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Isobaric Vapor—Liquid Equilibrium of the Binary Mixtures Toluene + Styrene and Styrene + α-Methylstyrene

Roshi Dahal,* Petri Uusi-Kyyyni, Juha-Pekka Pokki, and Ville Alopaeus

ABSTRACT: Isobaric vapor—liquid equilibria of the binary mixtures toluene + styrene at 30 and 40 kPa and styrene + α-methylstyrene at 20 and 25 kPa were measured applying a recirculation still. The measured vapor—liquid equilibrium data were modeled adopting the non-random two-liquid (NRTL) excess Gibbs energy model with the RK (Redlich–Kwong) equation of state. The NRTL binary interaction parameter optimization was carried out employing own measured data and literature data for the toluene + styrene system. The applied model correlates well with the experimental data at the pressure range of 101–30 kPa. Moreover, the NRTL binary parameter regression was performed applying own measured data and literature data separately for the styrene + α-methylstyrene system. The model fitted with the parameters obtained from own measured data described the multiphase behavior of the system better than the parameters obtained from literature data. Additionally, the binary systems showed ideal behavior over the whole range of investigation as the calculated activity coefficients approached unity and no azeotropes were observed.

1. INTRODUCTION

Chemical recycling technologies are promising platforms in transition from a linear toward a circular economy and closed-loop recycling of plastic waste. In addition, the chemical recycling technique is a suitable option for mixed plastic waste streams compared to mechanical recycling. One of the most important chemical recycling technologies is pyrolysis where plastics are thermally converted into liquid or wax that can be refined into chemicals or fuel, or even integrated into the petrochemical production schemes of virgin plastics.

Our current research is focused on the recovery of pure styrene monomers from the polystyrene pyrolysis oil applying distillation and to develop a continuous distillation model for scale-up of the process. Thus, a better understanding of the phase behavior of polystyrene pyrolysis oil components is required in the design and control of distillation systems. Within these objectives, this paper presents the phase equilibrium behavior of a few most relevant components of polystyrene pyrolysis oil. The parameters and the developed VLE model from this work will be adopted for the design of the distillation column in future work. In addition, these VLE data are also required for the traditional styrene distillations.

Isobaric vapor—liquid equilibrium (VLE) for the binary system toluene + styrene at 101.3 kPa measured by Martirosyan et al. has been provided in vapor—liquid data collection. Furthermore, isobaric vapor—liquid equilibrium for the binary system styrene + α-methylstyrene at 6.7 kPa has been presented by Laevskaya et al. Static vapor pressures of the α-methylstyrene-toluene mixture were measured from 293 to 333 K by Bui et al. where the system slightly deviates from ideality. From the literature, it was observed that the experimental VLE data for these binaries remain inadequate. Therefore, vapor—liquid measurements were performed to obtain new data at a wider range of temperature and pressure for toluene + styrene and styrene + α-methylstyrene systems. Besides, the vapor—liquid data measured by Laevskaya et al. showed anomalous behavior for the styrene + α-methylstyrene system at higher concentrations of styrene. A possible azeotrope formation was speculated for this system due to such a behavior prior to own VLE measurements. However, no azeotrope formation was observed during own measurements which is detailed in the following chapters.

This study reports isobaric vapor—liquid equilibrium data for the binary systems: toluene + styrene measured at 30 and 40 kPa and styrene + α-methylstyrene (αMS) measured at 20 and 25 kPa. The measured vapor—liquid equilibrium data were correlated employing the non-random two-liquid (NRTL) excess Gibbs energy model with the RK (Redlich–Kwong) equation of state. The VLE data were described well by the NRTL—RK model and a reasonable prediction was obtained even with the ideal liquid model.

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A good agreement was found. It shows that the performance of the recirculation apparatus as applied in this work is reliable. The liquid and vapor coexist in equilibrium at a constant temperature and pressure.

In the earlier work, the vapor–liquid equilibrium of 2-methylpentane + 2-butanol was measured with the same recirculation apparatus as applied in this work and a static total pressure apparatus. A good agreement was found between the measurements made with two different methods. It shows that the performance of the recirculation apparatus and the experimental method is reliable.

The experimental work began with the determination of the vapor pressure of component 1 of the binary mixture at isobaric conditions. Initially, approximately 80 mL of component 1 was loaded to the apparatus. The pressure was adjusted to experimental pressure for isobaric measurements. The liquid was left to boil for 30–45 min until the pressure and temperature were stabilized. Thereafter, the temperature and pressure were recorded. Vapor and liquid phase sampling were taken from septum sampling points using 1 mL Hamilton sample-lock syringes into 2 mL vials. The samples were immediately analyzed by GC. Vapor-phase sampling was performed after the condensation of the vapor phase. The measurements for the next composition were performed by withdrawing 3–5 mL of the component from the liquid or vapor sampling chamber and by injecting the same volume of component 2 of the binary mixture into the circulation still. During the VLE measurement, 4-tert-butylcatechol (0.008 wt %) was added to the mixtures as an inhibitor to prevent polymerization.

A calibrated Pt-100 temperature probe with an ASL F200 thermometer was applied for the temperature measurement. The expanded uncertainty of the temperature measurement obtained from the Finnish National Standards Laboratory (MIKES) calibration certificate was ±0.018 K with coverage factor $k = 2$. Moreover, the temperature fluctuations from 0.001 to 0.006 K were observed for the measured VLE data which were also included to calculate the overall temperature uncertainty. Therefore, the overall expanded uncertainty of the temperature measurement was estimated to be 0.02 K (with coverage factor $k = 2$), as shown in Table 2.

### Table 1. Supplier and the Purity of Components

<table>
<thead>
<tr>
<th>Component/CAS number</th>
<th>Supplier</th>
<th>Inhibitor</th>
<th>GC purity, mass %</th>
<th>Water content, mass %</th>
<th>Purification method</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene/108-88-3</td>
<td>VWR Chemicals, ≥99.5%, ≤0.3%</td>
<td></td>
<td>99.9 ± 0.1</td>
<td>0.017 ± 0.005</td>
<td>drying</td>
</tr>
<tr>
<td>styrene/100-42-5</td>
<td>Sigma-Aldrich, ≥99.9%</td>
<td>4-tert-butylcatechol</td>
<td>99.9 ± 0.1</td>
<td>0.018 ± 0.005</td>
<td>drying</td>
</tr>
<tr>
<td>α-methylstyrene/98-83-9</td>
<td>Sigma-Aldrich, ≥99%</td>
<td>4-tert-butylcatechol</td>
<td>99.8 ± 0.1</td>
<td>0.015 ± 0.005</td>
<td>drying</td>
</tr>
</tbody>
</table>

*Purity according to the supplier. ^Inhibitor content according to the supplier. ^Determined by Karl-Fisher titration. "Parts per million.

### Table 2. Uncertainty Components (with their Standard, Combined, and Expanded Uncertainties) of the VLE Measurements

<table>
<thead>
<tr>
<th>VLE measurements</th>
<th>Uncertainty component</th>
<th>Standard uncertainty (K)</th>
<th>Combined uncertainty, $u_c$ (K)</th>
<th>Expanded uncertainty, $u_e$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>$u_{\text{pressure}}$ (kPa)</td>
<td>0.07</td>
<td>0.10</td>
<td>0.20</td>
</tr>
<tr>
<td>Pressure calibration</td>
<td>$u_{\text{pressure calibration}}$</td>
<td>0.07</td>
<td>0.10</td>
<td>0.20</td>
</tr>
<tr>
<td>Pressure transducer</td>
<td>$u_{\text{pressure transducer}}$</td>
<td>0.07</td>
<td>0.10</td>
<td>0.20</td>
</tr>
<tr>
<td>Combined uncertainty</td>
<td>$u_{\text{combined}}$</td>
<td>0.018</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Temperature fluctuation</td>
<td>$u_{\text{temperature fluctuation}}$</td>
<td>0.001−0.006</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Combined uncertainty</td>
<td>$u_{\text{combined}}$</td>
<td>0.018</td>
<td>0.01</td>
<td>0.02</td>
</tr>
</tbody>
</table>

*The minimum and the maximum temperature uncertainty due to temperature fluctuations during the VLE measurements.

Similarly, a pressure transducer (PMP 4070, Druck, uncertainty of pressure measurement provided by the manufacturer was 0.07 kPa) and a Red Lion panel meter were employed for the pressure measurement. The pressure transducer (uncertainty of pressure measurement 0.07 kPa, provided by the manufacturer) was calibrated against a Beamex MC2-PE calibrator (pressure calibrator uncertainty 0.014 kPa, with coverage factor $k = 2$). The calibrator is periodically calibrated at the manufacturer Beamex Oy, Finland. Including the calibration uncertainty, the overall expanded uncertainty of the pressure measurement was estimated to be 0.20 kPa with the coverage factor $k = 2$, as shown in Table 2.

### 2.2.2. Gas Chromatography Analyses and Calibration

The condensed vapor phase and the liquid phase were analyzed applying Agilent 6850 gas chromatograph (GC) equipped with a flame ionization detector. The settings for Agilent 6850 GC are provided in Appendix Table A-1. The composition analysis of the components is based on the method of the GC peak area presented in eq 1.

$$w_1 = \frac{A_1 \times Q}{A_1 \times Q + A_2} \quad (1)$$

where $w_1$ is the mass fraction of component 1, and $A_1$ and $A_2$ are GC peak areas of components 1 and 2, respectively.

Gravimetric calibration mixtures were prepared to calculate the response factors for the binaries: toluene + styrene and styrene + α-methylstyrene and to confirm that the response factors are unity. These calibration mixtures were gravimetrically prepared in 2 mL vials with an analytical balance (Precisa, 410AM-FR) and the uncertainty of the measured mass was...
where \( m_1 \) and \( m_2 \) are the masses of component 1 and 2 in the gravimetrically prepared sample. \( A_1 \) and \( A_2 \) are the GC peak areas of components 1 and 2, respectively. The average of the GC response factor calculated from eight calibration mixtures was 0.99 for the toluene + styrene and 1.02 for the styrene + \( \alpha \)MSt system. It shows that the response factors were almost unity for the binaries. Therefore, the response factor \( Q \) was kept one in eq 1 for the binaries.

### 2.3. Uncertainty Estimation

The expanded experimental uncertainties \( U \) are calculated using eq 3,

\[
U = kU_i = k\sqrt{\sum U_i^2}
\]

(3)

where \( U_i \) is the standard uncertainty of each influencing component, \( U_i \) is the combined standard uncertainty of each influencing element, and \( k \) is the coverage factor. In this work, the coverage factor \( k = 2 \), which corresponds to a 95% degree of confidence, is applied to characterize the measurements. Table 2 lists the standard uncertainties of influencing components and calculated combined and expanded uncertainties for pressure and temperature measurement.

The uncertainties of activity coefficients were estimated by the total derivative method with respect to the measured variables. The derivatives of the activity coefficients were calculated using the reorganized eq 5 with respect to pressure and vapor and liquid mole fraction. The fugacity coefficient ratio \( (\phi_i/\phi_i^{sat}) \) and the Poynting correction in eq 5 were assumed to be unity for the uncertainty estimation.

The uncertainties in mass fractions were calculated by taking derivative of eq 1 with respect to areas \( A_1 \) and \( A_2 \).

### 3. MODELING

#### 3.1. Vapor Pressure Correlation

The measured vapor pressures of toluene, styrene, and \( \alpha \)MSt were compared with the values calculated from the DIPPR 101 equation \(^{15} \) presented in eq 4. Table 3 summarizes the pure component physical properties and the parameters of vapor pressure correlation \((A-E)\) applied in the modeling.

\[
P/\text{Pa} = \exp(A + B/(T/K) + C \ln(T/K) + D(T/K)^6)
\]

(4)

#### 3.2. Vapor and Liquid Phase Models

The measured vapor–liquid equilibrium (VLE) systems were modeled using the NRTL \(^{16} \) activity coefficient model. The NRTL–RK method uses the NRTL activity coefficient model for liquid phase and Redlich–Kwong (RK) equation of state for vapor phase calculation. \(^{17} \)

The vapor–liquid equilibrium criteria \(^{18} \) is defined as in eq 5.

\[
\gamma_{\phi_i^y} = \kappa_i \phi_i^{sat}/P_i^{sat} \text{POY}_i
\]

(5)

where \( x \) and \( y \) are liquid and vapor mole fractions, \( i \) refers to component \( i \), \( \phi_i^y \) is the vapor phase fugacity coefficient, \( \phi_i^{sat} \) is the fugacity coefficient of pure component at saturation, \( P \) is the pressure of the system, \( \gamma_i \) is the activity coefficient, \( P_i^{sat} \) is the vapor pressure of the pure component, \( \text{POY}_i \) refers to the Poynting pressure correction and index “\( sat \)” refers to the saturated state. Poynting correction was included during modeling. In this work, RK binary interaction parameters were not regressed and \( k_i \) was set to zero.

#### 4. RESULTS

4.1. Pure Component Vapor Pressures

Vapor pressures of pure components toluene, styrene, and \( \alpha \)MSt were measured applying the recirculation still apparatus, as illustrated in Table 4. Styrene and \( \alpha \)MSt contained a polymerization inhibitor, as presented in Table 1. Additionally, 4-tert-butylicatehol (0.005 wt %) was added to these pure components to prevent polymerization during the vapor pressure measurements. The amount inhibitor was applied in small amount so the effect on measured pressure with the composition was much smaller than measured pressure uncertainty. Furthermore, samples were taken from condensed vapor and liquid phases for the GC analysis. The GC analysis results confirmed that there was no polymerization of styrene and \( \alpha \)MSt during the vapor pressure measurements.

The measured vapor pressures agree well with the DIPPR correlation in Figure 1, and the deviations are within the experimental uncertainty and uncertainty of correlation applied.

### 4.2. Binary VLE Measurements

4.2.1. Toluene + Styrene

The measured VLE data and the calculated activity coefficients for toluene (1) + styrene (2) at 30 and 40 kPa are presented in Table 5 and Figures 2 and 3, respectively. The uncertainties of the pressure and the temperature measurements were calculated using eq 3. Similarly, uncertainties in the compositions and the activity coefficients were calculated by the total derivative method, as described in Section 2.3. In addition, the literature data \(^{3} \) and the calculated activity coefficients for toluene (1) + styrene (2) at 101 kPa are illustrated in Figure 4.
The expanded uncertainties of temperature and pressure were calculated using a coverage factor k = 2, u(T/K) = 0.02 K, and u(P/kPa) = 0.2 kPa. Values are calculated from the DIPPR correlation (eq 4). Pressure deviation, ΔP = P_\text{meas} - P_\text{lit} 44 45 Relative vapor pressure deviation P_\text{exp.,R} = |(P_{i\text{meas}} - P_{i\text{lit}})/P_{i\text{meas}}|, where P_{i\text{meas}} is the measured vapor pressure and P_{i\text{lit}} is the calculated vapor pressure from correlation.

The regressed parameters for the toluene (1) + styrene (2) system are provided in Table 7. The experimentally determined VLE from this work and the literature VLE data were included for the binary interaction parameter regression. However, the literature data4 showed deviation in vapor composition at x_{\text{toluene}} = 0.2 (Figure 4). Therefore, this VLE point was excluded during parameter fitting. The equal weighting factor was employed in the objective function for pressure, temperature, and mole fraction to balance different sets of experimental data.
Moreover, a similar ideal behavior has been reported in the literature for the mixtures containing styrene and toluene.23

4.2.2. Styrene + α-Methylstyrene (αMS). The measured VLE data and the calculated activity coefficients for styrene (1) + αMS (2) at 20 and 25 kPa are presented in Table 6 and Figures 5–8. The uncertainties of the pressure and the temperature measurements were calculated using eq 3. Similarly, uncertainties in the compositions and the activity coefficients were calculated by the total derivative method, as described in Section 2.3. In addition, the literature data and the calculated activity coefficients for styrene (1) + αMS (2) at 6.7 kPa are illustrated in Figures 9 and 10, respectively.

The regressed parameters for styrene (1) + αMS (2) are provided in Table 7. The parameter regression was carried out applying own measured VLE data and the literature data4 separately and designated as parameter sets I and II (Table 7).

The phase behavior of the styrene (1) + αMS (2) system is well described with both (i) the NRTL–RK model applying parameter set I and (ii) with ideal vapor and ideal liquid assumption in Figures 5 and 7. Similarly, the ideal behavior is also observed from the calculated activity coefficients which is almost unity in Table 5 and Figures 6a and 8a. However, the ability to describe the phase behavior of the styrene (1) + αMS (2) system with the NRTL–RK model applying parameter set II is not satisfactory for the measured system shown in Figures 5a and 7a. In addition, the activity coefficient plot in Figures 6b and 8b show that the predicted activity coefficient deviates from the unity.

It should be noted that the NRTL–RK parameter set II for the styrene (1) + αMS (2) system is obtained from the regression of literature data.6 The VLE plot in Figure 9a shows scatter in data and an anomalous trend at x_styrene = 0.9 where the equilibrium temperature is almost the same as the pure component boiling point. This concludes that the literature VLE data of styrene (1) + αMS (2) does not seem good enough. It might be a possible reason for the failure of the model predictions to correlate the measured data applying binary parameter set II in Figures 5a and 7a.

4.3. Regressed Parameters. The regressed NRTL–RK parameters for toluene (1) + styrene (2) and styrene (1) + αMS (2) systems as well as the temperature, pressure, and composition residuals are presented in Table 7. The parameter regression was performed employing own measured VLE data and the literature data of the pressure range of 101–30 kPa for the toluene (1) + styrene (2) system. Similarly, the parameter regression for the styrene (1) + αMS (2) system was performed applying own measured VLE data (20–25 kPa) and literature data (6.7 kPa) separately. These parameters obtained from the regression of own VLE data and literature data were designated as parameter sets I and parameter set II, respectively. Therefore, two parameters sets (I and II) were adopted to correlate the measured system of styrene (1) + αMS (2) in this work.

5. DISCUSSION

5.1. VLE Data of Styrene + αMS. The literature data8 for styrene + αMS shows deviation from ideality. This is rather unexpected, and indeed the present model predicts close to ideal behavior for this system, as shown in Figure 9a. It can also be speculated that the literature data of styrene + αMS is based on incorrect pure component vapor pressure (Figure 9a) or impure styrene. When applying the DIPPR correlation, anomalous interaction parameters seem to result in. Hence, we
carried out further investigation to clarify the potential problem with these data.

8

\( P \text{/kPa} \) & \( T / K \) & \( x_1 \) & \( y_1 \) & \( y_1 \pm u(y_1) \) & \( y_2 \pm u(y_2) \) \\
--- & --- & --- & --- & --- & --- \\
20.1 & 384.84 & 0 & 0 & 1.000 \\
20.2 & 382.38 & 0.104 & 0.175 & 0.970 ± 0.023 & 0.998 ± 0.035 \\
20.2 & 379.62 & 0.228 & 0.334 & 0.929 ± 0.008 & 1.032 ± 0.030 \\
20.1 & 377.48 & 0.330 & 0.487 & 1.001 ± 0.006 & 0.986 ± 0.024 \\
20.1 & 376.22 & 0.396 & 0.565 & 1.010 ± 0.005 & 0.969 ± 0.020 \\
20.1 & 373.90 & 0.521 & 0.687 & 1.008 ± 0.003 & 0.959 ± 0.013 \\
20.1 & 372.17 & 0.611 & 0.772 & 1.027 ± 0.002 & 0.914 ± 0.005 \\
20.1 & 370.93 & 0.678 & 0.816 & 1.020 ± 0.002 & 0.936 ± 0.001 \\
20.1 & 369.60 & 0.780 & 0.876 & 0.998 ± 0.001 & 0.967 ± 0.013 \\
20.1 & 367.65 & 0.898 & 0.949 & 1.005 ± 0.0004 & 0.921 ± 0.006 \\
25.1 & 391.13 & 0 & 0 & 1.000 \\
25.0 & 388.72 & 0.095 & 0.165 & 1.017 ± 0.029 & 0.998 ± 0.037 \\
25.0 & 386.66 & 0.197 & 0.308 & 0.976 ± 0.013 & 0.999 ± 0.033 \\
25.0 & 384.69 & 0.279 & 0.423 & 1.009 ± 0.009 & 0.992 ± 0.028 \\
25.0 & 383.28 & 0.355 & 0.506 & 0.990 ± 0.007 & 0.997 ± 0.025 \\
25.3 & 380.31 & 0.532 & 0.681 & 0.990 ± 0.004 & 0.994 ± 0.016 \\
25.2 & 378.83 & 0.611 & 0.752 & 0.997 ± 0.004 & 0.976 ± 0.010 \\
25.2 & 377.26 & 0.706 & 0.823 & 0.995 ± 0.003 & 0.974 ± 0.001 \\
25.2 & 375.49 & 0.795 & 0.883 & 1.000 ± 0.003 & 0.987 ± 0.013 \\
25.2 & 374.11 & 0.897 & 0.944 & 0.998 ± 0.002 & 0.993 ± 0.055 \\
25.2 & 372.54 & 1 & 1 & 1.000 \\

\( ^{a}u(x_1) = 0.006, u(y_1) = 0.006, u(P) = 0.2 \text{kPa}, u(T) = 0.02 \text{K}. \)

First, the vapor pressure equation parameter of styrene was regressed applying the literature VLE data\(^8\) to see if the apparent nonideality in VLE data\(^8\) could be explained by an
is out of the trend from the phase diagram.

1.35

+ the Van Ness test, 28 0.01 at 6.7 kPa (a) (are not able to reproduce the phase behavior for the complete

| =

| =

0.01

several tests: the area test, 1.01, and the infinite dilution test

0.01,

0.004, 15

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0.001, and (d) at 6.7 kPa:

(0) ln

from the NRTL model applying (a) parameter set I and (b)

from literature VLE data parameter set II presented in Table 7.

( )

Figure 10. Styrene (1) + αMS (2) activity coefficients at 6.7 kPa: calculated from literature VLE data (▲) γ1 and (Δ) γ2; (-----) γ1 and

(---) γ2 from the NRTL model applying (a) parameter set I and (b) parameter set II presented in Table 7.

Table 7. The NRTL Model Parameters Applying VLE Data and Deviations of Binary Systems

<table>
<thead>
<tr>
<th>component i</th>
<th>toluene</th>
<th>styrene</th>
<th>styrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>component j</td>
<td>styrene</td>
<td>αMS</td>
<td>αMS</td>
</tr>
<tr>
<td>parameter source</td>
<td>this work</td>
<td>αMS</td>
<td>αMS</td>
</tr>
<tr>
<td>data</td>
<td>this work, ref 6</td>
<td>this work from ref 8</td>
<td></td>
</tr>
<tr>
<td>number of parameters</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>parameter set</td>
<td>I</td>
<td>II</td>
<td></td>
</tr>
<tr>
<td>parameter/unit</td>
<td>α0</td>
<td>660.5</td>
<td>804.1</td>
</tr>
<tr>
<td></td>
<td>β0/K</td>
<td>275.9</td>
<td>−469.7</td>
</tr>
<tr>
<td></td>
<td>γ0</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>δ0</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ε0</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>f0/K</td>
<td>345.73</td>
<td>366.24</td>
</tr>
<tr>
<td></td>
<td>f0/K</td>
<td>338.55</td>
<td>350.95</td>
</tr>
<tr>
<td></td>
<td>Tm/°K</td>
<td>386.22</td>
<td>391.13</td>
</tr>
<tr>
<td></td>
<td>Tm/°K</td>
<td>391.13</td>
<td>399.05</td>
</tr>
<tr>
<td></td>
<td>Δy</td>
<td>0.005, 0.006</td>
<td>0.004, 0.005, 0.01, 0.01</td>
</tr>
<tr>
<td></td>
<td>ΔT°/K</td>
<td>0.05, 0.04, 0.01, 1.35, 1.01, 0.37</td>
<td></td>
</tr>
</tbody>
</table>

αNRTL binary interaction parameters available in the Aspen Plus: $\gamma = a_0 + b_0/T + c_0 \ln T + d_0$ $\Delta T = \sum_{i=1}^{N} (T_{exp} - T_{calc})$. $\Delta y = \sum_{i=1}^{N} (\gamma_{exp} - \gamma_{calc})$. Average absolute deviation of the vapor phase composition, $\Delta y = \sum_{i=1}^{N} (\gamma_{exp} - \gamma_{calc})$. Average absolute deviation of the temperature.

VLE data measured in this work. "Lit. VLE data." 8 "Lit. VLE data." 8

Figure 11. Styrene (1) + αMS (2) VLE data 8 at 6.7 kPa: (O) exp., (●) pure component vapor pressures calculated from the DIPPR correlation, (-----) from the NRTL model applying parameter set II in Table 7 and vapor pure pressure parameters presented in Table 3, (---) applying the ideal liquid model and re-calculated pure component vapor pressure parameter A (eq 4) for styrene using literature data.

Figure 9. Styrene (1) + αMS (2) VLE data 8 at 6.7 kPa: (O) exp., (●) pure component vapor pressure using DIPPR correlation, 14 from the NRTL model applying (-----) ideal model, (----) parameter set I, and (---) parameter set II presented in Table 7; (b) x-y diagram: (O) exp., applying NRTL model (-----) parameter set I, (---) parameter set II.

These phase diagrams are compared in Figure 11. Figure 11 shows that the boiling point of styrene predicted applying new

vapor pressure equation parameter does not match with the vapor pressure of styrene calculated from the DIPPR correlation and differs by 1 K. In addition, the VLE point where $x_{\text{styrene}} = 0.9$ is out of the trend from the phase diagram shown in Figure 11. Such problem and scatters in the VLE data may arise if the samples from the phases were taken before the system has reached equilibrium or due to higher uncertainty in pressure measurement. However, no such problems were addressed when referring to the original paper.

This clarifies that the parameters obtained from the literature data 8 are not able to reproduce the phase behavior of styrene + αMS very well due to the problem in the experimental data itself. On the other hand, we have observed from Figures 5a, 7a, and 9a that the parameters obtained from own measured VLE data describe the phase behavior of styrene + αMS very well at the pressure range of 6.7–25 kPa. Thus, VLE measured in this work seems to be a significant input for the design of separation units of the styrene + αMS system especially at high styrene purities.

5.2. Quality Assessment of Own VLE Data. Kang et al. suggested 17 several tests: the area test, 25 the Van Ness test, 26 the point test, 27 and the infinite dilution test 28 for the complete analysis of VLE data quality. However, the binary system of
Moreover, Laavie et al. have also explained that the infinite dilution test and the area test, respectively, were not applicable for their measured binaries because the activity coefficient range was very close to one.

Therefore, in this work, the Van Ness test method was applied for the analysis of measured VLE data. The data sets are considered consistent if the absolute average deviations between the measured and calculated vapor phase mole fractions and pressures are less than 1%. In addition, the pure component vapor pressure test was performed where the consistency between the endpoints of the VLE curve and the pure component vapor pressures was checked. It is evident from Table 8 that the data sets have passed both the Van Ness and the pure component vapor pressure tests as the consistency tests values are within the limits.

Table 8. The Consistency Tests Parameters\(^{24}\) (\(\Delta P_k^\%\), \(\Delta y_k^\%\), \(\Delta P_k^i\)) for the Measured Data of Two Binary Mixtures Containing Styrene

<table>
<thead>
<tr>
<th>system</th>
<th>Van Ness for NRTL</th>
<th>pure component consistency</th>
<th>tests</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\Delta P_k^%) (&lt;1)(^a)</td>
<td>(\Delta y_k^%) (&lt;1)(^b)</td>
<td>(\Delta P_k^i) (&lt;0.01)(^c)</td>
</tr>
<tr>
<td>toluene (1) + styrene (2)</td>
<td>30 kPa 0.34 0.47 0.009 0.008</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40 kPa 0.38 0.55 0.008 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20 kPa 0.46 0.60 0.002 0.005</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25 kPa 0.45 0.27 0.002 0.0004</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Relative vapor pressure deviation, \(\Delta P_k^\% = \left(100\times\frac{\sum_{i=1}^{m} y_i^{\exp}(P_k) - y_i^{\text{calc}}(P_k)}{P_k}\right)\), \(P_k\) is the total pressure in the measurement \(k\) experimental (exp) or calculated by a model (calc), \(N\) is the total number of measurements.

\(^b\) Vapor fraction deviation, \(\Delta y_k = \left(100\times\frac{\sum_{i=1}^{N} y_i^{\exp}_k - y_i^{\text{calc}}_k}{y_i^{\text{calc}}_k}\right)\). \(y_i\) is the vapor fraction of the first component in measurement \(k\), determined in experimental (exp) and calculated by a model (calc).

\(^c\) Relative vapor pressure deviation of pure component, \(\Delta P_k^i = |\Delta P_k^i\text{exp} - \Delta P_k^i\text{lit}|/\Delta P_k^i\text{lit}\), \(P_k^i\) is pure component \(i\) saturated vapor pressure; experimental (exp) and from literature (lit) for component 1 or 2.

6. CONCLUSIONS

In this work, a recirculation still apparatus was adopted to measure the VLE of toluene + styrene at 30 and 40 kPa and styrene + αMS at 20 and 25 kPa. The measured systems have been modeled applying the NRTL−RK model. The ideality of the system was observed from the calculated activity coefficients which equal unity over the whole range of investigation. It was determined that the experimental data are thermodynamically consistent according to the Van Ness test method. In addition, the pure component vapor pressure test showed consistency between the endpoints of the VLE curve and the pure component vapor pressures.

APPENDIX A

The settings for Agilent 6850 gas chromatograph are given in Table A-1.

Table A-1. Settings for Agilent 6850 Gas Chromatograph

<table>
<thead>
<tr>
<th>GC name</th>
<th>Agilent 6850</th>
</tr>
</thead>
<tbody>
<tr>
<td>type</td>
<td>Capillary</td>
</tr>
<tr>
<td>model number</td>
<td>Agilent 19,091 N-216E</td>
</tr>
<tr>
<td>column coating material</td>
<td>HP-INNOWax Polyethylene Glycol</td>
</tr>
<tr>
<td>nominal length/m</td>
<td>60</td>
</tr>
<tr>
<td>nominal diameter/μm</td>
<td>320</td>
</tr>
<tr>
<td>nominal film thickness/μm</td>
<td>0.5</td>
</tr>
<tr>
<td>Detector type</td>
<td>FID</td>
</tr>
<tr>
<td>temperature/K</td>
<td>573.15</td>
</tr>
<tr>
<td>mode</td>
<td>Split</td>
</tr>
<tr>
<td>temperature/K</td>
<td>548.15</td>
</tr>
<tr>
<td>pressure/kPa</td>
<td>92.0</td>
</tr>
<tr>
<td>split ratio</td>
<td>50:1</td>
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<tr>
<td>gas type</td>
<td>He</td>
</tr>
<tr>
<td>total flow/mL min(^{-1})</td>
<td>84.5</td>
</tr>
<tr>
<td>split flow/mL min(^{-1})</td>
<td>80.4</td>
</tr>
<tr>
<td>Oven initial/K</td>
<td>313.15</td>
</tr>
<tr>
<td>hold time/min</td>
<td>1</td>
</tr>
<tr>
<td>Ramp: ramp rate/C min(^{-1})</td>
<td>30</td>
</tr>
<tr>
<td>final temperature/K</td>
<td>523.15</td>
</tr>
<tr>
<td>run time/min</td>
<td>33</td>
</tr>
<tr>
<td>Post Run</td>
<td>523.15</td>
</tr>
<tr>
<td>run time/min</td>
<td>5</td>
</tr>
</tbody>
</table>

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Notes
The authors declare no competing financial interest.
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NOMENCLATURE

Abbreviations

\( \alpha \text{MS} \)
alpha-methylstyrene

\( \text{CAS} \)
chemical abstracts service registry number

\( \text{GC} \)
gas chromatography

\( \text{ppm} \)
parts per million

\( \text{VLE} \)
vapor–liquid equilibrium

Symbols

\( a_{ij} \)
nonrandomness constant for binary \( ij \) interactions in the NRTL model

\( A-E \)
parameters of the pure component vapor pressure correlation

\( M \)
molar mass (g mol\(^{-1}\))

\( mL \)
milliliter

\( n \)
number of moles (mol)

\( P \)
pressure (kPa)

\( T \)
temperature (K)

\( w \)
mass fraction

\( \text{wt} \)
weight

\( x \)
liquid mole fraction

\( y \)
vapor mole fraction

Greek Letters

\( \alpha_p, \alpha_i \)
nonrandomness constant for binary \( ij \) interactions in the NRTL model

\( \Delta \)
difference

\( \gamma_i \)
activity coefficient of component \( i \)

\( \phi_i \)
fugacity coefficient of component \( i \) at the system temperature and pressure

Subscripts

\( \text{calc} \)
calculated

\( \text{exp.} \)
experimental

\( i, j \)
components of a mixture

\( \text{lit} \)
literature

\( \text{meas} \)
measured

Superscripts

\( \text{sat} \)
saturated

REFERENCES


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