# Isobaric Vapor-Liquid Equilibria of the Water + 1-Propanol System at 30,60 , and $100 \mathbf{k P a}$ 

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#### Abstract

I sobaric vapor-liquid equilibria for the water + 1-propanol system are reported at 30,60, and 100 kPa . The results were found to be thermodynamically consistent according to Van Ness-Byer-Gibbs, K ojima, and Wisniak methods. The system shows a minimum boiling azeotrope, and the azeotropic composition is scarcely shifted with pressure. Results were compared with literature values. The data were correlated with Margules, Van Laar, Wilson, NRTL, and UNIQUAC liquid-phase activity coefficient models.


## Introduction

Distillation is the most common operation for the separation of liquid binary and multicomponent mixtures. The correct design of distillation columns requires the availability of accurate and, if possible, thermodynamically consistent vapor-liquid equilibria (VLE) data and the use of generalized methods to predict the properties of the mixtures.

The present work is part of a project studying the effect of pressure on the behavior of the azeotropic point in mixtures in which at least one component is an alcohol. For this purpose, the azeotropic system water + 1-propanol was selected. F or this system, isobaric and isothermal VLE data sets have been found in the literature, the majority of these included in the DECHEMA Chemistry Data Series (Gmehling and Onken, 1977, 1981) VLE compilation, and other more recently presented sources (Munday et al., 1980; Morrison et al., 1990; Zielkiewic and Konitz, 1991). Among these, seven isobaric and six isothermal sets of data have been reported in the DECHEMA as consistent according to the point-to-point thermodynamic consistency test of Van Ness-Byer-Gibbs (1973), modified by Fredenslund (1977). However, a detailed study on these data reveals differences with respect to the azeotropic values. The azeotropic points are plotted in Figure 1, showing how azeotropic compositions tend to be scattered. The object of our study is the accurate measurement of VLE and the determination of azeotropic data for the isobaric system at three pressures (30, 60, and 100 kPa ) not previously reported. The contribution presented in this paper includes VLE data that fulfill the thermodynamic consistency tests (Van Ness-Byer-Gibbs, 1973; K ojima et al. 1990; Wisniak, 1993).

## Experimental Section

Chemicals. Milli-Q water and 1-propanol high-purity grade purchased from Aldrich Chemical were used without further purification. The purities of all chemicals, checked by gas chromatography (GC), were as follows: water, 100.00 mass \%; 1-propanol, 99.80 mass \%. Experimental densities of the pure liquids at 293.15 K were measured in a digital precision densimeter, Anton Paar DMA55, with a thermostated bath controlled to 0.01 K . The refractive indexes at 293.15 K were measured using an Abbe refractometer (ATAGO 3T). The accuracies in density and refractive index measurements were $0.00001 \mathrm{~g} \mathrm{~cm}^{-3}$ and $\pm 0.0002$, respectively. The boiling points were determined


Figure 1. Variation of the azeotropic composition for the system water (1) + 1-propanol (2): (O) this work; (©) literature data (points numbered as indicated in Table 6).

Table 1. Physical Properties of Chemicals: Densities d, Refractive Indexes $\mathbf{n}$, and Boiling Points $\mathrm{T}_{\mathrm{b}}$

| compd | $\mathrm{d}(293.15 \mathrm{~K}) / \mathrm{g} \mathrm{cm}^{-3}$ |  | $\mathrm{n}(293.15 \mathrm{~K})$ |  | $\mathrm{T}_{\mathrm{b}}(100.00 \mathrm{kPa}) / \mathrm{K}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | exptl | lit. | exptI | lit. | exptI | lit. |
| water | 0.99806 | $0.99820^{\text {a }}$ | 1.3334 | $1.3330^{\text {a }}$ | 372.78 | $372.77^{\text {a }}$ |
| 1-propanol | 0.80366 | 0.803 75 ${ }^{\text {a }}$ | 1.3853 | $1.3855^{\text {a }}$ | 369.75 | 369.95 ${ }^{\text {a }}$ |

a TRC Thermodynamic Tables Hydrocarbons, 1994.
using the apparatus described below. The experimental values of these properties are listed in Table 1 together with the literature values (TRC, 1994).

Apparatus and Procedure. The equilibrium vessel used in this work is an all-glass, dynamic recirculating still described by Walas (1985), equipped with a Cottrell pump. Thestill (Labodest model), manufactured by Fischer Labor und Verfahrenstechnik (Bonn, Germany) is capable of handling pressures from 0.25 to 400 kPa and temperatures up to 523.15 K . In the boiler, vapor is generated by external heating. The Cottrell pump ensures the intimate contact between the liquid and vapor phases and also with the temperature sensing element. The equilibrium temperature is measured with a digital Ditel thermometer with an accuracy of $\pm 0.01 \mathrm{~K}$. For the pressure measurement,

Table 2. Antoine Coefficients $A$, $B$, and $C$

|  |  | Antoine coefficients |  |  |
| :--- | :---: | :---: | :---: | :---: |
| component | temp range/K | A | B | C |
| water | $274-373$ | 16.5700 | 3984.92 | -39.724 |
| 1-propanol | $303-370$ | 16.0353 | 3415.56 | -70.733 |

Table 3. Vapor-Liquid Equilibrium Data, Liquid-Phase Mole Fraction $\mathrm{x}_{1}$, Vapor-Phase Mole Fraction $\mathrm{y}_{1}$, Temperature T, and Activity Coefficients $\gamma_{i}$ for the Water (1) + 1-Propanol (2) System at 30 kPa

| $\mathrm{x}_{1}$ | $\mathrm{y}_{1}$ | $\mathrm{~T} / \mathrm{K}$ | $\gamma_{1}$ | $\gamma_{2}$ |
| :---: | :---: | :---: | :---: | :---: |
| 0.000 | 0.000 | 341.08 |  |  |
| 0.008 | 0.027 | 340.49 | 3.658 | 1.008 |
| 0.066 | 0.184 | 337.88 | 3.393 | 1.016 |
| 0.137 | 0.315 | 335.92 | 3.057 | 1.015 |
| 0.210 | 0.405 | 334.33 | 2.757 | 1.041 |
| 0.304 | 0.481 | 332.82 | 2.425 | 1.110 |
| 0.377 | 0.514 | 332.26 | 2.145 | 1.194 |
| 0.434 | 0.545 | 332.06 | 1.994 | 1.243 |
| 0.510 | 0.568 | 331.93 | 1.780 | 1.371 |
| 0.578 | 0.583 | 331.93 | 1.613 | 1.537 |
| 0.659 | 0.597 | 331.84 | 1.453 | 1.848 |
| 0.725 | 0.606 | 331.94 | 1.335 | 2.229 |
| 0.779 | 0.612 | 331.99 | 1.252 | 2.725 |
| 0.823 | 0.615 | 332.08 | 1.186 | 3.360 |
| 0.857 | 0.619 | 332.17 | 1.141 | 4.098 |
| 0.889 | 0.622 | 332.27 | 1.100 | 5.211 |
| 0.914 | 0.629 | 332.51 | 1.070 | 6.523 |
| 0.936 | 0.638 | 332.83 | 1.044 | 8.418 |
| 0.954 | 0.661 | 333.43 | 1.033 | 10.646 |
| 0.964 | 0.691 | 334.27 | 1.028 | 11.896 |
| 0.977 | 0.739 | 335.90 | 1.007 | 14.523 |
| 0.983 | 0.796 | 337.06 | 1.023 | 14.519 |
| 0.989 | 0.851 | 338.46 | 1.020 | 15.326 |
| 0.994 | 0.891 | 339.50 | 1.015 | 19.565 |
| 0.997 | 0.935 | 340.52 | 1.015 | 22.240 |
| 1.000 | 1.000 | 342.33 |  |  |
|  |  |  |  |  |

a digital manometer with an accuracy of $\pm 0.01 \mathrm{kPa}$ is used. The temperature probe was calibrated against the ice and steam points of distilled water. High-purity (>99.9 mass \%) hexane vapor pressures were used for the manometer calibration.

In each VLE experiment, the pressure was fixed and remained constant using a vacuum pump, and the heating and shaking systems of the liquid mixture were turned on. The system was kept at the boiling point at least for 30 min to ensure that the steady state was reached. At this moment, $0.2 \mathrm{~cm}^{3}$ samples of liquid and condensed vapor of the Cottrell pump were taken for analysis.

Analysis. All the samples were analyzed by using a Varian Star 3400 CX gas chromatograph with a thermal conductivity detector. The GC response was treated with a Star Chromatography Station. The chromatographic column ( $2 \mathrm{~m} \times 1 / 8 \mathrm{in}$.) was packed with Porapak P . The carrier gas was helium flowing at $50 \mathrm{~cm}^{3} \mathrm{~min}^{-1}$, and the col umn temperature was 383.15 K . The GC was calibrated with gravimetrically prepared standard solutions. The uncertainty of composition measurements was estimated to be $\pm 0.001$. At least two analyses were made for each liquid and each condensed vapor sample.

## Results and Discussion

Vapor pressures $\mathrm{P}_{\mathrm{i}}^{0}$ were calculated with the Antoine equation

$$
\begin{equation*}
\ln \left(\mathrm{P}_{\mathrm{i}}^{0} / \mathrm{kPa}\right)=\mathrm{A}-\frac{\mathrm{B}}{(\mathrm{C}+\mathrm{T} / \mathrm{K})} \tag{1}
\end{equation*}
$$

The Antoine constants for water were those given in DECHEMA Chemistry Data Series (Gmehling and Onken, 1977). For 1-propanol, the values given in Aucejo et al.

Table 4. Vapor-Liquid Equilibrium Data, Liquid-Phase Mole Fraction $x_{1}$, Vapor-Phase Mole Fraction $\mathbf{y}_{1}$, Temperature T, and Activity Coefficients $\gamma_{i}$ for the Water (1) + 1-Propanol (2) System at 60 kPa

| $\mathrm{x}_{1}$ | $\mathrm{y}_{1}$ | $\mathrm{~T} / \mathrm{K}$ | $\gamma_{1}$ | $\gamma_{2}$ |
| :---: | :---: | :---: | :---: | :---: |
| 0.000 | 0.000 | 356.78 |  |  |
| 0.009 | 0.031 | 356.35 | 3.845 | 0.995 |
| 0.045 | 0.123 | 354.53 | 3.318 | 1.009 |
| 0.103 | 0.245 | 352.44 | 3.107 | 1.011 |
| 0.168 | 0.340 | 350.70 | 2.839 | 1.028 |
| 0.231 | 0.408 | 349.51 | 2.603 | 1.051 |
| 0.294 | 0.461 | 348.63 | 2.397 | 1.083 |
| 0.361 | 0.501 | 347.63 | 2.212 | 1.158 |
| 0.417 | 0.527 | 347.74 | 2.005 | 1.197 |
| 0.487 | 0.551 | 347.50 | 1.814 | 1.306 |
| 0.557 | 0.571 | 347.52 | 1.642 | 1.443 |
| 0.621 | 0.585 | 347.53 | 1.508 | 1.631 |
| 0.686 | 0.594 | 347.55 | 1.385 | 1.925 |
| 0.747 | 0.602 | 347.73 | 1.279 | 2.323 |
| 0.796 | 0.605 | 347.80 | 1.203 | 2.850 |
| 0.833 | 0.609 | 347.91 | 1.152 | 3.430 |
| 0.869 | 0.612 | 348.14 | 1.099 | 4.294 |
| 0.892 | 0.620 | 348.28 | 1.078 | 5.070 |
| 0.925 | 0.630 | 348.51 | 1.046 | 7.036 |
| 0.946 | 0.646 | 348.99 | 1.028 | 9.154 |
| 0.960 | 0.672 | 349.92 | 1.014 | 10.992 |
| 0.970 | 0.704 | 350.93 | 1.009 | 12.655 |
| 0.981 | 0.760 | 352.78 | 0.998 | 14.956 |
| 0.988 | 0.806 | 354.43 | 0.983 | 17.840 |
| 0.993 | 0.872 | 356.06 | 0.992 | 18.838 |
| 0.996 | 0.923 | 357.30 | 0.996 | 18.830 |
| 0.999 | 0.974 | 358.02 | 1.019 | 24.684 |
| 1.000 | 1.000 | 359.14 |  |  |
|  |  | 2 |  |  |

(1995) were used. Antoine constants for both compounds are summarized in Table 2.

The experimental VLE data for the binary system at (30, 60 , and 100) kPa are given in Tables 3-5. The $T-x-y$ diagrams at the three pressures are shown in Figure 2. It can be observed that the system presents a minimum boiling azeotrope and the azeotropic composition is scarcely shifted with pressure.

The azeotropic composition, pressure, and temperature are listed in Table 6 along with thermodynamically consistent literature data from the DECHEMA Chemistry Data Series (Gmehling and Onken, 1977, 1981). In all cases, the azeotropic point has been calculated from the experimental data by fitting the function $z=x_{1} / y_{1}$ to a polynomial function of $x_{1}$ and solving for $x_{1}$ at $z=1$. Variation of azeotropic pressure with composition is shown in Figure 1. Azeotropic pressure is shifted to lower values as the water mole fraction increases. The values obtained in this work are in agreement with the tendency shown by the majority of the consistent data previously reported, contributing to reduce the moderate divergence among the different data.

Comparison of VLE data can be also performed by representing the value of $\mathrm{G}^{\mathrm{E}} / \mathrm{RT}$ at constant composition vs $1 / T$. Such a plot for 0.5 mole fraction is presented in Figure 3. The temperature dependence of $\mathrm{G}^{\mathrm{E}}$ may be established by means of $\mathrm{H}^{\mathrm{E}}$ data according to the GibssHelmholtz equation

$$
\begin{equation*}
\left(\frac{\partial\left(\mathrm{G}^{\mathrm{E}} / \mathrm{T}\right)}{\partial(1 / \mathrm{T})}\right)_{\mathrm{P}, \mathrm{n}}=\mathrm{H}^{\mathrm{E}} \tag{2}
\end{equation*}
$$

$\mathrm{H}^{\mathrm{E}}$ being the molar excess enthalpy. The $\mathrm{H}^{\mathrm{E}}$ variation with temperature at equimolar composition has been adjusted from literature $\mathrm{H}^{\mathrm{E}}$ data (Christensen et al., 1984). In Figure 3, two solid lines showing this tendency have been plotted, delimiting the experimental data.

To cal culate the liquid-phase activity coefficients, $\gamma_{i}$, the Poynting factor was considered as unity at the experimen-


Figure 2. Temperature $T$ vs composition ( $x_{1}, y_{1}$ ) for the system water (1) +1 -propanol (2) at constant pressure, $P=30,60$, and $100 \mathrm{kPa}:(\mathrm{O})$ experimental; ( - ) NRTL ( $\alpha_{12}$ adjustable) model.

Table 5. Vapor-Liquid Equilibrium Data, Liquid Phase Mole Fraction $\mathbf{x}_{1}$, Vapor Phase Mole Fraction $\mathbf{y}_{1}$, Temperature T, and Activity Coefficients $\gamma_{i}$ for the Water (1) + 1-Propanol (2) System at $\mathbf{1 0 0} \mathbf{~ k P a}$

| $\mathrm{x}_{1}$ | $\mathrm{y}_{1}$ | $\mathrm{~T} / \mathrm{K}$ | $\gamma_{1}$ | $\gamma_{2}$ |
| :---: | :---: | :---: | :---: | ---: |
| 0.000 | 0.000 | 369.75 |  |  |
| 0.013 | 0.025 | 369.40 | 2.174 | 0.994 |
| 0.038 | 0.097 | 367.84 | 3.056 | 1.003 |
| 0.083 | 0.194 | 366.07 | 2.989 | 1.006 |
| 0.160 | 0.317 | 363.80 | 2.760 | 1.018 |
| 0.226 | 0.390 | 362.46 | 2.530 | 1.041 |
| 0.283 | 0.437 | 361.63 | 2.337 | 1.072 |
| 0.356 | 0.487 | 360.82 | 2.136 | 1.124 |
| 0.426 | 0.522 | 360.47 | 1.939 | 1.192 |
| 0.500 | 0.550 | 360.33 | 1.750 | 1.295 |
| 0.583 | 0.572 | 360.28 | 1.564 | 1.480 |
| 0.648 | 0.585 | 360.27 | 1.440 | 1.701 |
| 0.708 | 0.595 | 360.32 | 1.338 | 1.997 |
| 0.763 | 0.603 | 360.44 | 1.252 | 2.400 |
| 0.817 | 0.608 | 360.62 | 1.171 | 3.047 |
| 0.853 | 0.613 | 360.78 | 1.124 | 3.720 |
| 0.883 | 0.619 | 360.93 | 1.090 | 4.574 |
| 0.911 | 0.627 | 361.12 | 1.062 | 5.841 |
| 0.926 | 0.632 | 361.43 | 1.041 | 6.844 |
| 0.945 | 0.643 | 361.77 | 1.024 | 8.812 |
| 0.957 | 0.663 | 362.41 | 1.018 | 10.369 |
| 0.967 | 0.683 | 363.30 | 1.003 | 12.265 |
| 0.978 | 0.739 | 365.06 | 1.004 | 14.126 |
| 0.985 | 0.794 | 366.87 | 1.000 | 15.232 |
| 0.991 | 0.854 | 368.71 | 0.999 | 16.756 |
| 0.996 | 0.905 | 370.23 | 0.996 | 23.145 |
| 0.999 | 0.984 | 371.95 | 1.015 | 24.348 |
| 1.000 | 1.000 | 372.78 |  |  |
|  |  |  |  |  |

tal conditions. The fugacity coefficients were calculated on the basis of the virial equation of state, with the second virial coefficient being estimated by means of the Pitzer

Table 6. Variation of the Azeotropic Composition and Temperature with Pressure for the System Water (1) + 1-Propanol (2)

|  | P/kPa | $\mathrm{x}_{1}$ | T/K | ref |
| ---: | ---: | :---: | :---: | :--- |
| 1 | 6.4 | 0.604 | 303.15 | Udovenko and Mazanko, 1972 |
| 2 | a |  |  |  |
| 2 | 18.7 | 0.591 | 323.07 | Vrevskii, 1910 |
| 3 | 26.7 | 0.583 | 329.83 | Smirnova, 1959 |
| 4 | 30.0 | 0.585 | 331.90 | this work |
| 5 | 31.2 | 0.574 | 333.15 | Schreiber et al., 1971a |
| 6 | 40.1 | 0.583 | 339.09 | Vrevskii, 1910a |
| 7 | 53.3 | 0.576 | 345.07 | Smirnova, 1959 |
| 8 | 60.0 | 0.575 | 347.52 | this work |
| 9 | 66.7 | 0.550 | 350.66 | Goelles and Still, 1979 |
| 10 | 73.3 | 0.571 | 352.95 | Vrevskii, 1910 |
| 11 | 80.0 | 0.567 | 354.83 | Smirnova, 1959 |
| 12 | 100.0 | 0.569 | 360.29 | this work |
| 13 | 101.1 | 0.599 | 360.57 | Dawe et al., 1973a |
| 14 | 101.3 | 0.567 | 360.81 | Smirnova, 1959a |
| 15 | 101.3 | 0.565 | 360.77 | Kojima et al., 1968 |
| 16 | 110.1 | 0.567 | 363.15 | Ratcliff and Chao, 1969a |

a Data from the DECHEMA Chemistry Data Series (Gmehling and Onken, 1977). ${ }^{\text {b }}$ Data from the DECHEMA Chemistry Data Series (Gmehling and Onken, 1981).


Figure 3. Comparison of $\mathrm{G}^{\mathrm{E}}(\mathrm{x}=0.5) / \mathrm{RT}$ at various temperatures: ( O ) this work; ( $\bullet$ ) literature data (points numbered as indicated in Table 6).
and Curl equations (1957) with the correction proposed by Tsonopoulos (1974). For every experimental pressure-temperature-composition condition, the cal culated fugacity coefficients were close to unity ( 0.9998 maximum, 0.9666 minimum) and were not considered in the analysis of the VLE data. So, the experimental liquid-phase activity coefficients $\gamma_{i}$ were calculated from

$$
\begin{equation*}
\gamma_{i}=\frac{P y_{i}}{x_{i} P_{i}^{0}} \tag{3}
\end{equation*}
$$

The thermodynamic consistency of the VLE experimental data was checked by the following methods: the point-topoint test of Van Ness-Byer-Gibbs (1973), the infinite dilution test proposed by K ojima et al. (1990), modified by J ackson and Wilsak (1995), and the L-W method of Wisniak (1993).

For the point-to-point test of Van Ness-Byer-Gibbs a four-parameter Legendre polynomial was used for the excess Gibbs free energy. Thetemperature dependence of the excess Gibbs free energy was allowed for by the term $\Delta H / R T^{2} d T$ from the Gibbs-Duhem equation. Heat of mixing data were taken from the literature (Christensen et al., 1984). The selected objective function to minimize was the sum of the squared relative deviations in the total pressure. The consistency criteria in this test are that the mean absolute deviation between calculated and measured mole fractions of component 1 in the vapor phase, MAD$(y)$, is less than 0.01, and that deviations scatter randomly about zero. To check the absence of bias in the data, a graphical inspection of the error in $\mathrm{y}_{1}$ is performed, $\mathrm{y}_{1}$

Table 7. Thermodynamic Consistency Tests

| P/kPa | Van Ness-Byer-Gibbs |  | Kojima |  | Wisniak |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | error for dilute component 1 (\%) | error for dilute component 2 (\%) |  |  |  |
|  | MAD(y) | BIAS |  |  | L | W | D |
| 30 | 0.0098 | -0.0054 | 20.4 | 21.4 | 8.23 | 8.66 | 2.58 |
| 60 | 0.0071 | -0.0007 | 6.1 | 1.8 | 8.79 | 9.27 | 2.65 |
| 100 | 0.0070 | 0.0003 | 5.4 | 0.2 | 9.16 | 9.67 | 2.74 |

Table 8. Correlation Parameters for Activity Coefficients, Activity Coefficients at Infinite Dilution $\gamma_{i}^{\infty}$, and Mean Absolute Deviations MAD(y) and MAD(T)

| P/kPa | model | $\mathrm{A}_{12}$ | $\mathrm{A}_{21}$ | $\alpha_{12}$ | $\gamma_{1}^{\infty}$ | $\gamma_{2}^{\infty}$ | MAD(y) | MAD(T) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 30.00 | Margules | $0.9388^{\text {a }}$ | $2.6214^{\text {a }}$ |  | 2.56 | 13.75 | 0.0291 | 0.64 |
|  | Van Laar | $1.2133^{\text {a }}$ | $2.9060^{\text {a }}$ |  | 3.36 | 18.28 | 0.0109 | 0.33 |
|  | Wilson | $5451.42^{\text {b }}$ | $4019.48^{\text {b }}$ |  | 4.19 | 25.24 | 0.0107 | 0.37 |
|  | NRTLC | $8103.12^{\text {b }}$ | $-5.61{ }^{\text {b }}$ | $0.30^{\text {a }}$ | 3.35 | 17.19 | 0.0115 | 0.35 |
|  | NRTL ${ }^{\text {d }}$ | $1048.05^{\text {b }}$ | $2190.39^{\text {b }}$ | $-1.56{ }^{\text {a }}$ | 4.16 | 18.91 | 0.0062 | 0.29 |
|  | UNIQUAC | 1867.76 ${ }^{\text {b }}$ | $194.98{ }^{\text {b }}$ |  | 3.12 | 19.00 | 0.0117 | 0.39 |
| 60.00 | Margules | $0.9000^{\text {a }}$ | $2.6011^{\text {a }}$ |  | 2.46 | 13.48 | 0.0297 | 0.74 |
|  | Van Laar | $1.1578{ }^{\text {a }}$ | $2.9373{ }^{\text {a }}$ |  | 3.18 | 18.86 | 0.0101 | 0.31 |
|  | Wilson | $5442.05^{\text {b }}$ | $4521.85{ }^{\text {b }}$ |  | 3.85 | 26.47 | 0.0088 | 0.31 |
|  | NRTL ${ }^{\text {c }}$ | $8738.57{ }^{\text {b }}$ | $-198.20^{\text {b }}$ | $0.30^{\text {a }}$ | 3.16 | 17.42 | 0.0120 | 0.35 |
|  | NRTL ${ }^{\text {d }}$ | $977.32^{\text {b }}$ | $2313.63{ }^{\text {b }}$ | $-1.56{ }^{\text {a }}$ | 3.76 | 19.29 | 0.0064 | 0.21 |
|  | UNIQUAC | $2127.32^{\text {b }}$ | 37.79 ${ }^{\text {b }}$ |  | 3.00 | 19.11 | 0.0113 | 0.37 |
| 100.00 | Margules | $0.8164^{\text {a }}$ | $2.5933{ }^{\text {a }}$ |  | 2.26 | 13.37 | 0.0299 | 0.86 |
|  | Van Laar | $1.1010^{\text {a }}$ | 2.9219a |  | 3.01 | 18.58 | 0.0099 | 0.31 |
|  | Wilson | 5457.66 ${ }^{\text {b }}$ | $4505.32^{\text {b }}$ |  | 3.60 | 23.93 | 0.0109 | 0.34 |
|  | NRTLC | $9218.80^{\text {b }}$ | -414.77 ${ }^{\text {b }}$ | $0.30^{\text {a }}$ | 2.96 | 17.00 | 0.0117 | 0.34 |
|  | NRTL ${ }^{\text {d }}$ | $874.58{ }^{\text {b }}$ | $2399.76^{\text {b }}$ | $-1.57{ }^{\text {a }}$ | 3.39 | 18.78 | 0.0062 | 0.21 |
|  | UNIQUAC | $2132.80^{\text {b }}$ | $37.71^{\text {b }}$ |  | 2.95 | 17.98 | 0.0109 | 0.33 |

${ }^{\text {a }}$ Dimensionless. ${ }^{\mathrm{b}} \mathrm{J}$ mol ${ }^{-1}$. ${ }^{\mathrm{c}}$ With recommended $\alpha_{12}$ value. ${ }^{\mathrm{d}}$ With adjustable $\alpha_{12}$.


Figure 4. Deviation between calculated and measured vaporphase mole fraction $\left(y_{1}\right)$ vs liquid-phase mole fraction $\left(x_{1}\right)$ for the water (1) + 1-propanol (2) system at constant pressure, $P=60$ kPa.
residuals being plotted vs $\mathrm{x}_{1}$. This plot for the 60 kPa data is shown, as an example, in Figure 4. Similar plots were obtained at 30 kPa and at 100 kPa . Experimental VLE data were found thermodynamically consistent according to this test, with the values of MAD(y) and sum of $\mathrm{y}_{1}$ residuals (BIAS) as listed in Table 7.

The application of the infinite dilution test of K ojima (1990) includes the calculation of the excess Gibbs free energy from the experimental data, and the extrapolation to infinite dilution using smoothing functions. The extrapolated values are then compared with those extrapolated of $\ln \gamma_{1}$ and $\ln \gamma_{2}$ at infinite dilution, and thermodynamic consistency is achieved if the values agree to within $30 \%$. The results at 60 kPa are shown in Figure 5 where $\mathrm{G}^{\mathrm{E}} / \mathrm{RT} \mathrm{x}_{1} \mathrm{x}_{2}$, In $\gamma_{1}$, and In $\gamma_{2}$ have been plotted vs $\mathrm{x}_{1}$. Deviations of the extrapol ated values at the three pressures (Table 7) were within the method tolerance.


Figure 5. Infinite dilution test for the water (1) + 1-propanol (2) binary system at constant pressure, $\mathrm{P}=60 \mathrm{kPa}$ : ( O ) $\operatorname{In} \gamma_{1} ;(\diamond) \mathrm{In}$ $\gamma_{2}$; (口) $\mathrm{G}^{\mathrm{E}} / \mathrm{RTx}_{1} \mathrm{x}_{2}$; (-) NRTL ( $\alpha_{12}$ adjustable) model; (---) polynomial regression; $(+)$ excluded points.

The $L-W$ method of Wisniak requires the evaluation of the integrals $L$ and $W$ as described in the paper by Wisniak (1993), and values of the deviation D defined as

$$
\begin{equation*}
\mathrm{D}=100 \frac{|\mathrm{~L}-\mathrm{W}|}{\mathrm{L}+\mathrm{W}} \tag{4}
\end{equation*}
$$

less than 3-5 indi cate thermodynamic consistency. As can be observed in Table 7, experimental VLE data were also found consistent according to the Wisniak test.

The activity coefficients were correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations (Gmehling and Onken, 1977). To fit the binary parameters, a nonlinear optimization method was used to minimize the function

$$
\begin{equation*}
\mathrm{F}=\sum_{\mathrm{n}} \sum_{\mathrm{i}}\left(\frac{\gamma_{\text {exptl }}-\gamma_{\text {calcd }}}{\gamma_{\text {exptl }}}\right)_{\mathrm{i}, \mathrm{n}}^{2} \tag{5}
\end{equation*}
$$

where n is the number of data points. For the NRTL model, two alternatives were selected: using the recommended value for $\alpha_{12}$ of 0.30 (Renon and Prausnitz, 1968) or adjusting $\alpha_{12}$ in the fitting process. The parameters $\mathrm{A}_{12}$, $\mathrm{A}_{21}$, and $\alpha_{12}$ for the correlation equations, mean absolute deviations, and activity coefficients at infinite dilution $\gamma_{i}^{\infty}$ are given in Table 8. The systems show positive deviations from ideality, as can be observed from the activity coefficients at infinite dilution. At the three pressures, Van Laar, Wilson, NRTL with $\alpha_{12}=0.30$, and UNIQUAC models yield similar deviations between experimental and calculated vapor compositions and temperatures, while Margules shows greater deviations in both variables. Better results were obtained with the NRTL equation using adjustable $\alpha_{12}$.

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