# Density, Refractive Index, Speed of Sound at 298.15 K, and Vapor−Liquid Equilibria at 101.3 kPa for Binary Mixtures of Ethyl Acetate + Ethyl Lactate and Methyl Acetate + Ethyl Lactate

**José M. Resa,* José M. Goenaga, and Ana I. Sánchez-Ruiz**

Departamento de Ingeniería Química, Universidad del País Vasco, Apartado 450, 01006, Vitoria, Spain

**Miguel Iglesias**

Departament d'Enginyeria Química, Escola Tècnica Superior d'Enginyeria Química, Universitat Rovira i Virgili,
Avinguda Països Catalans 26, Campus Sescelades, 43007 Tarragona, España

Densities, refractive indices, speeds of sound, and isentropic compressibility at 298.15 K and isobaric vapor−liquid equilibria data at 101.3 kPa were reported for the binary mixtures ethyl acetate + ethyl lactate and methyl acetate + ethyl lactate. Excess molar volumes, refractive index deviations, changes of speed of sound, and changes of isentropic compressibility on mixing were calculated from the measurement results that were fitted with Redlich−Kister polynomials. VLE experimental data were tested for thermodynamic consistency by means of Dechema test and were demonstrated to be consistent. The activity coefficients were correlated with the Margules, van Laar, UNIQUAC, NRTL, and Wilson equations. The ASOG model also was used for prediction.

## Introduction

This work is part of a research project[1−5] whose objective is to measure thermodynamic properties for binary systems involved in the wine distillation processes for further simulation. In this process, multicomponent mixtures are encountered. The main components are water and ethanol, and several minor compounds such as higher alcohols, aldehydes, and acetates are also present. These minor compounds are called congeners. For modeling and process simulation in which mixtures appear, binary data are needed. By this, it is very important to have available vapor−liquid equilibrium (VLE) data of mixtures formed by water + congeners, ethanol + congeners, and congeners + congeners. From the measurements, parameters of some classic correlations such as Wilson, NRTL, and UNIQUAC would be calculated, and results can be applied to study the distillation of wine.

## Experimental Section

***Materials.*** Ethyl Lactate ($x > 99.0$) was supplied by Fluka. Ethyl acetate ($x > 99.9$) from Fluka and methyl acetate ($x = 99$) from Riedel-de Haën were purified by distillation in a laboratory column of 100 plates. The purity of the material was checked by gas−liquid chromatography, and mole fraction $x$ was higher than 99.6. All products were degassed using ultrasound and dried on molecular sieves (pore diameter 3 Å from Fluka) before use. Densities, refractive indexes, and normal boiling points of the pure substances are given in Table 1 and compared with literature values of Riddick et al.[6]

***Apparatus and Procedure.*** The still used to measure VLE data was our own design of a dynamic recirculating apparatus that combines the features of Rock and Sieg[7] and those of Othmer.[8] Figure 1 shows the different parts of this VLE apparatus. The equilibrium temperature was measured with a digital platinum 100 resistance thermometer with an uncertainty of ± 0.01 K. For the pressure measurement, a digital manometer regulator (Divatronic DT1 model) manufactured by Leybold with an uncertainty of ± 0.1 kPa was used. Both vapor- and liquid-phase compositions for the two systems were determined by densimetry and refractometry. Densities were measured at 298.15 K using an Anton Paar DMA 58 vibrating-tube densimeter with an uncertainty of ± 0.00001 $g\cdot cm^{-3}$ that had been calibrated at atmospheric pressure with twice distilled water and dry air. The temperature of the densimeter was maintained at 298.15 K with a uncertainty of ± 0.01 K by means a semiconductor Peltier element and measured by a calibrated platinum resistance thermometer. Refractive indices were measured with a Mettler RE50 refractometer with an uncertainty of ± 0.00001, and temperature was controlled, like the densimeter, with a temperature uncertainty of ± 0.01 K. Speeds of sound were measured with an Anton Paar DSA 48 sound analyzer with an uncertainty of ± 0.1 $m\cdot s^{-1}$, and temperature was controlled by a Peltier cooler to a uncertainty of ± 0.1 K. Prior to measurements, density calibration, refractive index, and speed of sound curves for these systems were obtained to calculate the compositions of the vapor and liquid phases. The binary mixtures were prepared by directly weighing the constituent components with an electronic balance (Salter model ER-182A) that has an uncertainty of ± 0.0001 g. Precautions were taken in order to minimize evaporation losses during storage and preparation of the solutions. The estimated uncertainty in the determination of both liquid- and vapor-phase mole fractions is ± 0.001.

## Results and Discussion

***Density, Refractive Index, and Speed of Sound.*** Table 2 lists the measured density $\rho$, refractive index $n_D$, speed of sound $u$, and isentropic compressibility data at 298.15 K with the corresponding excess molar volume $V^E$, refractive index deviation $\delta n_D$, speed sound deviation $\delta u$, and isentropic compress-

---

* Corresponding author. E-mail: iqpredij@vc.ehu.es.

10.1021/je060052p CCC: \$33.50

**Table 1. Physical Properties of Pure Compounds: Densities $\rho$, Refractive Indices $n_D$, Speed of Sound $u$ at 298.15 K, and Normal Boiling Points $T_b$**

| | $\rho$/(kg·m$^{-3}$) | | $n_D$ | | $u$/(m·s$^{-1}$) | | $T_b$/K | |
|---|---|---|---|---|---|---|---|---|
| | obs | lit.[a] | obs | lit.[a] | obs | lit.[a] | obs | lit.[a] |
| ethyl acetate | 894.29 | 894.55 | 1.36978 | 1.36978 | 1138 | 1138[b] | 350.25 | 350.261 |
| methyl acetate | 926.96 | 927.9 | 1.35865 | 1.3589 | 1148 | 1150[c] | 330.03 | 330.018 |
| ethyl lactate | 1028.02 | 1027.2 | 1.41050 | not avaliable | 1277 | not avaliable | 424.98 | 427.70 |

[a] Riddick et al.[6] [b] Resa et al.[5] [c] Nandhibatla et al.[19]

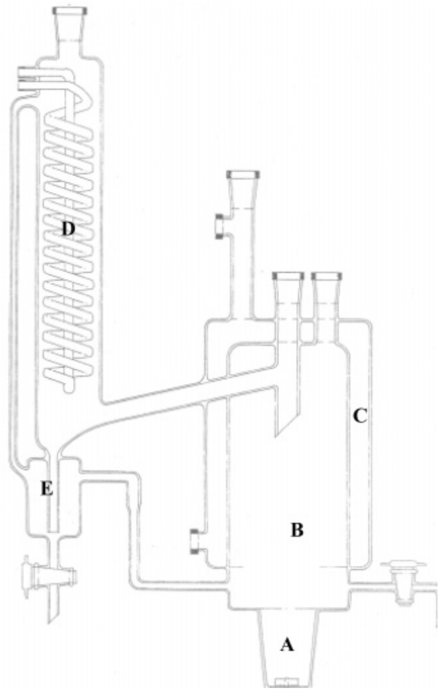

**Figure 1.** Equilibrium recirculation still used to measurement (vapor + liquid) equilibrium (VLE). A, heater; B, liquid-phase tank; C, oil jacket; D, condenser; E, vapor phase tank.

**Table 2. Densities, Refractive Indices, Speed Sounds, and Isentropic Compressibility for Ethyl Acetate (1) + Ethyl Lactate (2) and Methyl Acetate (1) + Ethyl Lactate (2) at 298.15 K with Excess Molar Volume $V^E$, Refractive Index Deviation $\delta n_D$, Speed of Sound Deviation $\delta u$, and Isentropic Compressibility Deviation $\delta k_s$**

| | $\rho$ | $V^E$ | | | $u$ | $\delta u$ | $k_s$ | $\delta k_s$ |
|---|---|---|---|---|---|---|---|---|
| $x_1$ | g·cm$^{-3}$ | cm$^3$·mol$^{-1}$ | $n_D$ | $\delta n_D$ | m·s$^{-1}$ | m·s$^{-1}$ | TPa$^{-1}$ | TPa$^{-1}$ |
| | | | Ethyl Acetate (1) + Ethyl Lactate (2) | | | | | |
| 0.049 | 1.02250 | −0.019 | 1.40880 | 0.000 | 1267 | −1 | 607 | −3 |
| 0.100 | 1.01677 | −0.038 | 1.40722 | 0.001 | 1263 | −0 | 617 | −6 |
| 0.150 | 1.01085 | −0.044 | 1.40535 | 0.001 | 1256 | −0 | 627 | −9 |
| 0.200 | 1.00494 | −0.057 | 1.40357 | 0.001 | 1249 | 0 | 638 | −12 |
| 0.251 | 0.99880 | −0.066 | 1.40168 | 0.001 | 1243 | 0 | 648 | −15 |
| 0.300 | 0.99268 | −0.065 | 1.40005 | 0.002 | 1236 | 0 | 659 | −17 |
| 0.350 | 0.98640 | −0.068 | 1.39819 | 0.002 | 1229 | 0 | 672 | −18 |
| 0.400 | 0.97987 | −0.057 | 1.39623 | 0.002 | 1222 | 0 | 684 | −20 |
| 0.450 | 0.97359 | −0.072 | 1.39451 | 0.002 | 1215 | 0 | 696 | −20 |
| 0.500 | 0.96698 | −0.080 | 1.39263 | 0.003 | 1208 | 0 | 709 | −21 |
| 0.550 | 0.96041 | −0.088 | 1.39060 | 0.002 | 1201 | 1 | 722 | −22 |
| 0.600 | 0.95346 | −0.078 | 1.38855 | 0.002 | 1194 | 1 | 735 | −22 |
| 0.650 | 0.94664 | −0.082 | 1.38645 | 0.002 | 1188 | 1 | 749 | −21 |
| 0.700 | 0.93960 | −0.074 | 1.38420 | 0.002 | 1180 | 1 | 764 | −19 |
| 0.756 | 0.93141 | −0.064 | 1.38126 | 0.002 | 1173 | 1 | 781 | −18 |
| 0.800 | 0.92484 | −0.037 | 1.37923 | 0.001 | 1167 | 1 | 794 | −16 |
| 0.849 | 0.91772 | −0.055 | 1.37694 | 0.001 | 1160 | 1 | 810 | −13 |
| 0.900 | 0.91003 | −0.039 | 1.37470 | 0.001 | 1153 | 1 | 827 | −10 |
| 0.950 | 0.90237 | −0.031 | 1.37220 | 0.000 | 1145 | 0 | 845 | −5 |
| | | | Methyl Acetate (1) + Ethyl Lactate (2) | | | | | |
| 0.058 | 1.02462 | −0.023 | 1.40872 | 0.001 | 1272 | 2 | 603 | −6 |
| 0.100 | 1.02103 | −0.029 | 1.40699 | 0.002 | 1266 | 2 | 611 | −7 |
| 0.150 | 1.01730 | −0.038 | 1.40595 | 0.003 | 1261 | 3 | 618 | −12 |
| 0.200 | 1.01363 | −0.061 | 1.40379 | 0.004 | 1255 | 4 | 626 | −15 |
| 0.250 | 1.00978 | −0.071 | 1.40230 | 0.005 | 1250 | 5 | 634 | −18 |
| 0.300 | 1.00546 | −0.068 | 1.39968 | 0.005 | 1244 | 6 | 643 | −20 |
| 0.350 | 1.00113 | −0.069 | 1.39787 | 0.006 | 1238 | 6 | 652 | −22 |
| 0.400 | 0.99659 | −0.069 | 1.39628 | 0.007 | 1232 | 7 | 661 | −25 |
| 0.450 | 0.99220 | −0.080 | 1.39379 | 0.007 | 1226 | 7 | 670 | −26 |
| 0.500 | 0.98741 | −0.082 | 1.39125 | 0.007 | 1220 | 7 | 680 | −27 |
| 0.550 | 0.98234 | −0.074 | 1.38790 | 0.006 | 1213 | 7 | 692 | −26 |
| 0.600 | 0.97725 | −0.081 | 1.38498 | 0.006 | 1207 | 7 | 703 | −26 |
| 0.650 | 0.97203 | −0.087 | 1.38197 | 0.005 | 1200 | 7 | 714 | −26 |
| 0.700 | 0.96630 | −0.078 | 1.37916 | 0.005 | 1193 | 6 | 727 | −25 |
| 0.750 | 0.96047 | −0.072 | 1.37601 | 0.004 | 1186 | 6 | 740 | −23 |
| 0.800 | 0.95434 | −0.060 | 1.37278 | 0.004 | 1180 | 6 | 753 | −21 |
| 0.850 | 0.94787 | −0.040 | 1.36960 | 0.003 | 1172 | 4 | 768 | −17 |
| 0.900 | 0.94128 | −0.035 | 1.36642 | 0.003 | 1164 | 3 | 784 | −12 |
| 0.950 | 0.93427 | −0.018 | 1.36248 | 0.001 | 1157 | 2 | 800 | −7 |

ibility $\delta k_s$ deviation for the binary mixtures of ethyl acetate + ethyl lactate and methyl acetate + ethyl lactate.

The excess molar volumes of binary mixtures were calculated from density measurements by applying the equation

$$V^E = x_1 M_1(1/\rho - 1/\rho_1) + x_2 M_2(1/\rho - 1/\rho_2) \qquad (1)$$

where $\rho$ is the density of the mixture, $\rho_1$ and $\rho_2$ are the densities of the pure substances, $M_1$ and $M_2$ are the molar masses, and $x_1$ and $x_2$ are the mole fractions. The uncertainty in the calculation of $V^E$ from density measurements was estimated to be ± 0.001 cm$^3$·mol$^{-1}$. Figure 2 illustrates the excess molar volumes of the two binary systems at 298.15 K.

The changes of refractive index $\delta n_D$ at 298.15 K from the linear additive value of the mole fraction is obtained by

$$\delta n_D = n_D - (x_1 n_{D1} + x_2 n_{D2}) \qquad (2)$$

where $n_D$ is the refractive index of the mixture and $n_{D1}$ and $n_{D2}$ are the refractive indices of the pure compounds. The plot of $\delta n_D$ versus the mole fraction $x_1$ of the most volatile compound of each binary system is given in Figure 3.

In the same way, the changes of speed of sound on mixing were calculated by the equation

$$\delta u = u - (x_1 u_1 + x_2 u_2) \qquad (3)$$

where $u$ is the speed of sound of the mixture and $u_1$ and $u_2$ are the speeds of sound of the pure compounds. The plot of $\delta u$ versus the mole fraction $x_1$ of the more volatile compound of each binary system is given in Figure 4.

Isentropic compressibility deviation were calculated by equation

$$\delta k_s = k_s - (x_1 k_{s1} + x_2 k_{s2}) \qquad (4)$$

where $k_s$ is the isentropic compressibilty of the mixture and $k_{s1}$ and $k_{s2}$ are the isentropic compressibilties of the pure compounds. The plot of $\delta k_s$ versus the mole fraction $x_1$ of the more volatile compound of each binary system is given in Figure 5.

Excess molar volumes, changes of refractive index, speeds of sound, and isentropic compressibility deviation on mixing

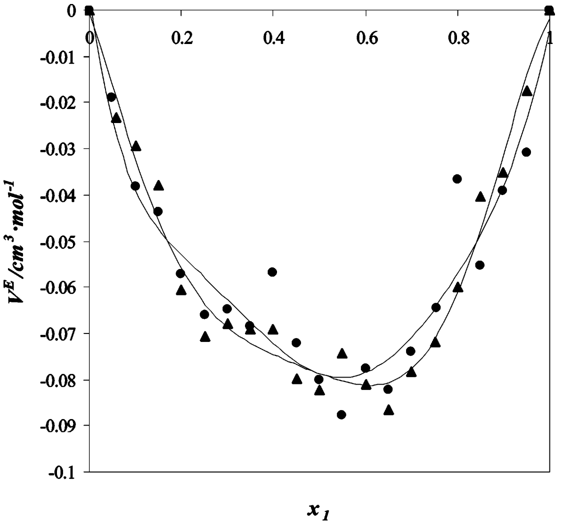

**Figure 2.** Excess molar volumes of mixtures of ethyl acetate (1) + ethyl lactate (2) ▲ and methyl acetate (1) + ethyl lactate (2) ● at 298.15 K.

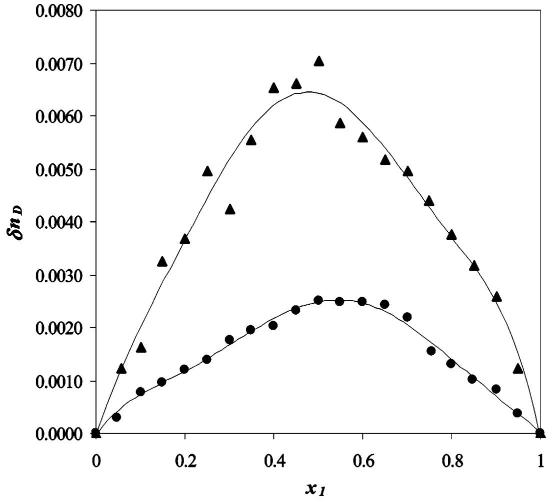

**Figure 3.** Change of refractive indices on ethyl acetate (1) + ethyl lactate (2) ▲ and methyl acetate (1) + ethyl lactate (2) ● at 298.15 K.

of the binary systems were fitted to Redlich−Kister polynomials of the form

$$(V^{\mathrm{E}} \text{ or } \delta_{\mathrm{D}} \text{ or } \delta u \text{ or } \delta k_{\mathrm{s}}) = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k \qquad (5)$$

where $a_k$ is the adjustable parameters obtained by a least-squares fit method and $k$ is the degree of the polynomial expansion. Table 3 lists the parameters with their standard deviations $\sigma$. The coefficients $a_k$ were used to calculate the solid curves (see Figures 2 to 5). The standard deviations $\sigma$ are defined as follows:

$$\sigma = \sqrt{\frac{\sum (Z_{\mathrm{cal}} - Z_{\mathrm{exp}})_i^2}{N - m}} \qquad (6)$$

where $N$ is the number of experimental data, $m$ is the number of equation parameters, and $Z$ is the considered property ($V^{\mathrm{E}}$ or $\delta n_{\mathrm{D}}$ or $\delta u$ or $\delta k_{\mathrm{s}}$) as shown in Table 3.

***VLE Data.*** Vapor−liquid equilibrium data ($T$, $x_1$, $y_1$) for ethyl lactate (1) + ethyl acetate (2) and ethyl lactate (1) + methyl acetate (2) binary systems at 101.3 kPa are presented in Table 4. The $T$−$x_1$−$y_1$ phase diagrams are shown in Figures 6 and 7.

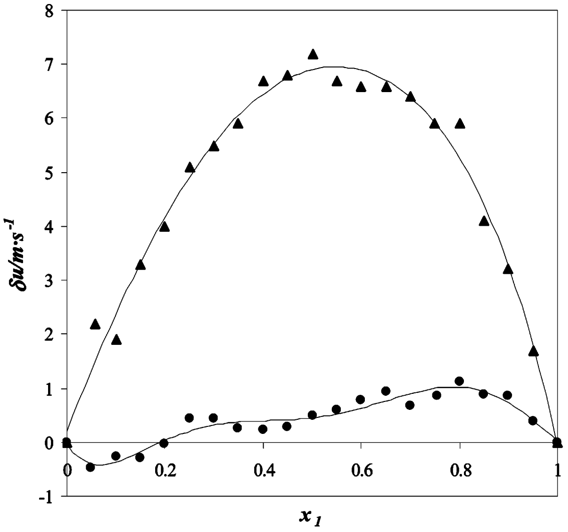

**Figure 4.** Change of speed sounds on mixing Ethyl acetate (1) + ethyl lactate (2) ▲ and methyl acetate (1) + ethyl lactate (2) ● at 298.15 K.

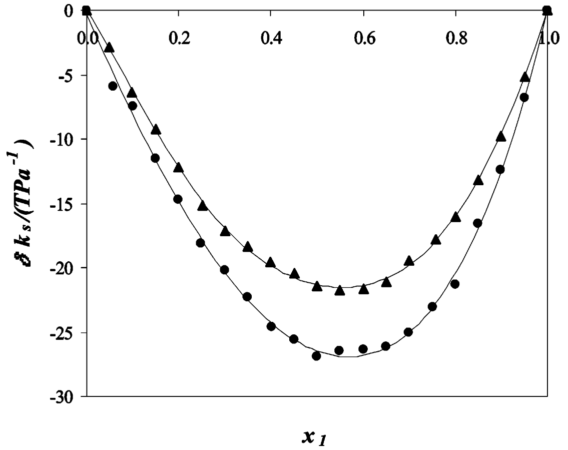

**Figure 5.** Isentropic compressibility deviation of ethyl acetate (1) + ethyl lactate (2) ▲ and methyl acetate (1) + ethyl lactate (2) ● at 298.15 K.

**Table 3. Adjustable Parameters $a_k$ with Standard Deviations $\sigma$ for Excess Molar Volumes $V^{\mathrm{E}}$, Refractive Index Deviations $\delta n_{\mathrm{D}}$, Speeds of Sound Deviations $\delta u$, and Isentropic Compressibility Deviation $\delta k_{\mathrm{s}}$**

| | $V^{\mathrm{E}}$ / cm$^3$·mol$^{-1}$ | $\delta n_{\mathrm{D}}$ | $\delta u$ / m·s$^{-1}$ | $\delta k_{\mathrm{s}}$ / TPa$^{-1}$ |
|---|---|---|---|---|
| | Ethyl Acetate (1) + Ethyl Lactate (2) | | | |
| $a_0$ | −0.315 | 0.009 | 2 | −85 |
| $a_1$ | −0.064 | 0.001 | 2 | −15 |
| $a_2$ | 0.041 | −0.004 | 9 | −15 |
| $a_3$ | 0.109 | −0.002 | 9 | −12 |
| $a_4$ | −0.335 | 0.002 | −14 | 17 |
| $\sigma$ | 0.007 | 0.000 | 0.1 | 0.2 |
| | Methyl Acetate (1) + Ethyl Lactate (2) | | | |
| $a_0$ | −0.324 | 0.027 | 28 | −103 |
| $a_1$ | −0.149 | −0.007 | 5 | −27 |
| $a_2$ | −0.038 | −0.016 | 4 | −13 |
| $a_3$ | 0.439 | 0.019 | 2 | −6 |
| $a_4$ | −0.300 | 0.020 | 2 | −2 |
| $\sigma$ | 0.013 | 0.000 | 0.3 | 0.4 |

The activity coefficients $\gamma_i$ of the components were calculated from

$$\gamma_i = \frac{y_i \Phi_i P}{x_i P_i^0} \qquad (7)$$

where $x_i$ and $y_i$ are the liquid and vapor mole fractions in equilibrium, $\Phi_i$ is a vapor phase correction factor, $P$ is the total

**Table 4. Vapor−Liquid Equilibrium Data for Ethyl Acetate (1) + Ethyl Lactate (2) and Methyl Acetate (1) + Ethyl Lactate (2) Systems: Liquid-Phase Mole Fraction $x_1$, Vapor-Phase Mole Fraction $y_1$, Boiling Temperature $T$, Activity Coefficients $\gamma_1$ and $\gamma_2$ at 101.3 kPa**

| $x_1$ | $y_1$ | $T$/K | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|
| | | Ethyl Acetate (1) + Ethyl Lactate (2) | | |
| 0.000 | 0.000 | 424.98 | | |
| 0.015 | 0.116 | 421.19 | 1.371 | 1.061 |
| 0.035 | 0.238 | 417.39 | 1.258 | 1.055 |
| 0.050 | 0.315 | 414.54 | 1.241 | 1.058 |
| 0.098 | 0.514 | 405.28 | 1.244 | 1.081 |
| 0.152 | 0.624 | 398.08 | 1.142 | 1.145 |
| 0.185 | 0.686 | 393.89 | 1.135 | 1.158 |
| 0.202 | 0.717 | 391.81 | 1.141 | 1.150 |
| 0.246 | 0.765 | 387.77 | 1.101 | 1.175 |
| 0.307 | 0.826 | 381.69 | 1.107 | 1.195 |
| 0.350 | 0.855 | 378.46 | 1.091 | 1.204 |
| 0.417 | 0.890 | 373.82 | 1.077 | 1.226 |
| 0.514 | 0.927 | 367.89 | 1.069 | 1.245 |
| 0.556 | 0.938 | 365.70 | 1.064 | 1.269 |
| 0.604 | 0.948 | 363.83 | 1.044 | 1.292 |
| 0.688 | 0.964 | 360.36 | 1.030 | 1.318 |
| 0.727 | 0.969 | 359.03 | 1.019 | 1.374 |
| 0.766 | 0.975 | 357.43 | 1.021 | 1.387 |
| 0.810 | 0.981 | 355.93 | 1.016 | 1.388 |
| 0.855 | 0.986 | 354.57 | 1.009 | 1.424 |
| 0.943 | 0.995 | 351.87 | 1.003 | 1.461 |
| 0.977 | 0.998 | 350.84 | 1.003 | 1.518 |
| 1.000 | 1.000 | 350.25 | | |
| | | Methyl Acetate (1) + Ethyl Lactate (2) | | |
| 0.000 | 0.000 | 424.98 | | |
| 0.011 | 0.154 | 419.85 | 1.511 | 1.056 |
| 0.043 | 0.401 | 409.96 | 1.207 | 1.071 |
| 0.077 | 0.562 | 401.45 | 1.117 | 1.089 |
| 0.112 | 0.681 | 393.12 | 1.106 | 1.112 |
| 0.153 | 0.775 | 384.62 | 1.112 | 1.132 |
| 0.185 | 0.807 | 381.00 | 1.041 | 1.161 |
| 0.261 | 0.880 | 370.56 | 1.035 | 1.210 |
| 0.289 | 0.898 | 367.01 | 1.044 | 1.239 |
| 0.323 | 0.917 | 363.53 | 1.044 | 1.227 |
| 0.350 | 0.929 | 360.78 | 1.050 | 1.231 |
| 0.409 | 0.947 | 355.74 | 1.052 | 1.261 |
| 0.464 | 0.961 | 351.45 | 1.062 | 1.242 |
| 0.540 | 0.971 | 347.50 | 1.035 | 1.291 |
| 0.596 | 0.978 | 344.49 | 1.033 | 1.285 |
| 0.695 | 0.986 | 340.14 | 1.021 | 1.335 |
| 0.743 | 0.989 | 338.20 | 1.019 | 1.369 |
| 0.785 | 0.991 | 336.72 | 1.013 | 1.440 |
| 0.822 | 0.993 | 335.33 | 1.013 | 1.450 |
| 0.914 | 0.997 | 332.03 | 1.020 | 1.519 |
| 0.955 | 0.999 | 331.01 | 1.012 | 1.019 |
| 0.979 | 0.999 | 330.48 | 1.005 | 2.245 |
| 1.000 | 1.000 | 330.03 | | |

pressure, and $P_i^0$ is the vapor pressure of pure component $i$. These vapor pressures were calculated from the Antoine equation:

$$\log(P_i^0/\text{kPa}) = A_i - \frac{B_i}{(T/\text{K}) + C_i} \tag{8}$$

The constants $A_i$, $B_i$, and $C_i$ are reported in Table 5, and their values were obtained from Riddick et al.[6]

The vapor-phase correction factor is given by

$$\Phi_i = \frac{\phi_i}{\phi_i^{\text{sat}}} \exp\left[-\frac{V_i(P - P_i^0)}{RT}\right] \tag{9}$$

where $\phi_i$ is the fugacity coefficient of component $i$ in the mixture, $\phi_i^{\text{sat}}$ is the fugacity coefficient at saturation, and $V_i$ is the molar volume of component $i$ in the liquid phase.

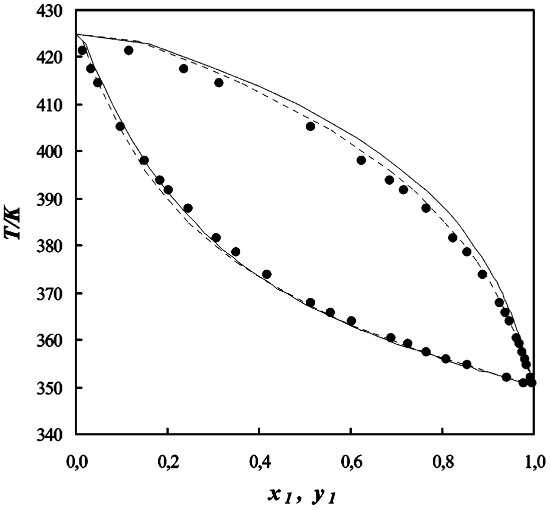

**Figure 6.** $T$−$x_1$−$y_1$ diagram for ethyl acetate (1) + ethyl lactate (2) at 101.3 kPa: ●, experimental data; - - -, Wilson correlation; —, ASOG prediction.

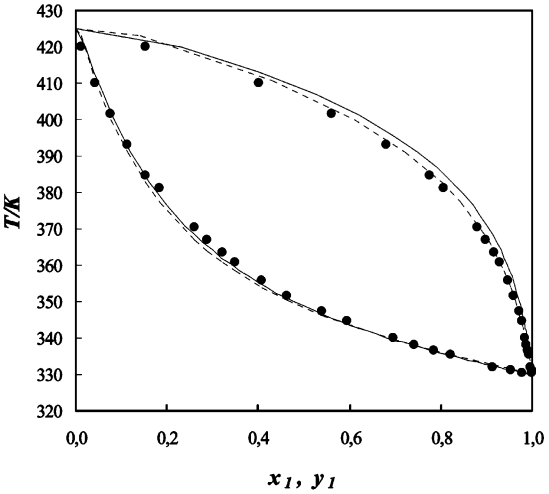

**Figure 7.** $T$−$x_1$−$y_1$ diagram for methyl acetate (1) + ethyl lactate (2) at 101.3 kPa: ●, experimental data; - - -, Wilson correlation; —, ASOG prediction.

**Table 5. Antoine Coefficients, Equation 7**

| compound | $A_i$ | $B_i$ | $C_i$ |
|---|---|---|---|
| ethyl acetate | 6.18799 | 1224.673 | 215.712 |
| methyl acetate | 6.24410 | 1183.700 | 222.414 |
| ethyl lactate | 7.82690 | 2489.700 | 0 |

The activity coefficients were correlated with the Margules,[9] van Laar,[10] Wilson,[11] NRTL,[12] and UNIQUAC[13] equations. To determine the constants of each model, we have used the method "VLE calc" suggested by Gess et al.[14] Estimation of the parameters for the equation was based on the iterative solution, using the maximum likelihood regression of the objective function $Q_i$,[15] with the activity coefficients obtained from the consistency test as experimental values:

$$Q_i = \sum\left(\frac{\gamma_{\text{exptl}} - \gamma_{\text{calcd}}}{\gamma_{\text{exptl}}}\right)^2 \tag{10}$$

where $\gamma_{\text{exptl}}$ is the activity coefficients calculated from experimental data and $\gamma_{\text{calcd}}$ is the coefficients calculated with the correlations. The parameters, the average deviation in $T$ ($\Delta T$), and the average deviation in $y$ ($\Delta y$) are listed in Table 6. Also, the ASOG[16] method was used to obtain predictions in Figures 6 and 7.

**Table 6. Correlation Parameters for Activity Coefficients and Average Deviation for the Studied Systems**

| equation | $A_{12}$ | $A_{21}$ | $\Delta T$/K | $\Delta y_1$ |
|---|---|---|---|---|
| Ethyl Acetate (1) + Ethyl Lactate (2) | | | | |
| Margules[a] | 0.275 | 0.310 | 0.55 | 0.006 |
| van Laar[a] | 0.269 | 0.316 | 0.54 | 0.006 |
| Wilson[b] | 4415.1 | −3426.1 | 0.61 | 0.006 |
| NRTL[c] ($\alpha_{12} = 0.30$) | 814.5 | 149.1 | 0.56 | 0.006 |
| UNIQUAC[d] | 1195.9 | −772.0 | 0.73 | 0.006 |
| Methyl Acetate (1) + Ethyl Lactate (2) | | | | |
| Margules[a] | 0.118 | 0.280 | 0.94 | 0.006 |
| van Laar[a] | 0.120 | 0.408 | 0.85 | 0.006 |
| Wilson[b] | 3603.7 | −2620.7 | 1.05 | 0.008 |
| NRTL[c] ($\alpha_{12} = 0.10$) | 9047.4 | −6455.6 | 0.82 | 0.006 |
| UNIQUAC[d] | 1857.9 | −1186.9 | 0.87 | 0.007 |

[a] Margules and van Laar constants (dimensionless). [b] Wilson's interaction parameters (J·mol$^{-1}$). [c] NRTL's interaction parameters (J·mol$^{-1}$). [d] UNIQUAC's interaction parameters (J·mol$^{-1}$).

**Table 7. Results of the Thermodynamic Consistency Test and of the Margules Constant Test**

| system | avg deviation $\Delta y_1$ | Margules constant |
|---|---|---|
| ethyl acetate (1) + ethyl lactate (2) | 0.008 | 0.3877 |
| methyl acetate (1) + ethyl lactate (2) | 0.004 | 0.2629 |

The thermodynamic consistency of the experimental data was checked by means of a modified Dechema test[17] where the fugacity coefficients are calculated by the method of Hayden and O'Connel,[18] and activity coefficients are calculated by using the four-suffix Margules equation:

$$\bar{G}^{\,E}/RT = x_1x_2[Ax_2 + Bx_1 - Dx_1x_2] \tag{11}$$

with the corresponding activity coefficients

$$\ln \gamma_1 = x_2^{\,2}[A + 2(B - A - D)x_1 + 3Dx_1^{\,2}] \tag{12}$$

$$\ln \gamma_2 = x_1^{\,2}[B + 2(A - B - D)x_2 + 3Dx_2^{\,2}] \tag{13}$$

Parameters $A$, $B$, and $D$ were estimated using the error-in-variables regression maximum likelihood technique. The constraint equation for the regression was

$$F = P - \left(\frac{x_1\gamma_1{}^*f_1^{\,0}}{\phi_1} + \frac{x_2\gamma_2{}^*f_2^{\,0}}{\phi_2}\right) \tag{14}$$

Here the asterisk (*) denotes a calculated or predicted value. An experimental value has no asterisk; $f_1^0$ and $f_2^0$ are the standard state fugacities. The errors in the prediction of $y_1$ were calculated. Predicted $y_1$* values were obtained using the equation

$$y_1{}^* = \frac{x_1\gamma_1{}^*f_1^{\,0}}{\phi_1 P^*} \tag{15}$$

An average deviation was calculated from

$$\text{average deviation} = \frac{\sum_{i=1}^{n} |\Delta y|}{n} \tag{16}$$

Here $\Delta y = y_1 - y_1{}^*$ and $n =$ the number of experimental data points. To pass the consistency test, a system must have an average deviation less than 0.01. The two systems included in this work have passed this consistency test (see Table 7).

We also carried out the Margules constant test using the program of Gess et al.[14] The Margules constant can be used to indicate the ideality of a system. Systems that yield a Margules constant whose absolute value is less than 0.60 can be considered ideal, while those which yield an absolute value greater than 0.60 can be considered nonideal. This criterion for classification, however, is not rigorous. Table 7, shows the values of this constant.

## Conclusions

New VLE data not previously reported in the literature have been measured for the systems ethyl acetate + ethyl lactate and methyl acetate + ethyl lactate as well as binary parameters, values of different correlations, and necessary physical properties for modeling and simulation of wine distillation.

Both systems present ideal behavior. The ASOG method prediction has good agreement with experimental data in both cases.

Correlations for the ethyl acetate + ethyl lactate system are very similar except UNIQUAC correlation, with Van Laar correlation lightly better than the others. Better correlation for the methyl acetate + ethyl lactate system is NRTL, being Wilson correlation the one that has higher deviation from the experimental correlation.

Excess molar volume trend is very similar between the two systems. In fact, we have two compounds (ethyl acetate and methyl acetate) that are from the same family and have a very similar aliphatic chain. One of them has an ethyl group, and the other one has a methyl group. We would anticipate that the behavior was similar between them. Both systems (ethyl acetate + ethyl lactate and methyl acetate + ethyl lactate) have interactions of London dispersion weak forces. Then the $V^E$ values are very small, that is very close to zero. They have a near ideality trend. Our newly designed apparatus of VLE is presented in this paper.

## Literature Cited

(1) Resa, J. M.; González, C.; Juez, M.; Ortiz de Landaluce S. Density, refractive index and speed of sound for mixtures of ethyl acetate with 2-butanol and 3-methyl-1-butanol vapor−liquid equilibrium of the ethyl acetate + 3-methyl-1-butanol system *Fluid Phase Equilib.* **2004**, *217*, 175−180.

(2) Resa, J. M.; González, C.; Goenaga, J. M. Density, refractive index, speed of sound at 298.15 K, and vapor−liquid equilibria at 101.3 kPa for binary mixtures of methanol + 2-methyl-1-butanol and ethanol + 2-methyl-1-butanol. *J. Chem. Eng. Data* **2005**, *50*, 1570−1575.

(3) Resa, J. M.; González, C.; Goenaga, J. M. Density, refractive index, speed of sound at 298.15 K, and vapor−liquid equilibria at 101.3 kPa for binary mixtures of propanol + 2-methyl-1-butanol and propanol + 3-methyl-1-butanol. *J. Chem. Eng. Data* **2006**, *51*, 73−78.

(4) Resa, J. M.; Goenaga, J. M,; Lanz, J.; Iglesias. M. Vapor−liquid equilibrium of binary mixtures containing ethyl acetate + 2-methyl-1-propanol and ethyl acetate + 2-methyl-1-butanol at 101.3 kPa *J. Chem. Eng. Data* **2006**, *51*, 595−598.

(5) Resa, J. M.; González, C.; Goenaga, J. M.; Iglesias. M. Density, refractive index, and speed of sound at 298.15 K and vapor−liquid equilibria at 101.3 kPa for binary mixtures of ethyl acetate + 1-pentanol and ethanol + 2-methyl-1-propanol. *J. Chem. Eng. Data* **2004**, *49*, 804−808.

(6) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*; Wiley-Interscience: New York, 1986.

(7) Rock, H.; Sieg, L.. Measurement of evaporation equilibria in a modernized by-pass apparatus. *Z. Phys. Chem.* (*Muenchen*) **1955**, *3*, 355−64.

(8) Othmer, D. F. Compositions of vapors from boiling binary solutions. *Ind. Eng. Chem.* **1928**, *20*, 743−746.

(9) Margules, M. S. *Akad. B Wien. Math-Naturwiss. KI. II* **1895**, *104*, 1234−1239.

(10) van Laar, J. J. The vapor pressure of binary mixtures. *Z. Phys. Chem.* **1910**, *72*, 723−751.

(11) Wilson, G. M. Vapor−liquid equilibrium. XI. A new expression for the excess free energy of mixing. *J. Am. Chem. Soc.* **1964**, *86*, 6, 127−130.
(12) Renon, H.; Prausnitz, J. M. Estimation of parameters for the NRTL equation for excess Gibbs energies of strongly non-ideal liquid mixtures. *Ind. Eng. Chem. Process. Des. Dev.* **1969**, *8*, 413−419.
(13) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partially or completely miscible systems. *AIChE J.* **1975**, *21*, 116−128.
(14) Gess. M. A.; Danner, R. P.; Nagvekar, M. *Thermodynamic Analysis of Vapor−Liquid Equilibria*: *Recommended Models and a Standard Data Base*; DIPPR/AIChE: 1991.
(15) Patino-Leal, H; Reilly, P. Statistical estimation of parameters in vapor−liquid equilibrium. *AIChE J.* **1982**, *28*, 580−584.
(16) Kojima, K.; Tochigi, K. *Prediction of Vapor−Liquid Equilibria by the ASOG Method*; Kodansha Ltd.: Tokyo, 1979.
(17) Gmehling, J.; Onken, U. *Vapor−Liquid Equilibrium Data Collection*; DECHEMA Chemistry Data Series; DECHEMA: Frankfurt, 1977; Vols. 1−8.
(18) Hayden, J. G.; O'Connell, J. P. A generalized method for predicting second virial coefficients. *Ind. Eng. Chem. Process. Des. Dev.* **1975**, *14*, 209−216.
(19) Sastry, N. V.; Patel, M. C. Densities, excess molar volumes, viscosities, speeds of sound, excess isentropic compressibilities, and relative permittivities for alkyl (methyl, ethyl, butyl, and isoamyl) acetates + glycols at different temperatures *J. Chem. Eng. Data* **2003**, *48*, 1019−1027.

Received for review February 8, 2006. Accepted May 3, 2006.

JE060052P