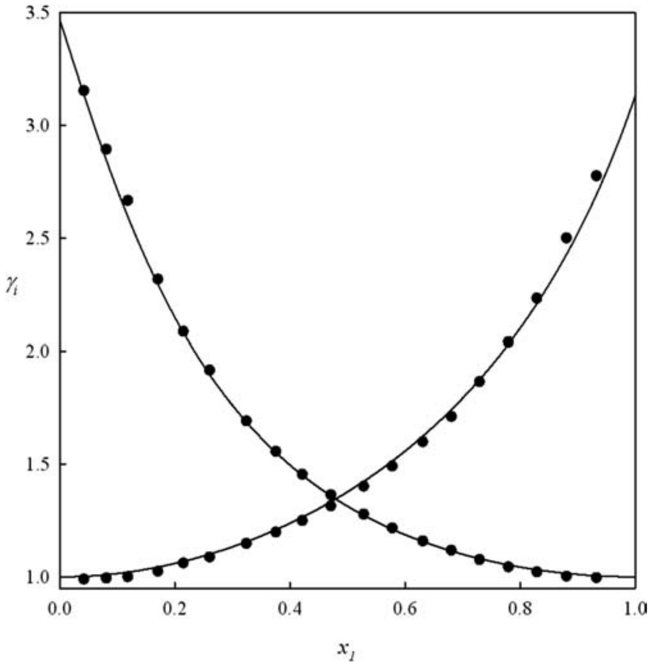

**Figure 2.** Activity coefficient plot for the system ethanol (1) + TAME (2) at 50.00 kPa. ●, experimental data; —, predicted from the two-parameter Legendre polynomial used in consistency analysis.

where the Antoine constants $A_i$, $B_i$, and $C_i$ are summarized in Table 5. The activity coefficients presented in Tables 2 and 4 are estimated accurate to within ± 1.4 %.

The experimental data reported in these tables allow concluding that the binary mixtures exhibit positive deviation from ideal behavior, and azeotropic behavior is present for each isobar. The

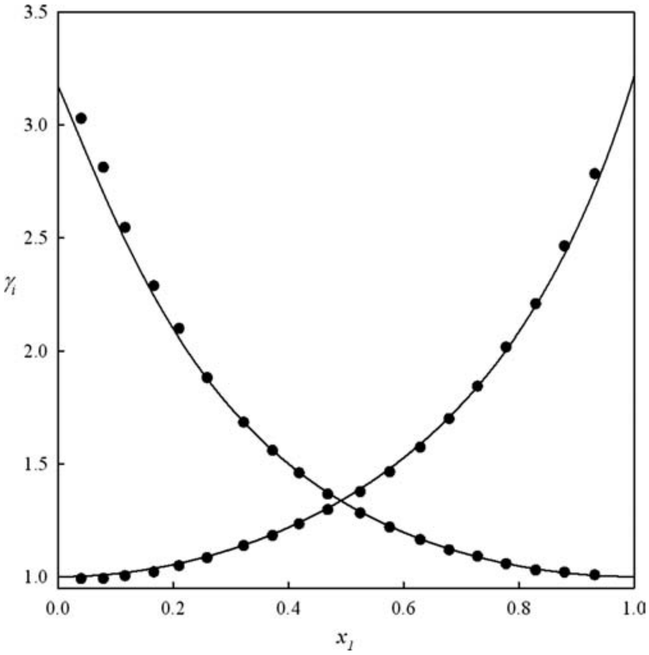

**Figure 3.** Activity coefficient plot for the system ethanol (1) + TAME (2) at 75.00 kPa. ●, experimental data; —, predicted from the two-parameter Legendre polynomial used in consistency analysis.

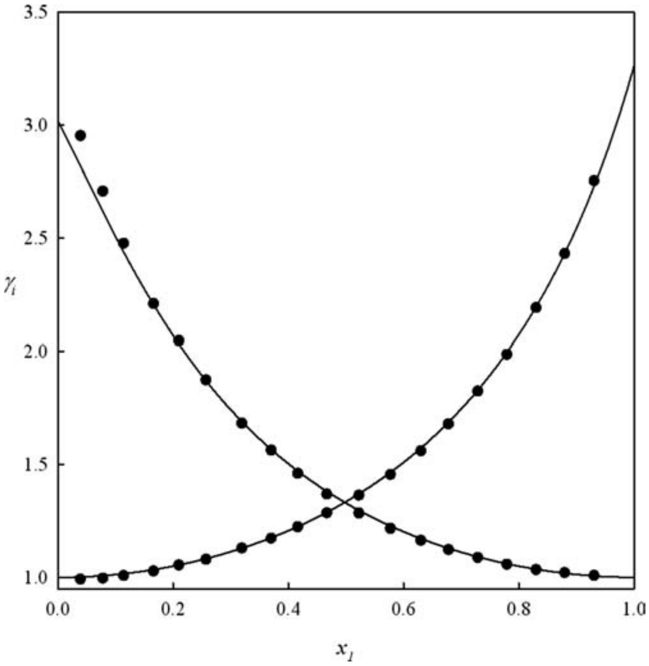

**Figure 4.** Activity coefficient plot for the system ethanol (1) + TAME (2) at 94.00 kPa. ●, experimental data; —, predicted from the two-parameter Legendre polynomial used in consistency analysis.

azeotropic concentrations of the measured binaries were estimated by fitting the function

$$f(x) = 100\left(\frac{y-x}{x}\right) \tag{5}$$

where $f(x)$ is an empirical interpolating function, and $x$ and $y$ have been taken from the experimental data. Azeotropic concentrations, as determined by solving $f(x) = 0$, are indicated in Table 6, from which it is concluded that the mole fraction of the azeotrope impoverishes in ethanol as pressure (or temperature) increases, as it is shown in Figure 1. The reported azeotropic coordinates are in good agreement to results presented by other authors.[5−8]

**Table 5. Antoine Coefficients ($A_i$, $B_i$, and $C_i$) in eq 4[a]**

| compound | $A_i$ | $B_i$ | $C_i$ | temperature range/K |
|---|---|---|---|---|
| ethanol | 7.16178 | 1549.6973 | −50.890 | 310.89 to 351.65 |
| TAME | 5.92939 | 1184.0816 | −57.5413 | 313.24 to 359.33 |

[a] Parameters have been taken from ref 18 for ethanol and from ref 9 for TAME.

**Table 6. Estimated Azeotropic Coordinates for the System Ethanol (1) + TAME (2)[a]**

| $P$/kPa | $x_1^{\mathrm{Az}}$ | $T^{\mathrm{Az}}$/K |
|---|---|---|
| 50 | 0.503 | 328.63 |
| 75 | 0.554 | 338.76 |
| 94 | 0.583 | 344.66 |

[a] $P$ is the pressure of the system; $x_1^{\mathrm{Az}}$ is the azeotropic mole fraction, and $T^{\mathrm{AZ}}$ is the azeotropic temperature.

**Table 7. Consistency Test Statistics for the Binary System Ethanol (1) + TAME (2)**

| $P$/kPa | $L_1$[a] | $L_2$[a] | 100 $\Delta y$[b] | $\delta P$[c]/kPa |
|---|---|---|---|---|
| 50.00 | 1.1644 | −5.6803 | 0.4 | 0.1 |
| 75.00 | 1.1506 | −0.3137 | 0.4 | 0.2 |
| 94.00 | 1.1338 | 0.6575 | 0.2 | 0.2 |

[a] Parameters for the Legendre polynomial[20] used in consistency. [b] Average absolute deviation in vapor phase mole fractions $\Delta y = (1/N)\Sigma_{i=1}^{N}|y_i^{\mathrm{exp}} - y_i^{\mathrm{cal}}|$ ($N$: number of data points). [c] Average absolute deviation in vapor pressure $\delta P = (1/N)\Sigma_{i=1}^{N}|P_i^{\mathrm{exp}} - P_i^{\mathrm{cal}}|$ .

The VLE data reported in Tables 2 to 4 were found to be thermodynamically consistent by the point-to-point method of Van Ness et al.[19] as modified by Fredenslund et al.[20] For each isobaric condition, consistency criterion ($\Delta y < 0.01$) was met by fitting the equilibrium vapor pressure according to the Barker's[21] reduction method. Statistical analysis reveals that a two-parameter Legendre polynomial is adequate for fitting the equilibrium vapor pressure in each case. Pertinent consistency statistics and Legendre polynomial parameters are presented in Table 7.

The VLE data reported in Tables 2 to 4 were correlated with the Wohl, nonrandom two-liquid (NRTL), Wilson, and universal quasichemical (UNIQUAC) equations,[22] whose adjustable parameters were obtained by minimizing the following objective function (OF):

$$\mathrm{OF} = \sum_{i=1}^{N}(|P_i^{\mathrm{exp}} - P_i^{\mathrm{cal}}|/P_i^{\mathrm{exp}} + |y_i^{\mathrm{exp}} - y_i^{\mathrm{cal}}|)^2 \qquad (6)$$

In eq 6, the superscript exp stands for experimental data while cal means calculated quantity. $N$ is the number of data points. The parameters of the different activity coefficient models are reported in Table 8, together with the relative deviation for the case of bubble and dew point pressures. From the results presented in Table 8, it is possible to conclude that all of the fitted models gave a reasonable correlation of the binary system and that the best fit is obtained with the Wohl model. The capability of simultaneously predicting the bubble- and dew-point pressures and the vapor and liquid phase mole fractions, respectively, has been used as the ranking factor. To establish the coherency of the present binary data and to test the predictive capability of the parameters reported in Table 8, we have used the best ranked model (Wohl's model) to predict the binary VLE data reported in other sources. For the case of atmospheric isobaric conditions[5] we obtained a good agreement both in the predicted bubble-point ($\Delta P < 0.91$ %, $\Delta y_i < 0.7$ %) and dew-point pressures ($\Delta P < 0.69$ %, $\Delta x_i < 0.5$ %). For the case of case of isothermal data[6−8] a good agreement

**Table 8. Parameters and Prediction Statistics for Different Gibbs Excess ($G^{\mathrm{E}}$) Models in Ethanol (1) + TAME (2)[a]**

| | | | | | bubble-point pressures | | dew-point pressures | |
|---|---|---|---|---|---|---|---|---|
| model | $P$/kPa | $A_{12}$ | $A_{21}$ | $\alpha_{12}$ | $\Delta P$ (%)[f] | 100 $\Delta y_i$[g] | $\Delta P$ (%)[f] | 100 $\Delta x_i$[g] |
| Wohl | 50.00 | 1.232 | 1.109 | 0.959[d] | 0.27 | 0.4 | 0.45 | 0.4 |
| | 75.00 | 1.185 | 1.134 | 1.045[d] | 0.41 | 0.3 | 0.49 | 0.3 |
| | 94.00 | 1.146 | 1.128 | 1.013[d] | 0.30 | 0.2 | 0.34 | 0.2 |
| NRTL | 50.00 | 1305.66 | 2299.04 | 0.300[e] | 0.33 | 0.4 | 0.52 | 0.4 |
| | 75.00 | 1583.39 | 2051.64 | 0.300[e] | 0.43 | 0.3 | 0.53 | 0.3 |
| | 94.00 | 1701.65 | 1910.23 | 0.300[e] | 0.31 | 0.2 | 0.36 | 0.2 |
| Wilson[b] | 50.00 | 4728.65 | −775.63 | | 0.52 | 0.3 | 0.72 | 0.3 |
| | 75.00 | 4640.20 | −661.00 | | 0.50 | 0.2 | 0.63 | 0.2 |
| | 94.00 | 4608.12 | −658.35 | | 0.40 | 0.1 | 0.45 | 0.1 |
| UNIQUAC[c] | 50.00 | −855.98 | 3047.18 | | 0.26 | 0.4 | 0.45 | 0.4 |
| | 75.00 | −802.20 | 2951.96 | | 0.34 | 0.4 | 0.44 | 0.4 |
| | 94.00 | −795.38 | 2934.12 | | 0.30 | 0.3 | 0.36 | 0.3 |

[a] $A_{12}$ and $A_{21}$ are the $G^{\mathrm{E}}$ model parameters in J·mol$^{-1}$. [b] Liquid molar volumes have been estimated from the Rackett equation.[15] [c] Molecular parameters are those calculated from UNIFAC[20,23] using the following $r$ and $q$ parameters: $r_1 = 2.1055$, $r_2 = 4.7422$, $q_1 = 1.9720$, $q_2 = 4.1720$. [d] $q$ parameter for Wohl's model. [e] $\alpha_{12}$ parameter for the NRTL model. [f] $\Delta P = (100/N)\Sigma_i^N|P_i^{\mathrm{exp}} - P_i^{\mathrm{cal}}|/P_i^{\mathrm{exp}}$. [g] $\Delta\delta = 1/N\Sigma_i^N|\delta_i^{\mathrm{exp}} - \delta_i^{\mathrm{cal}}|$ with $\delta = y$ or $x$.

**Table 9. Interfacial Tensions ($\sigma$) as a Function of the Liquid Mole Fraction ($x_1$) for the Binary System Ethanol (1) + TAME (2) at 303.15 K and 101.3 kPa**

| $x_1$ | $\sigma$ <br> $\text{mN}\cdot\text{m}^{-1}$ |
|---|---|
| 0.000 | 22.00 |
| 0.040 | 21.97 |
| 0.071 | 21.95 |
| 0.137 | 21.93 |
| 0.198 | 21.90 |
| 0.252 | 21.88 |
| 0.303 | 21.86 |
| 0.410 | 21.84 |
| 0.508 | 21.81 |
| 0.611 | 21.78 |
| 0.708 | 21.76 |
| 0.803 | 21.73 |
| 0.898 | 21.71 |
| 1.000 | 21.70 |

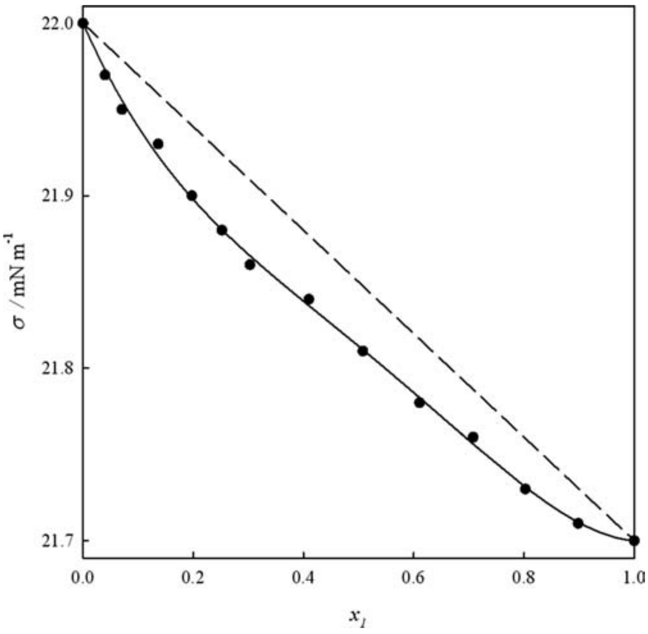

**Figure 5.** Interfacial tension ($\sigma$) as a function of the liquid mole fraction ($x_1$) for the system ethanol (1) + TAME (2) at 303.15 K and 101.3 kPa. ●, experimental data; - - -, lineal behavior ($x_1\sigma_1 + x_2\sigma_2$); —, smoothed by a Redlich–Kister expansion with the parameters shown in Table 9.

both in the predicted bubble-point ($\Delta T < 0.12$ %, $\Delta y_i < 1.0$ %) and dew-point temperatures ($\Delta T < 0.11$ %, $\Delta x_i < 1.3$ %). According to the previous results, we can conclude that the Gibbs excess ($G^E$) parameters reported in this work can be used to accurately and consistently predict the VLE of this binary system.

*Interfacial Tension Data.* The interfacial tension measurements at $T = 303.15$ K and $P = 101.3$ kPa are reported in Table 9 and depicted in Figure 5. These experimental data were correlated using the following Redlich–Kister expansion[24]

$$\sigma = x_1 x_2 \sum_{k=0}^{m} c_k (x_1 - x_2)^k + x_1\sigma_1 + x_2\sigma_2 \qquad (7)$$

In eq 7 $\sigma$ is the interfacial tension of the mixture while $\sigma_i$ is the interfacial tension of the pure components. $m$ denotes the number of $c_k$ parameters. The $c_k$ parameters of eq 7 were obtained by a Simplex optimization technique, and pertinent results together with the correlation statistics are reported in Table 10. From Figure 5 it is possible to conclude that the interfacial tensions of the mixture ethanol + TAME exhibit a negative deviation from the lineal behavior ($x_1\sigma_1 + x_2\sigma_2$).

**Table 10. Coefficients ($c_0$, $c_1$, and $c_2$) and Deviations (Maximum (max dev), Average (avg dev), and Standard (st dev)) Obtained in Correlation of Interfacial Tension, eq 7, for Ethanol (1) + TAME (2) at 303.15 K and 101.3 kPa**

| $c_0$ | $c_1$ | $c_2$ | max dev | avg dev | st dev |
|---|---|---|---|---|---|
| $\text{mN}\cdot\text{m}^{-1}$ | | | $10^3\ \text{mN}\cdot\text{m}^{-1}$ | | |
| −0.1488 | −0.0725 | −0.1971 | 0.05 | 0.01 | 0.01 |

## CONCLUSIONS

Isobaric VLE data [at (50, 75, and 94) kPa] and atmospheric interfacial tensions at 303.15 K have been measured for ethanol + TAME. Experimental results revealed that the phase equilibrium data for this binary mixture exhibits positive deviations from ideal behavior and azeotropic behavior is present. The mole fraction of the azeotrope impoverishes in ethanol as pressure (or temperature) increases in good agreement with previous measurements. In addition, the determined interfacial tensions exhibit negative deviation from the linear behavior.

The activity coefficients and boiling points of ethanol + TAME were well-correlated with the mole fraction using the Wohl, NRTL, Wilson, and UNIQUAC equations, the best fit corresponding to the Wohl model. The interfacial tensions of this mixture were smoothed using the Redlich–Kister equation.

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