

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

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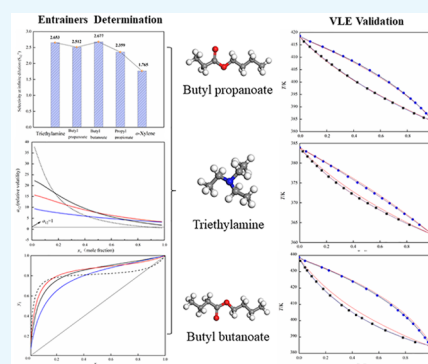


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**ABSTRACT:** For separating the azeotropic mixture methanol and toluene, an extractive distillation is applied with butyl propanoate, triethylamine, and butyl butanoate as the extractive solvents, which were screened by relative volatility, selectivity, 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,<sup>1,2</sup> such as in the manufacture of styrene, which is prepared by side-chain alkylation with methanol and toluene as raw materials, and *p*-xylene, which can also be prepared with methanol and toluene.<sup>1,3,4</sup> 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.<sup>1</sup> In general, special distillation technologies are utilized in the chemical industry for separating azeotropic mixtures, including azeotropic distillation,<sup>5</sup> salt distillation,<sup>6</sup> extractive distillation,<sup>7–9</sup> and pressure-swing distillation.<sup>10</sup> 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.<sup>11</sup> investigated the VLE behavior of the system (toluene + methanol) under 101.3 kPa. Wang et al.<sup>12</sup> 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.<sup>13</sup> 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,<sup>14</sup> NRTL,<sup>15</sup> and Wilson.<sup>16</sup> Besides, the COSMO-UNIFAC<sup>17</sup> 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<sup>18</sup>

$$S_{12}^{\infty} = \frac{\gamma_1^{\infty}}{\gamma_2^{\infty}} \quad (1)$$

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where  $\gamma_1^\infty$  and  $\gamma_2^\infty$  stand for the infinite dilution activity coefficients, which were determined using the UNIFAC model.<sup>18</sup> The infinite dilution activity coefficient is expressed as follows<sup>19</sup>

$$\ln \gamma_i^\infty = \lim_{x_i \rightarrow 0} \ln \gamma_i^C + \lim_{x_i \rightarrow 0} \ln \gamma_i^R \quad (2)$$

where

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_j l_j x_j \quad (3)$$

and

$$\ln \gamma_i^R = q_i \left[ 1 - \ln \left( \sum_j \theta_j \tau_{ji} \right) - \sum_j \left( \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \right) \right] \quad (4)$$

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

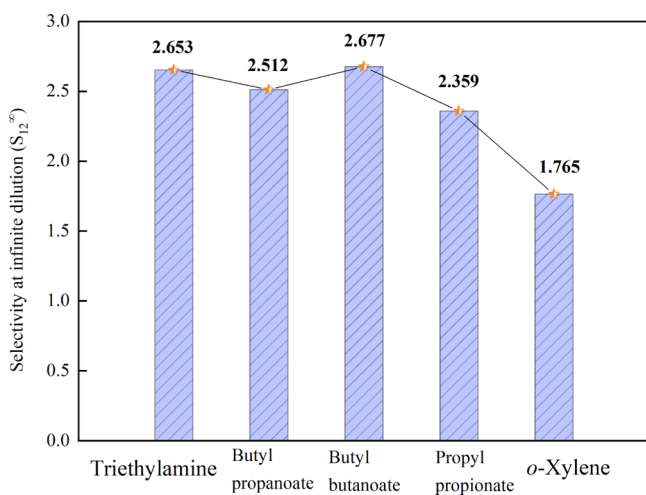


Figure 1.  $S_{12}^\infty$  by the UNIFAC model at  $T = 298.15$  K.

methanol (1) + toluene (2), the capacity of the different entrainers follows the order butyl butanoate > triethylamine > butyl propanoate > propyl propionate > *o*-xylene. The calculated selectivity values of butyl butanoate, butyl propanoate, and triethylamine are higher than those of *o*-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<sup>7</sup>

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} \quad (5)$$

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

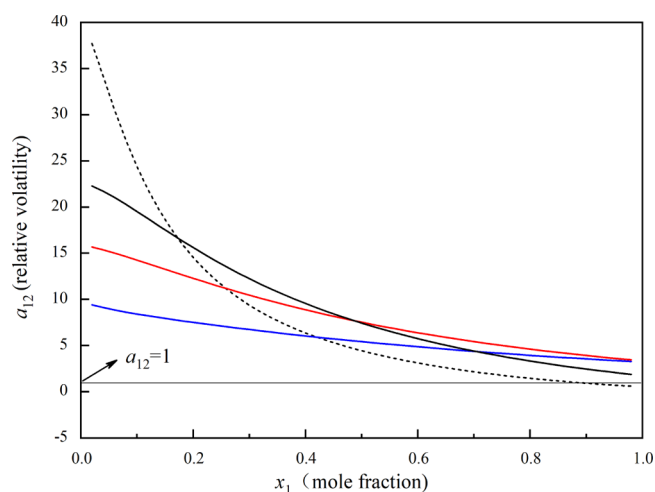


Figure 2.  $\alpha_{12}$  vs  $x_1$  for methanol (1) + toluene (2) with the three entrainers calculated using the UNIFAC model: —, triethylamine; red —, butyl butanoate; blue —, butyl propanoate; and ---, without entrainer.

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

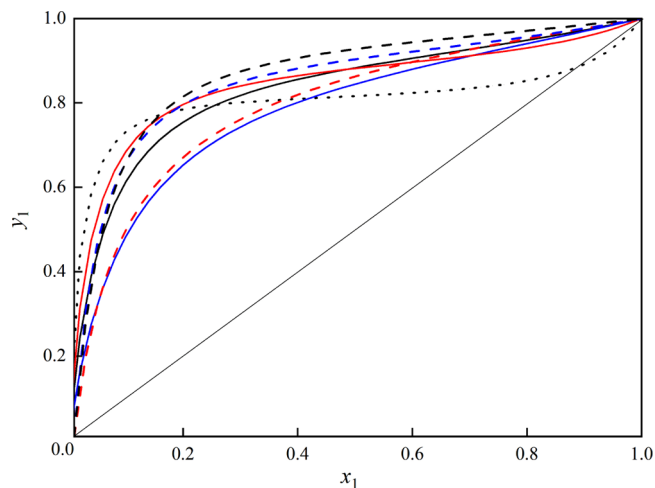


Figure 3. Effect of the different entrainers on VLE for methanol (1) + toluene (2) calculated with the UNIFAC model, red —, triethylamine; —, butyl butanoate; and blue —, butyl propanoate, and using the NRTL activity coefficient model with the regressed parameters: red ---, triethylamine; ---, butyl butanoate; blue ---, butyl propanoate; and ---, without the entrainer.

methanol and toluene 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

**Table 1. Isobaric VLE Data of the Mixture Toluene (1) + Butyl Propanoate (2) under 101.3 kPa<sup>a</sup>**

T/K	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$
383.55	1.0000	1.0000		
385.58	0.9228	0.9708	1.0012	1.0424
387.34	0.8516	0.9413	1.0013	1.0262
389.47	0.7701	0.9029	1.0015	1.0198
391.64	0.6916	0.8606	1.0017	1.0151
393.31	0.6338	0.8253	1.0020	1.0140
395.60	0.5585	0.7732	1.0021	1.0134
397.38	0.5021	0.7299	1.0038	1.0105
399.88	0.4280	0.6647	1.0048	1.0086
402.56	0.3534	0.5882	1.0052	1.0078
404.72	0.2964	0.5215	1.0061	1.0070
407.04	0.2382	0.4447	1.0075	1.0061
408.68	0.1990	0.3872	1.0082	1.0051
410.42	0.1589	0.3229	1.0091	1.0044
412.26	0.1179	0.2509	1.0106	1.0037
414.22	0.0737	0.1698	1.0438	1.0007
416.31	0.0299	0.0770	1.1103	1.0005
418.37	0.0000	0.0000		

<sup>a</sup>The standard uncertainties of  $u$  are  $u(P) = 0.35$  kPa,  $u(T) = 0.35$  K,  $u(x) = 0.0069$ , and  $u(y) = 0.0082$ .

**Table 2. Isobaric VLE Data of the Mixture Triethylamine (1) + Toluene (2) under 101.3 kPa<sup>a</sup>**

T/K	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$
383.55	0.0000	0.0000		
382.93	0.0226	0.0471	1.1486	1.0002
381.64	0.0579	0.1140	1.1228	1.0012
380.42	0.0929	0.1753	1.1117	1.0027
379.26	0.1283	0.2334	1.1057	1.0033
378.15	0.1644	0.2882	1.0980	1.0041
376.57	0.2148	0.3595	1.0944	1.0074
375.09	0.2709	0.4307	1.0829	1.0080
373.69	0.3284	0.4966	1.0709	1.0094
372.35	0.3866	0.5583	1.0616	1.0098
371.09	0.4457	0.6158	1.0527	1.0105
369.87	0.5079	0.6711	1.0421	1.0116
368.71	0.5698	0.7224	1.0339	1.0127
367.23	0.6491	0.7826	1.0263	1.0186
365.81	0.7379	0.8439	1.0145	1.0240
364.46	0.8195	0.8940	1.0071	1.0544
361.96	1.0000	1.0000		

<sup>a</sup>The standard uncertainties of  $u$  are  $u(P) = 0.35$  kPa,  $u(T) = 0.35$  K, and  $u(x) = u(y) = 0.0061$ .

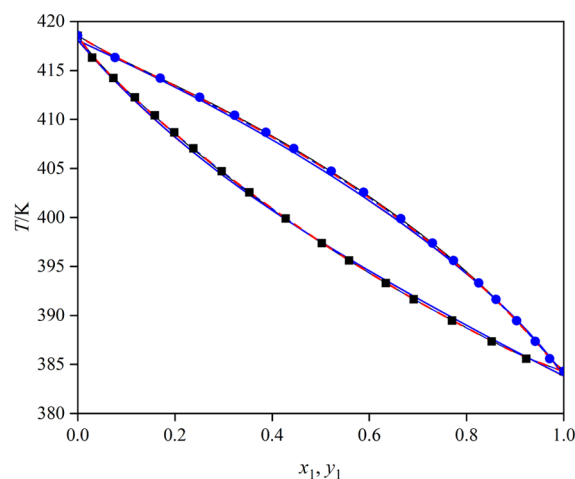
liquid mole fraction and  $y_1$  stands for vapor mole fraction. Besides, the  $x$ – $y$  curves for the three mixtures are displayed in Figure 7. As shown in Figure 7, all the  $x$ – $y$  curves deviate from the diagonal line, indicating that the solvents can be recovered by a common distillation technology.

**3.2. VLE Calculation.** For the investigated mixtures, the liquid phase is a non-ideal solution, and the vapor phase can be

**Table 3. Isobaric VLE Data of the Mixture Toluene (1) + Butyl Butanoate (2) under 101.3 kPa<sup>a</sup>**

T/K	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$
438.29	0.0000	0.0000		
436.65	0.0091	0.0446	1.3413	1.0014
432.64	0.0439	0.1706	1.1589	1.0021
430.75	0.0601	0.2238	1.1566	1.0039
427.21	0.0948	0.3208	1.1362	1.0050
423.94	0.1295	0.4037	1.1262	1.0053
419.47	0.1814	0.5056	1.1152	1.0071
415.44	0.2332	0.5878	1.1083	1.0087
409.54	0.3199	0.6920	1.0964	1.0152
406.37	0.3747	0.7432	1.0871	1.0156
403.50	0.4289	0.7857	1.0789	1.0159
401.59	0.4725	0.8138	1.0636	1.0183
398.11	0.5505	0.8582	1.0535	1.0180
394.08	0.6488	0.9029	1.0463	1.0206
389.61	0.7814	0.9466	1.0281	1.0501
386.85	0.8736	0.9705	1.0164	1.1140
383.55	1.0000	1.0000		

<sup>a</sup>The standard uncertainties of  $u$  are  $u(P) = 0.35$  kPa,  $u(T) = 0.35$  K, and  $u(x) = u(y) = 0.0062$ .



**Figure 4.**  $T$ – $x$ – $y$  curves for the mixture toluene (1) + butyl propanoate (2): blue ●,  $T$ – $y$  (experimental); ■,  $T$ – $x$  (experimental); red ---, UNIQUAC model; —, NRTL model; blue ---, Wilson model; red —, COSMO-UNIFAC model; and blue —, UNIFAC model.

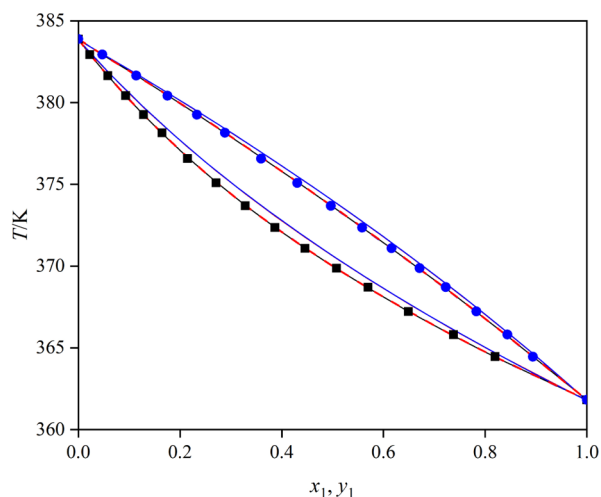
assumed as an ideal gas at 101.3 kPa for VLE calculation. The VLE relation is defined as<sup>20,21</sup>

$$\gamma_i = \frac{P y_i}{P_i^s x_i} \quad (6)$$

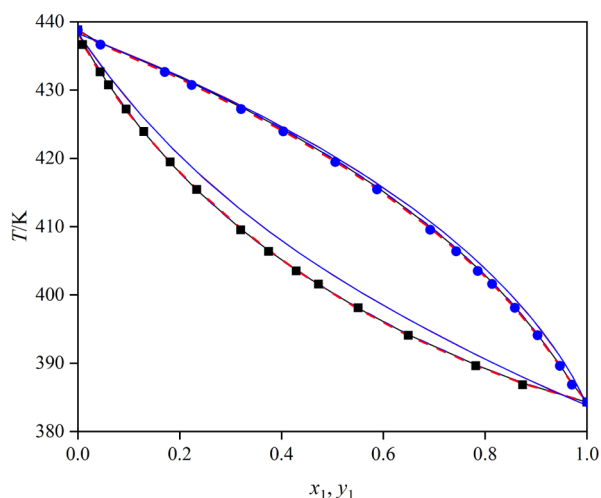
where  $\gamma_i$  refers to the activity coefficient,  $x_i$  stands for the mole fraction in the liquid phase,  $y_i$  stands for the mole fraction in the vapor phase, and  $P_i^s$  stands for saturation vapor pressure of the pure component and was determined using the extended Antoine equation, which is defined as<sup>22</sup>

$$\ln(P_i^s/\text{kPa}) = C_{1i} + \frac{C_{2i}}{T/K + C_{3i}} + C_{4i}(T/K) + C_{5i}$$

$$\ln(T/K) + C_{6i}(T/K)^{C_{7i}} C_{8i} \leq T/K \leq C_{9i} \quad (7)$$



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

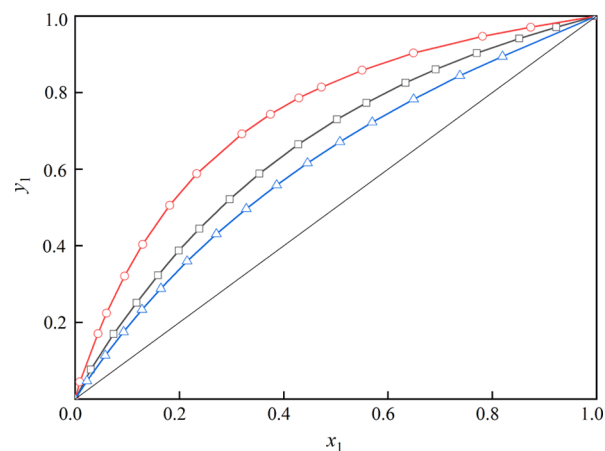
where  $C_{1i}$  to  $C_{9i}$  are the coefficients of the equation, and the values are presented in Table 4. The results of activity coefficient ( $\gamma_i$ ) of the mixtures are presented in Tables 1–3

**3.3. Thermodynamic Consistency Test.** The consistency test of van Ness<sup>24</sup> was utilized to verify the reliability of the determined VLE data. The van Ness test is represented as

$$\Delta y = \frac{1}{N} \sum_{i=1}^N 100 |y_i^{\text{exp}} - y_i^{\text{cal}}| \quad (8)$$

$$\Delta P = \frac{1}{N} \sum_{i=1}^N 100 \left| \frac{P_i^{\text{exp}} - P_i^{\text{cal}}}{P_i^{\text{exp}}} \right| \quad (9)$$

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.



**Figure 7.**  $x$ - $y$  curves of the mixtures: red -○-, toluene (1) + butyl butanoate (2); blue -△-, toluene (1) + triethylamine (2); and -□-, toluene (1) + butyl propanoate (2).

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<sup>26</sup>

$$F = \sum_i^N \left[ \left( \frac{P_i^{\text{exp}} - P_i^{\text{cal}}}{\sigma_P} \right)^2 + \left( \frac{T_i^{\text{exp}} - T_i^{\text{cal}}}{\sigma_T} \right)^2 + \left( \frac{x_i^{\text{exp}} - x_i^{\text{cal}}}{\sigma_x} \right)^2 + \left( \frac{y_i^{\text{exp}} - y_i^{\text{cal}}}{\sigma_y} \right)^2 \right] \quad (10)$$

where  $\sigma$ ,  $T$ , and  $P$  denote the standard deviation, temperature, and pressure. The values of standard deviation<sup>23</sup> 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  $\text{RMSDs}(T)$  and  $\text{RMSDs}(y_i)$  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<sup>28,29</sup> 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

Table 4. Coefficients of the Extended Antoine Model<sup>a</sup>

component	C <sub>1i</sub>	C <sub>2i</sub>	C <sub>3i</sub>	C <sub>4i</sub>	C <sub>5i</sub>	C <sub>6i</sub>	C <sub>7i</sub>	C <sub>8i</sub> /K	C <sub>9i</sub> /K
triethylamine	49.64	-5681.90	0	0	-4.98	1.24 × 10 <sup>-17</sup>	6	158.45	535.15
toluene	70.04	-6729.80	0	0	-8.18	5.30 × 10 <sup>-6</sup>	2	178.18	591.75
butyl butanoate	102.27	-9384.00	0	0	-12.77	7.47 × 10 <sup>-6</sup>	2	181.15	616.00
butyl propanoate	64.32	-7709.80	0	0	-6.84	6.36 × 10 <sup>-18</sup>	6	183.63	594.60

<sup>a</sup>Collected from the Aspen databank.<sup>23</sup>

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<sup>a</sup>

component	<i>r</i>	<i>q</i>
toluene	3.9229	2.9680
butyl propanoate	5.5017	4.7360
triethylamine	5.0119	4.2560
butyl butanoate	6.1892	5.2760

<sup>a</sup>Taken from the Aspen property databank.<sup>25</sup>

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 entrainers 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 UNIQUAC 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.

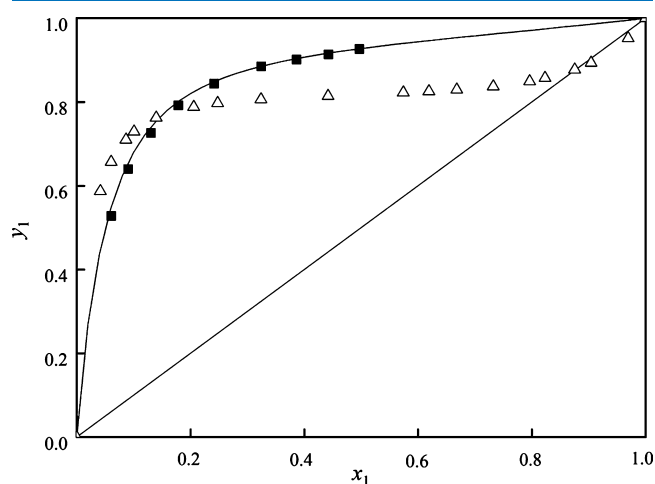


Figure 8. *x*-*y* curves for the mixture methanol (1) + toluene (2): ■, experimental data with butyl butanoate; —, by the NRTL model with the regressed parameters; and △, from ref 30.

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

Table 7. Binary Parameters for the Mixtures under 101.3 kPa

model	parameters				RMSD	
	<i>a</i> <sub>12</sub>	<i>a</i> <sub>21</sub>	<i>b</i> <sub>12</sub> /K	<i>b</i> <sub>21</sub> /K	<i>y</i> <sub>1</sub> <sup>a</sup>	<i>T</i> /K <sup>b</sup>
toluene + butyl propanoate						
NRTL <sup>c</sup>	0.1941	0.1581	-32.14	-112.16	0.0026	0.16
UNIQUAC <sup>d</sup>	22.45	-6.2300	-2285.03	2185.63	0.0023	0.15
Wilson <sup>e</sup>	7.9342	5.3700	2880.91	-1892.58	0.0025	0.15
triethylamine + toluene						
NRTL	-15.77	11.76	6211.83	-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
toluene + butyl butanoate						
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

<sup>a</sup>RMSD(*y*<sub>1</sub>) =  $\sqrt{\frac{\sum_{i=1}^N (y_{1i}^{exp} - y_{1i}^{cal})^2}{N}}$  <sup>b</sup>RMSD(*T*) =  $\sqrt{\frac{\sum_{i=1}^N (T_i^{exp} - T_i^{cal})^2}{N}}$  <sup>c</sup>NRTL,  $\tau_{ij} = a_{ij} + b_{ij}/T$ , the  $\alpha_{ij}$  value was fixed at 0.3. <sup>d</sup>UNIQUAC,  $\tau_{ij} = \exp(a_{ij} + b_{ij}/T)$ . <sup>e</sup>Wilson,  $\ln A_{ij} = a_{ij} + b_{ij}/T$ .

Table 8. Specifications of the Chemicals

component	CAS	suppliers	mass fraction	T/K		analysis method <sup>b</sup>
				exp <sup>a</sup>	lit	
toluene	108-88-3	Tianjin Yuanli Chemical Co., Ltd.	0.998	383.55	383.60 <sup>36</sup> 382.95 <sup>37</sup>	GC
methanol	67-56-1	Aladdin reagent Shanghai Co., Ltd.	0.998	337.67	337.75 <sup>11</sup> 337.42 <sup>13</sup>	GC
butyl propanoate	590-01-2	Aladdin reagent Shanghai Co., Ltd.	0.990	418.37	418.26 <sup>38</sup> 418.69 <sup>39</sup>	GC
butyl butanoate	109-21-7	Shanghai Macklin Biochemical Co., Ltd.	0.990	438.29	438.32 <sup>38</sup> 438.15 <sup>39</sup>	GC
triethylamine	121-44-8	Aladdin reagent Shanghai Co., Ltd.	0.998	361.96	361.92 <sup>40</sup> 361.97 <sup>41</sup>	GC

<sup>a</sup>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. <sup>b</sup>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  $\text{RMSD}(T)$  and  $\text{RMSD}(y_i)$  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,<sup>31,32</sup> 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.<sup>33–35</sup>

**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
	specification	Porapak Q (3 mm × 2 m)
carrier gas	type	hydrogen (22 mL/min)
	pressure	0.18 MPa
injection port	temperature	463.15 K
	volume	0.3 $\mu$ L
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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## Notes

The authors declare no competing financial interest.

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