Separation of the Azeotropic Mixture Methanol and Toluene Using Extractive Distillation: Entrainer Determination, Vapor–Liquid Equilibrium Measurement, and Modeling

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ABSTRACT: For separating the azeotropic mixture methanol and toluene, an extractive distillation is applied with butyl propanoate, triethylamine, and butyl butanoate as the extractive solvents, which were screened by relative volatility, selectivity, and the x−y curve. The vapor–liquid equilibrium data of the binary and ternary systems for (toluene + butyl propanoate), (toluene + triethylamine), (toluene + butyl butanoate), and (methanol + toluene + butyl butanoate) were determined. The reliability for the experimental vapor–liquid equilibrium (VLE) data was assessed with the van Ness method. The measured data was fitted by the UNIQUAC, Wilson, and NRTL models, and the correlated results were consistent with the determined VLE data. In addition, the COSMO-UNIFAC model was used to predict the VLE data for comparison.

1. INTRODUCTION

Methanol and toluene are extensively applied raw materials, such as in the manufacture of styrene, which is prepared by side-chain alkylation with methanol and toluene as raw materials, and p-xylene. From such production processes, a liquid mixture containing methanol and toluene can be produced. To maintain sustainable production, it is necessary to separate the mixture. However, methanol and toluene can form an azeotrope with the azeotropic composition (toluene/methanol = 0.113:0.887, mole fraction) at 337.02 K under 101.3 kPa. In general, special distillation technologies are utilized in the chemical industry for separating azeotropic mixtures, including azeotropic distillation, salt distillation, extractive distillation, and pressure-swing distillation. Here, extractive distillation is considered for separating the azeotropic mixture methanol and toluene.

To develop the extractive distillation to separate the mixture methanol and toluene, the vapor–liquid equilibrium (VLE) data including methanol, toluene, and the entrainers are required. In a previous work, Burke et al. investigated the VLE behavior of the system (toluene + methanol) under 101.3 kPa. Wang et al. studied the VLE behavior of the mixture (triethylamine + methanol) at 99.3 kPa. The VLE data for the systems (methanol + butyl propanoate) and (methanol + butyl butanoate) were determined by Espiau et al. So far, the isobaric VLE data of the binary systems (toluene + butyl propanoate), (toluene + triethylamine), and (toluene + butyl butanoate) has not been found in the literature.

In this paper, the index selectivity at infinite dilution ($S_{12}^{\infty}$), the relative volatility ($\alpha_{12}$), and the x−y diagram were adopted to select entrainers for separating the azeotropic mixture methanol and toluene. The isobaric VLE data of the mixtures (toluene + butyl butanoate), (triethylamine + toluene), and (toluene + butyl propanoate) were determined under 101.3 kPa. In the meantime, the determined VLE data were correlated by UNIQUAC, NRTL, and Wilson. Besides, the COSMO-UNIFAC model was used to generate the VLE values for the systems for comparison.

2. ENTRAINER DETERMINATION

2.1. Selectivity. The index selectivity at infinite dilution $S_{12}^{\infty}$ was applied to assess the capacity of entrainers, which is defined as follows:

$$S_{12}^{\infty} = \frac{y_2^{\infty}}{y_1^{\infty}}$$

(1)
where $\gamma_1^\infty$ and $\gamma_2^\infty$ stand for the infinite dilution activity coefficients, which were determined using the UNIFAC model. The infinite dilution activity coefficient is expressed as follows:

$$\ln \gamma_i^\infty = \lim_{\xi_i \to 0} \ln \gamma_i^C + \lim_{\xi_i \to 0} \ln \gamma_i^R$$

where

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + \sum_j \left( \frac{\theta_{ij}}{x_i} \sum_k \frac{\tau_{ik}}{x_j} \right)$$

and

$$\ln \gamma_i^R = q_i \left[ 1 - \ln \left( \sum_j \theta_{ij} \tau_{ji} \right) - \sum_j \left( \frac{\theta_{ij}}{x_i} \sum_k \frac{\tau_{ik}}{x_j} \right) \right]$$

where $\theta_i$ and $\Phi_i$ are the area fraction and segment fraction, respectively, $x_i$ is the mole fraction of component $i$, $r_i$ and $q_i$ are the pure component parameters, and $\tau_{ij}$ and $\tau_{ji}$ are the adjustable parameters.

Figure 1 shows the calculated results of $S_{12}^\infty$ with the entrainers. From Figure 1, it can be seen that for the system methanol (1) + toluene (2), the capacity of the different entrainers follows the order butyl butanoate > triethylamine > butyl propanoate > propyl propionate > $\alpha$-xylene. The calculated selectivity values of butyl butanoate, butyl propanoate, and triethylamine are higher than those of $\alpha$-xylene and propyl propionate. Therefore, the three entrainers were chosen for further analysis.

2.2. Relative Volatility. For selection of entrainers, the relative volatility ($\alpha_{12}$) of methanol and toluene with different entrainers was calculated by the UNIFAC model, which is expressed as follows:

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2}$$

where $x_i$ stands for liquid mole fraction and $y_i$ stands for vapor mole fraction.

Figure 2 illustrates the relative volatility for the system methanol (1) + toluene (2) with the entrainers. As displayed in Figure 2, the $\alpha_{12}$ values of butyl butanoate, triethylamine, and butyl propanoate reveal apparent deviations from unity, indicating that the three entrainers have the potential to break the azeotropic point of the mixture methanol and toluene.

2.3. Effect of Entrainers on VLE. Figure 3 shows the $x$-$y$ diagram calculated by the UNIFAC model for the mixture methanol (1) + toluene (2) with the selected entrainers. As can be seen from Figure 3, the $x$-$y$ curves for the mixture are deviated from the diagonal line, indicating that the azeotropic point of the mixture can be broken by the entrainers.

Consequently, depending on the analysis of $S_{12}^\infty$, $\alpha_{12}$, and the $x$-$y$ curve, butyl butanoate, triethylamine, and butyl propanoate can be the potential alternatives to separate the azeotropic mixture methanol and toluene using extractive distillation.
3. RESULTS AND DISCUSSION

3.1. VLE Data. The measured VLE data of the systems (toluene + butyl propanoate), (triethylamine + toluene), and (toluene + butyl butanoate) under 101.3 kPa is summarized in Tables 1–3 and illustrated in Figures 4–6, where \( x_1 \) stands for liquid mole fraction and \( y_1 \) stands for vapor mole fraction. Besides, the \( x-y \) curves for the three mixtures are displayed in Figure 7. As shown in Figure 7, all the \( x-y \) curves deviate from the diagonal line, indicating that the solvents can be recovered by a common distillation technology.

3.2. VLE Calculation. For the investigated mixtures, the liquid phase is a non-ideal solution, and the vapor phase can be assumed as an ideal gas at 101.3 kPa for VLE calculation. The VLE relation is defined as

\[
\gamma_i = \frac{P_i}{P_i^*} \frac{1}{x_i} \tag{6}
\]

where \( \gamma_i \) refers to the activity coefficient, \( x_i \) stands for the mole fraction in the liquid phase, \( y_i \) stands for the mole fraction in the vapor phase, and \( P_i^* \) stands for saturation vapor pressure of the pure component and was determined using the extended Antoine equation, which is defined as

\[
\ln(P_i/kPa) = C_{i1} + \frac{C_{i2}}{T/K + C_{i3}} + C_{i4}(T/K) + C_{i5} \ln(T/K) + C_{i6}(T/K)^{2.5} \leq T/K \leq C_{i7} \tag{7}
\]
3.3. Thermodynamic Consistency Test. The consistency test of van Ness was utilized to verify the reliability of the determined VLE data. The van Ness test is represented as

$$\Delta y = \frac{1}{N} \sum_{i=1}^{N} 100(y_i^{exp} - y_i^{cal})$$

(8)

$$\Delta P = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{P_i^{exp} - P_i^{cal}}{P_i^{exp}} \right|$$

(9)

where cal and exp refer to the values of calculation and experiments and N indicates the data point number. If all the values of $\Delta P$ and $\Delta y$ do not exceed unity, it signifies that the VLE data are thermodynamically consistent.

where $C_i$ to $C_n$ are the coefficients of the equation, and the values are presented in Table 4. The results of activity coefficient ($y_i$) of the mixtures are presented in Tables 1–3.

Figure 5. $T=x$-$y$ curves for the mixture triethylamine (1) + toluene (2): blue ○, $T=x$ (experimental); ■, $T=x$ (experimental); red −, UNIQUAC model; −, NRTL model; blue −, Wilson model; red −, COSMO-UNIFAC model; and blue −, UNIFAC model.

Figure 6. $T=x$-$y$ curves for the mixture toluene (1) + butyl butanoate (2): blue ○, $T=x$ (experimental); ■, $T=x$ (experimental); red −, UNIQUAC model; −, NRTL model; blue −, Wilson model; red −, COSMO-UNIFAC model; and blue −, UNIFAC model.

where cal and exp refer to the values of calculation and experiments and N indicates the data point number. If all the values of $\Delta P$ and $\Delta y$ do not exceed unity, it signifies that the VLE data are thermodynamically consistent.

Table 5 lists the values of $\Delta P$ and $\Delta y$. As given in Table 5, all the values of $\Delta P$, $\Delta y$ do not exceed unity, indicating that the obtained VLE data for the systems is thermodynamically consistent.

3.4. VLE Data Correlation. The activity coefficient models of NRTL, UNIQUAC, and Wilson were adopted to correlate the isobaric VLE data for (toluene + butyl propanoate), (triethylamine + toluene), and (toluene + butyl butanoate) using Aspen Plus. The correlated results of the three systems using the activity coefficient models are shown in Figures 4–7. The parameters $r$ and $q$ of the components for the UNIQUAC model are provided in Table 6. To fit the measured VLE data, the following expression is adopted

$$F = \sum_{i} \left[ \left( \frac{y_i^{exp} - y_i^{cal}}{\sigma_p} \right)^2 + \left( \frac{T_i^{exp} - T_i^{cal}}{\sigma_T} \right)^2 \right]$$

$$+ \left( \frac{x_i^{exp} - x_i^{cal}}{\sigma_x} \right)^2 + \left( \frac{y_i^{exp} - y_i^{cal}}{\sigma_y} \right)^2$$

where $\sigma$, $T$, and $P$ denote the standard deviation, temperature, and pressure. The values of standard deviation are $\sigma_p$ 0.35 kPa; $\sigma_T$, 0.35 K; $\sigma_x$, 0.008; and $\sigma_y$, 0.006, respectively.

The RMSDs (root-mean-square deviations) and the correlated interaction parameter values are presented in Table 7. As displayed in Table 7, the largest values of RMSDs($T$) and RMSDs($y_i$) are 0.23 K and 0.0054, indicating that the three models can fit the determined VLE data well. Furthermore, the experimental vapor pressures of the system (toluene + triethylamine) at $T = 298.14$–333.13 K were predicted using the regressed parameters of the Wilson model and compared with the data reported in ref 27. The results are provided in Figure S1 in the Supporting Information. From Figure S1, it can be seen that the predicted results agree with the experimental data in the literature, indicating the reliability of the regressed model parameters. The UNIFAC and COSMO-UNIFAC models were used to generate the isobaric VLE values of the three binary mixtures for comparison. As can be seen from Figures 4–6, for the mixture toluene and butyl propanoate, the prediction results from the UNIFAC and COSMO-UNIFAC model agree with the VLE data of the mixtures. For the mixtures (toluene + butyl propanoate), the prediction results from the UNIFAC and COSMO-UNIFAC model agree with the VLE data of the mixtures.
The Supporting Information. The pseudo-binary UNIFAC models, which are provided in Tables S1 and S2 in butanoate = 0.25:0.25:0.5 and calculated by the NRTL and with the feed ratio (mole fraction) of methanol/toluene/butyl entrainer (butyl butanoate) was determined at 101.3 kPa (methanol + toluene + butyl butanoate) with the best

Also, the experimental ternary VLE data of the system toluene with the three entrainers, which is added in Figure 3. The values of relative volatility were calculated and are presented in Table S1 in the Supporting Information.

Table 4. Coefficients of the Extended Antoine Model

| component            | C_u  | C_v  | C_w  | C_h  | C_i  | C_j  | C_k  |
|----------------------|------|------|------|------|------|------|------|
| triethylamine        | 49.64| -5681.90 | 0    | 0    | -4.98| 1.24 × 10^{-17} | 6    | 158.45 | 535.15 |
| toluene              | 70.04| -6729.80 | 0    | 0    | -8.18| 5.30 × 10^{-6}   | 2    | 178.18 | 591.75 |
| butyl butanoate      | 102.27| -9384.00 | 0    | 0    | -12.77| 7.47 × 10^{-6}   | 2    | 181.15 | 616.00 |
| butyl propanoate     | 64.32| -7709.80 | 0    | 0    | -6.84| 6.36 × 10^{-18}  | 2    | 183.63 | 594.60 |

Table 5. Validated Values of the van Ness Test

| system                | ΔP  | Δy  |
|----------------------|-----|-----|
| toluene + butyl propanoate | 0.03| 0.19|
| triethylamine + toluene    | 0.02| 0.08|
| toluene + butyl butanoate | 0.06| 0.18|

Table 6. Parameters r and q of the Components for the UNIQUAC Model

| component            | r   | q   |
|----------------------|-----|-----|
| toluene              | 3.9229| 2.9680 |
| butyl propanoate     | 5.5017| 4.7360 |
| triethylamine        | 5.0119| 4.2560 |
| butyl butanoate      | 6.1892| 5.2760 |

butanoate) and (toluene + triethylamine), the predicted values of the vapor phase are in agreement with the measured values, while the predicted values of the liquid phase show little deviations compared to the measured values.

To validate the UNIFAC prediction of the effect of these entertainers on VLE of methanol and toluene, the NRTL activity coefficient model with the regressed parameter was used to generate the VLE data of the mixture methanol and toluene with the three entrainers, which is added in Figure 3. Also, the experimental ternary VLE data of the system (methanol + toluene + butyl butanoate) with the best entrainer (butyl butanoate) was determined at 101.3 kPa with the feed ratio (mole fraction) of methanol/toluene/butyl butanoate = 0.25:0.25:0.5 and calculated by the NRTL and UNIFAC models, which are provided in Tables S1 and S2 in the Supporting Information. The pseudo-binary x−y diagram of methanol + toluene with butyl butanoate is plotted with the feed ratio (mole fraction) of methanol/toluene/butyl butanoate = 0.25:0.25:0.5 in Figure 8. The values of relative volatility were calculated and are presented in Table S1 in the Supporting Information.

As displayed in Figure 8, with the help of the entrainer butyl butanoate, the x−y curve shows a large deviation from the diagonal line with the feed ratio (mole fraction) of methanol/toluene/butyl butanoate = 0.25:0.25:0.5, which indicates that the entrainer butyl butanoate can enlarge the relative volatility of the system methanol and toluene compared to the VLE data.

Figure 8. x−y curves for the mixture methanol (1) + toluene (2): ■, experimental data with butyl butanoate; —, by the NRTL model with the regressed parameters; and △, from ref 30.

Table 7. Binary Parameters for the Mixtures under 101.3 kPa

| model      | a_12  | a_21  | b_12/K | b_21/K | y_1  | T/K  |
|------------|-------|-------|--------|--------|------|------|
| NRTL       | 0.1941| 0.1581| -32.14 | -112.16| 0.0026| 0.16 |
| UNIQUAC    | 22.45 | -6.2300| -2285.03| 2185.63| 0.0023| 0.15 |
| Wilson     | 7.9342| 5.3700| 2880.91| -1892.58| 0.0025| 0.15 |
| NRTL       | -15.77| 11.76 | 621.83 | -4602.33| 0.0024| 0.18 |
| UNIQUAC    | -3.0611| -4.4827| -2421.73| 1850.92| 0.0025| 0.12 |
| Wilson     | 9.8052| 12.65 | 2453.72| -4973.45| 0.0016| 0.17 |
| NRTL       | 5.9800| 2.3171| -2160.88| -926.69| 0.0028| 0.23 |
| UNIQUAC    | 19.41 | -0.5803| -1538.96| 407.64| 0.0054| 0.19 |
| Wilson     | 17.06 | 2.3345| -97.81 | -1438.50| 0.0053| 0.20 |

RMSD(y) = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (y_{i}^\text{exp} - y_{i}^\text{cal})^2} \quad \text{RMSD}(T) = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (T_{i}^\text{exp} - T_{i}^\text{cal})^2} \quad \text{NRTL}, \quad y_{i} = a_{i} + b_{i}/T, \quad \text{the } a_{i} \text{ value was fixed at 0.3.} \quad \text{UNIQUAC}, \quad y_{i} = \exp(a_{i} + b_{i}/T). \quad \text{Wilson, } \ln A_{i} = a_{i} + b_{i}/T. \quad \text{Wilson, } A_{i} = a_{i} + b_{i}/T.
Table 8. Specifications of the Chemicals

| component       | CAS     | suppliers                            | mass fraction | T/K exp | lit     | analysis method |
|-----------------|---------|--------------------------------------|---------------|---------|---------|-----------------|
| toluene         | 108-88-3| Tianjin Yuanli Chemical Co., Ltd.    | 0.998         | 383.55  | 383.60  | GC              |
| methanol        | 67-56-1 | Aladdin reagent Shanghai Co., Ltd.   | 0.998         | 337.67  | 337.75  | GC              |
| butyl propanoate| 590-01-2| Aladdin reagent Shanghai Co., Ltd.   | 0.990         | 418.37  | 418.26  | GC              |
| butyl butanoate | 109-21-7| Shanghai Macklin Biochemical Co., Ltd.| 0.990         | 438.29  | 438.32  | GC              |
| triethylamine   | 121-44-8| Aladdin reagent Shanghai Co., Ltd.   | 0.998         | 361.96  | 361.92  | GC              |

*The standard uncertainties of u are u(P) = 0.35 kPa and u(T) = 0.35 K, and the boiling temperature for the chemicals was determined to be under 101.3 kPa. *Gas chromatograph.

For the system at 101.3 kPa reported in ref 30. Also, from Table S1, the values of relative volatility are greater than unity, suggesting that butyl butanoate can effectively break the azeotropic point of the mixture methanol and toluene.

4. CONCLUSIONS

For separating the azeotropic mixture methanol and toluene through extractive distillation, the extractive solvents butyl butanoate, triethylamine, and butyl propanoate were chosen according to selectivity, relative volatility, and the x−y curve. With the selected extractive solvents, the isobaric VLE data for the mixtures (toluene + butyl propanoate), (triethylamine + toluene) (butyl butanoate + toluene), and (methanol + toluene + butyl butanoate) were determined under 101.3 kPa. The validated results by the van Ness test show that the VLE data measured in this work are of thermodynamic consistency. Besides, the UNIQUAC, NRTL, and Wilson equations were applied in fitting the isobaric VLE data. The largest values of RMSD(T) and RMSD(yi) are 0.23 K and 0.0054, respectively. Furthermore, the predictive model COSMO-UNIFAC was used to generate the isobaric VLE data of the three mixtures, and the predicted results show less deviation from the measured values. Compared to butyl propanoate and triethylamine, butyl butanoate displays the best effect on the separation of methanol and toluene. In addition, the ternary VLE data for (methanol + toluene + butyl butanoate) was determined under 101.3 kPa with the feed ratio (mole fraction) of methanol/toluene/butyl butanoate = 0.25:0.25:0.5. The values of relative volatility are larger than unity, showing that butyl butanoate can effectively eliminate the azeotropic point of the system. The determined VLE data and the optimized model parameters are helpful for designing the separation process.

5. EXPERIMENTAL SECTION

5.1. Materials. The materials butyl butanoate, toluene, triethylamine, and butyl propanoate were commercially obtained. The purity of the chemicals was verified using GC and utilized directly. Table 8 lists the specific descriptions of the materials.

5.2. Apparatus and Procedures. Measurements of the binary VLE data of the mixtures (toluene + butyl propanoate), (toluene + triethylamine), and (toluene + butyl butanoate) were conducted in a Rose-Williams still under 101.3 kPa. When the temperature of the prepared system in the still was maintained stable over 50 min,37,32 the mixture reached the equilibrium state. Afterward, the samples from the vapor and liquid phases were gathered for analysis by GC. The more specific experimental procedures can be referred to the literature 33–35.

5.3. Sample Analysis. To determine the sample composition, GC (SP-6890) was used, and the information of the column type, carrier gas, and the temperatures of the injector, detector, and column is given in Table 9.

Table 9. Analysis Conditions of GC

| name      | characteristic | description                          |
|-----------|----------------|--------------------------------------|
| column    | type           | packing column                       |
| carrier   | specification  | Porapak Q (3 mm × 2 m)               |
| gas       | type           | hydrogen (22 mL/min)                 |
| pressure  |                | 0.18 MPa                             |
| injection | temperature   | 463.15 K                             |
| port      | volume         | 0.3 μL                               |
| column    | temperature   | 403.15 K                             |
| detector  | type           | thermal conductivity detector (TCD)  |
| temperature |             | 473.15 K                             |

ASSOCIATED CONTENT

 Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05164.

Comparison of the isothermal VLE data for the mixture (toluene + triethylamine), experimental isobaric VLE data, and predicted values by the NRTL and UNIFAC models for the mixture (methanol + toluene + butyl butanoate) (PDF)

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