

## Isobaric Vapor–Liquid Equilibrium of Methylcyclohexane + Toluene with Gamma-Valerolactone as a Biobased Entrainer and 1-Methylpyrrolidin-2-one as a Conventional Entrainer

Hartanto, D.; Schuur, Boelo; Schuttevaer, Tim ; Kiss, A.A.; de Haan, A.B.

### DOI

[10.1021/acs.jced.4c00509](https://doi.org/10.1021/acs.jced.4c00509)

### Publication date

2025

### Document Version

Final published version

### Published in

Journal of Chemical and Engineering Data

### Citation (APA)

Hartanto, D., Schuur, B., Schuttevaer, T., Kiss, A. A., & de Haan, A. B. (2025). Isobaric Vapor–Liquid Equilibrium of Methylcyclohexane + Toluene with Gamma-Valerolactone as a Biobased Entrainer and 1-Methylpyrrolidin-2-one as a Conventional Entrainer. *Journal of Chemical and Engineering Data*, 70(3), 1339-1351. <https://doi.org/10.1021/acs.jced.4c00509>

### Important note

To cite this publication, please use the final published version (if applicable).  
Please check the document version above.

### Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

### Takedown policy

Please contact us and provide details if you believe this document breaches copyrights.  
We will remove access to the work immediately and investigate your claim.

# Isobaric Vapor–Liquid Equilibrium of Methylcyclohexane + Toluene with Gamma-Valerolactone as a Biobased Entrainer and 1-Methylpyrrolidin-2-one as a Conventional Entrainer

Dhoni Hartanto,\* Boelo Schuur, Tim Schuttevaer, Anton A. Kiss, and André B. de Haan



Cite This: *J. Chem. Eng. Data* 2025, 70, 1339–1351



Read Online

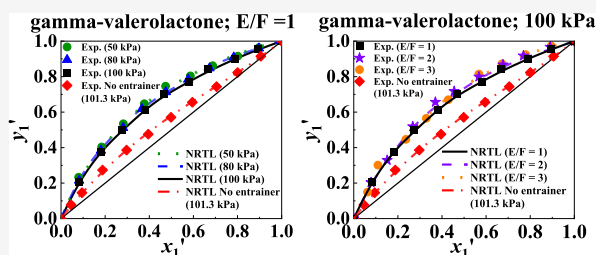
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

**ABSTRACT:** The isobaric vapor–liquid equilibrium (VLE) data of the binary mixture of methylcyclohexane (1) + toluene (2) at 101.3 kPa; the pseudoternary mixture of methylcyclohexane (1) + toluene (2) + gamma-valerolactone (GVL) (3) with the entrainer-to-feed ratio ( $E/F$ ) = 1 (mass basis) at 50, 80, and 100 kPa, and  $E/F$  = 2 and 3 at 100 kPa; and the pseudoternary mixture of methylcyclohexane (1) + toluene (2) + 1-methylpyrrolidin-2-one (NMP) (3) with  $E/F$  = 1 at 100 kPa were measured using a Fischer Labodest VLE602 ebulliometer. The reliability of the experimental VLE data was tested and confirmed by Van Ness and Fredenslund thermodynamic consistency tests. The experimental results indicate that the presence of GVL and NMP increases the relative volatility of methylcyclohexane to toluene; therefore, both entrainers remove a close-boiling behavior in the mixture. Non-random two-liquid (NRTL) and universal quasi chemical (UNIQUAC) thermodynamic models were applied in the experimental data correlation to obtain the optimum binary interaction parameters. For the mixture involving GVL, the experimental VLE data were accurately correlated by NRTL and UNIQUAC. However, NRTL has more accurate results compared with UNIQUAC. For the mixture containing NMP, both the UNIQUAC and NRTL models show favorable regression results.



## 1. INTRODUCTION

Distillation is a widely employed separation technology in the chemical industry due to its versatility in handling various feed flow rates and concentrations, efficient mass transfer capabilities, applicability in many applications of complex mixtures, and ability to produce high-purity products.<sup>1,2</sup> Over 100,000 distillation columns are in operation globally, corresponding to more than 50% of the overall plant cost.<sup>2,3</sup> Distillation, on the other hand, although it is a well-established technology, consumes a lot of energy and water and is therefore costly. It can also generate significant quantities of CO<sub>2</sub> emissions, especially when utilized in difficult separations involving azeotropes, and close-boiling or low-relative-volatility mixtures. In petrochemicals, methylcyclohexane and toluene are aliphatic and aromatic mixtures with close-boiling behavior. Extractive distillation, an advanced distillation technology, is often used, in which an entrainer with high-boiling and decomposition temperature properties is added to overcome the separation obstacles by enhancing the relative volatility of the mixtures. Consequently, cost, energy and water consumption, and CO<sub>2</sub> emissions can be minimized as an easier separation can be achieved.

1-Methylpyrrolidin-2-one (NMP) is a well-known and widely applied solvent in industry, as well as a common conventional organic entrainer in extractive distillation. Unfortunately, this entrainer is categorized as a high-toxicity

compound, which is set to be restricted for specific applications in the industry under the Regulation on the Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) and Environmental Protection Agency (EPA) regulations.<sup>4,5</sup> Thus, employing alternative entrainers with greener properties in extractive distillation has received greater exposure to enhance process sustainability, decrease energy needs, and mitigate the adverse environmental impacts of conventional organic entrainers. Examples of investigated alternative entrainers include ionic liquids (ILs),<sup>6–11</sup> biological buffers,<sup>12</sup> deep eutectic solvents (DESS),<sup>13–17</sup> and natural deep eutectic solvents (NADESS).<sup>18</sup> Biobased solvents are also gaining more interest in being used as entrainers in extractive distillation. Brower and Schuur<sup>19</sup> investigated the use of Cyrene as an effective biobased entrainer in aromatic/aliphatic and olefin/paraffin separation represented by methylcyclohexane/toluene and *n*-heptane/1-heptene mixtures, respectively. Brower and Schuur<sup>20</sup> also investigated the use of DL-limonene, water, and ethylene carbonate as biobased entrainers in

Received: September 10, 2024

Revised: February 5, 2025

Accepted: February 20, 2025

Published: February 27, 2025



Table 1. Specification of Chemicals

| chemicals                | CAS registry number | molecular weight (g/mol) | $T_{\text{boiling}}$ (K) <sup>a,b</sup> | density (g/cm <sup>3</sup> ) <sup>a,c</sup> | suppliers     | purity (mass fraction) <sup>a</sup> | purity analysis method | purification method |
|--------------------------|---------------------|--------------------------|-----------------------------------------|---------------------------------------------|---------------|-------------------------------------|------------------------|---------------------|
| methylcyclohexane        | 108-87-2            | 98.19                    | 374.15                                  | 0.770                                       | Sigma-Aldrich | ≥0.990                              | GC <sup>d</sup>        | none                |
| toluene                  | 108-88-3            | 92.14                    | 383.15                                  | 0.865                                       | Sigma-Aldrich | 0.999                               | GC <sup>d</sup>        | none                |
| gamma-valerolactone      | 108-29-2            | 100.12                   | 479.15                                  | 1.052                                       | Sigma-Aldrich | ≥0.999                              | GC <sup>d</sup>        | none                |
| 1-methylpyrrolidin-2-one | 872-50-4            | 99.13                    | 475.15                                  | 1.028                                       | Sigma-Aldrich | ≥0.995                              | GC <sup>d</sup>        | none                |
| acetone                  | 67-64-1             | 58.08                    | 329.15                                  | 0.791                                       | Merck         | ≥0.998                              | GC <sup>d</sup>        | none                |

<sup>a</sup>Specified by the suppliers. <sup>b</sup>At a pressure of 101.3 kPa. <sup>c</sup>At a temperature of 298.15 and a pressure of 101.3 kPa. <sup>d</sup>GC (gas chromatography).

acetone/diisopropyl separation. There are other various biobased entrainers that can be utilized in extractive distillation, such as gamma-valerolactone (GVL). GVL can be readily produced from lignocellulosic biomass and possesses crucial characteristics that make it a viable biobased substitute for restricted conventional organic entrainers due to its environmentally friendly properties such as biodegradability, nontoxicity, and sustainability.<sup>21,22</sup> Moreover, GVL offers favorable properties, including a liquid phase at room temperature, good polarity, and hydrogen bond acceptor capability (K-T parameters: polarizability ( $\pi^*$ ) = 0.83, hydrogen bond acceptor ( $\beta$ ) = 0.6, and hydrogen bond donor ( $\alpha$ ) = 0.20), high boiling point (480.15 K at 101.3 kPa), high decomposition temperatures (873.15 K at pressure of 170 kPa), good chemical stability, and low vapor pressure (2.67 kPa at 370.4 K), making it a well-suited entrainer for extractive distillation.<sup>23–28</sup>

Vapor–liquid equilibrium (VLE) is essential for thermodynamic data for designing and optimizing extractive distillation. However, there is no existing VLE data in the literature on the mixture of methylcyclohexane and toluene using GVL as a biobased entrainer and NMP as a conventional organic entrainer. The VLE data for the methylcyclohexane-toluene with the addition of morpholine as an entrainer was provided by Coca and Pis.<sup>29</sup> Brower and Schuur<sup>19</sup> studied the VLE data of methylcyclohexane-toluene with Cyrene as an entrainer. The effect of some ionic liquids as entrainers on methylcyclohexane-toluene VLE data behavior was investigated by Liebert et al.<sup>30</sup> Gutierrez et al.<sup>31</sup> reported the NMP effect at molar ratios of 0.1 and 0.3 on the relative volatility of methylcyclohexane to toluene; however, the publication did not provide complete VLE data. Other researchers reported the separation of methylcyclohexane and toluene mixtures using extractive distillation in either a pilot plant or a process simulation evaluation. Quijada-Maldonado et al.<sup>32</sup> studied the use of ILs and NMP as effective entrainers to separate methylcyclohexane from toluene in the pilot plant extractive distillation. Anwani and Shirsat<sup>33</sup> also simulated the use of phenol as an entrainer in the extractive distillation process for separating methylcyclohexane and toluene. Some other conventional organic entrainers, such as acetophenone, methyl *n*-amyl ketone, cyclohexanone, *o*-cresol, dimethylformamide (DMF), propylene glycol, furfural, phenol, and aniline, have been evaluated using process simulation for the separation of methylcyclohexane-toluene by extractive distillation.<sup>34</sup>

In this study, GVL was evaluated for the first time as a biobased entrainer for the methylcyclohexane and toluene separation by extractive distillation. The evaluation was

conducted by measuring the VLE data. The VLE data of methylcyclohexane and toluene with NMP as an entrainer was investigated as a benchmark. The consistency of the VLE data was tested using Van Ness<sup>35</sup> and Fredenslund<sup>36</sup> to confirm the reliability of the data. Furthermore, the experimental VLE data were correlated with activity coefficient thermodynamic models such as NRTL<sup>37</sup> and UNIQUAC<sup>38</sup> to obtain the optimum binary parameters for the investigated system.

## 2. METHODS

**2.1. Chemicals.** All chemicals were purchased from commercial suppliers. Gas chromatography (GC) was utilized to check the purity of the chemicals. All chemicals were used as received without performing any additional purifications since no detectable impurities were found. The detailed chemical specifications, such as name, CAS registry number, molecular weight, boiling point, density, suppliers, purity, and purity analysis method, are presented in Table 1.

**2.2. Experimental Procedures.** A Fischer Labodest VLE602 ebulliometer was used to measure the vapor–liquid equilibrium of a binary mixture of methylcyclohexane and toluene and pseudoternary mixtures of methylcyclohexane and toluene with gamma-valerolactone and 1-methylpyrrolidin-2-one, respectively. The temperature and pressure uncertainties of the apparatus, as stated by the supplier, are  $\pm 0.01$  K and  $\pm 0.01$  kPa, respectively. The feed mixture as well as the amounts of entrainers for the pseudoternary mixtures were prepared using an analytical balance (Mettler Toledo AE200, United States) with a precision of 0.0001 g. In each experiment, a mixture with a total volume of 100 mL was charged into the ebulliometer to ensure that the proper amount of liquid and vapor circulating in the setup. The magnetic stirrer was activated during the experiment to provide the supplied mixture with adequate heating and mixing. The vacuum pressure was controlled by using a vacuum pump (Pfeiffer DUO 3, Germany) and a pressure controller (Burkert 2871, Germany) coupled to the ebulliometer. The desired vacuum pressure was digitally set using an i-Fischer Unicontrol VLE. Next, the vacuum pump was turned on during the VLE measurements. Once the specific vacuum pressure was obtained, the pressure inside the ebulliometer was maintained with a pressure controller. The mixture was considered to have achieved equilibrium when the temperature in the ebulliometer remained constant ( $\pm 60$  min). Liquid and condensed vapor samples in amounts of approximately 0.1 mL were collected by opening the liquid phase sampling valve and using a syringe to get the liquid droplet, respectively. Each sample was diluted with analytical-grade acetone for composition analysis by gas

chromatography (GC). A similar method has been utilized in the literature.<sup>19,20,39</sup>

**2.3. Analytical Methods.** The composition of diluted liquid and vapor samples was analyzed using a gas chromatograph of a Thermo Scientific Trace 1300, Switzerland, equipped with two parallel ovens and a TriPlus 100 Liquid Samples (LS) Autosampler. The diluted samples were analyzed using a column of Agilent DB-1MS with dimensions of length, diameter, and film thickness of 60 m, 0.25 mm, and 0.25  $\mu\text{m}$ , respectively. The inlet type was a Split–Splitless (SSL) injector, and the injection volume was 1  $\mu\text{m}$ . A ramped temperature mode was used in the GC with the following profile, in which the initial temperature was 30  $^{\circ}\text{C}$ . After the injection, it shortly started with a ramp of 10  $^{\circ}\text{C}/\text{min}$  to 45  $^{\circ}\text{C}$ , followed by the next ramp of 5  $^{\circ}\text{C}/\text{min}$  to 60  $^{\circ}\text{C}$ . The third ramp was 2.5  $^{\circ}\text{C}/\text{min}$  to 80  $^{\circ}\text{C}$ , followed by the fourth ramp of 5  $^{\circ}\text{C}/\text{min}$  to 95  $^{\circ}\text{C}$ . The last ramp was 50  $^{\circ}\text{C}/\text{min}$  to the final temperature of 320  $^{\circ}\text{C}$ , and total ramps took place for 21 min. A flame ionization detector (FID) type was used as a detector with a temperature of 440  $^{\circ}\text{C}$ . A column flow of 2 mL/min and a split flow of 300 mL/min with a split ratio of 150 were used. An airflow of 350 mL/min, helium as a makeup flow of 40 mL/min, and a hydrogen flow of 50 mL/min with a carrier pressure of 213.2 kPa were used as gas references. Composition analysis was conducted in triplicate to exclude possible errors in the analytical method. The final sample composition was defined by the mean values of those replications. The standard uncertainty calculations for temperature, pressure, and liquid and vapor composition were based on NIST Technical Note 1297<sup>40</sup> and Joint Committee for Guides in Metrology (JCGM),<sup>41</sup> which are listed in eqs S1–S6 in the Supporting Information. The standard uncertainties are provided in the VLE data tabulation in Section 3.1.

### 3. RESULTS AND DISCUSSION

**3.1. Experimental Results.** The VLE data for the binary mixture of methylcyclohexane and toluene were measured at a pressure of 101.3 kPa. The experimental values consist of the mole fraction of methylcyclohexane in a liquid phase ( $x_1$ ) and a vapor phase ( $y_1$ ), equilibrium temperature ( $T$ ), the activity coefficient of methylcyclohexane ( $\gamma_1$ ) and toluene ( $\gamma_2$ ), and the relative volatility of methylcyclohexane to toluene ( $\alpha_{12}$ ), which are tabulated in Table 2.

Ideal gas behavior was assumed to be applicable because the VLE data of the binary mixture were investigated at atmospheric pressure. The activity coefficient of the component  $i$  ( $\gamma_i$ ) in the binary mixture as a representation of the nonideal behavior of the compound in the mixture was calculated using eq 1:

$$\gamma_i = \frac{y_i P}{x_i P_i^{\text{sat}}} \quad (1)$$

where  $x_i$  and  $y_i$  are a liquid-phase and a vapor-phase mole fraction of the component  $i$ , respectively,  $P$  is the total pressure in the system, and  $P_i^{\text{sat}}$  is the saturated vapor pressure of the component  $i$ . The saturated vapor pressure of component  $i$  ( $P_i^{\text{sat}}$ ) was calculated using the extended Antoine parameters taken from the Aspen Plus physical property databank listed in Table 3.

The relative volatility of methylcyclohexane to toluene ( $\alpha_{12}$ ) in the binary mixture was defined by eq 2:

**Table 2. VLE Data for Methylcyclohexane (1) + Toluene (2) at 101.3 kPa<sup>a,b</sup>**

| $T/\text{K}$ | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $\alpha_{12}$ |
|--------------|-------|-------|------------|------------|---------------|
| 383.87       | 0.000 | 0.000 |            | 1.000      |               |
| 382.50       | 0.046 | 0.078 | 1.344      | 1.004      | 1.76          |
| 381.50       | 0.095 | 0.146 | 1.243      | 1.009      | 1.62          |
| 379.87       | 0.188 | 0.273 | 1.230      | 1.003      | 1.62          |
| 378.43       | 0.297 | 0.386 | 1.145      | 1.021      | 1.49          |
| 377.45       | 0.396 | 0.476 | 1.088      | 1.044      | 1.39          |
| 376.42       | 0.498 | 0.571 | 1.066      | 1.063      | 1.34          |
| 375.60       | 0.595 | 0.655 | 1.049      | 1.083      | 1.29          |
| 375.03       | 0.705 | 0.743 | 1.021      | 1.125      | 1.21          |
| 374.62       | 0.800 | 0.823 | 1.007      | 1.160      | 1.16          |
| 374.16       | 0.906 | 0.915 | 1.002      | 1.199      | 1.12          |
| 373.92       | 1.000 | 1.000 | 1.000      |            |               |

<sup>a</sup> $T$  is the equilibrium temperature;  $x_1$  is a liquid-phase mole fraction of methylcyclohexane;  $y_1$  is a vapor-phase mole fraction of methylcyclohexane;  $\gamma_1$  is the activity coefficient of methylcyclohexane;  $\gamma_2$  is the activity coefficient of toluene; and  $\alpha_{12}$  is the relative volatility of methylcyclohexane to toluene. <sup>b</sup>Expanded combined uncertainties  $U$  with  $k = 2$  are  $U(T) = 0.2$  K,  $U(P) = 0.20$  kPa, and  $U(x_1) = U(y_1) = 0.006$ .

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} \quad (2)$$

The experimental results were compared with the VLE data from the literature.<sup>29,42</sup> The graphical comparison of the VLE data is depicted in Figure 1.

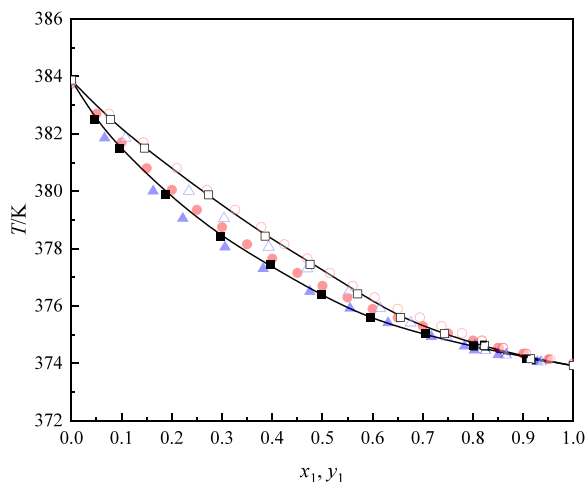
The results indicate that the VLE data obtained in this study are in better agreement with the VLE data reported by Coca and Pis<sup>29</sup> than those by Quiggle and Fenske.<sup>42</sup> The equilibrium temperature provided by Quiggle and Fenske is slightly higher than ours and that of Coca and Pis. In addition, the  $x$ – $y$  diagram is presented in Figure S1 in the Supporting Information. The vapor pressure of methylcyclohexane and toluene was measured and compared with literature values.<sup>43,44</sup> The results show that the vapor pressure from this work aligns well with the literature data, as provided in parts S2 and S3 of the Supporting Information. These results confirmed the reliability of the experimental apparatus and method. Moreover, the VLE data of the binary mixture from this work are consistent according to the Van Ness and Fredenslund thermodynamic consistency tests. A more detailed description of the thermodynamic consistency test is provided in Section 3.2. The VLE data of the binary mixture at 53.3 kPa were taken from the literature,<sup>45</sup> as shown in Figure 2. Figures 2 and S1 also show that a reduced pressure of 53.3 kPa did not significantly change the close-boiling behavior of the mixture. This data, along with the VLE data of the binary mixture at 101.3 kPa obtained from this work, were used for the regression analysis.

The apparatus was further utilized to measure the vapor–liquid equilibrium for the pseudoternary mixture of methylcyclohexane (1) + toluene (2) + GVL (3) with the entrainer-to-feed ratio ( $E/F$ ) = 1 at pressures of 50, 80, and 100 kPa, respectively. The  $E/F$  describes the mass-based ratio of the entrainer added to the binary mixture, which is expressed as the mass of the entrainer divided by the mass of the binary mixture. The experimental VLE data for the pseudoternary mixture are provided in Table 4, where  $x_1'$  and  $y_1'$  represent the mole fractions of methylcyclohexane in the liquid and

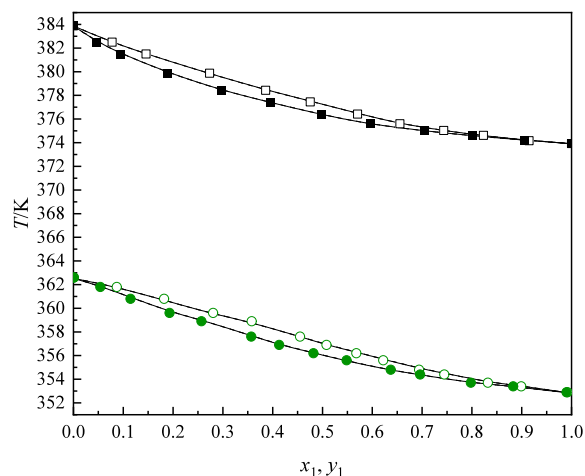
Table 3. Parameters of the Extended Antoine Equation<sup>a,b</sup>

| compound          | $A_1$  | $A_2$   | $A_3$ | $A_4$ | $A_5$   | $10^6 A_6$ | $A_7$ | $A_8$  | $A_9$ |
|-------------------|--------|---------|-------|-------|---------|------------|-------|--------|-------|
| methylcyclohexane | 85.776 | −7080.8 | 0     | 0     | −10.695 | 8.14       | 2.0   | 146.58 | 572.1 |
| toluene           | 70.037 | −6729.8 | 0     | 0     | −8.179  | 5.30       | 2.0   | 178.18 | 591.8 |

<sup>a</sup>Taken from the Aspen Plus physical property databank;  $A_1$ ,  $A_2$ ,  $A_3$ ,  $A_4$ ,  $A_5$ ,  $A_6$ ,  $A_7$ ,  $A_8$ , and  $A_9$  are Extended Antoine constants. <sup>b</sup>Extended Antoine equation:  $\ln(P^s) = A_1 + A_2/(T + A_3) + A_4T + A_5 \ln T + A_6T^{A_7}$  for  $A_8 < T < A_9$ , where  $P^s$  is in kPa and  $T$  in K.



**Figure 1.**  $T$ – $xy$  diagram for methylcyclohexane (1) + toluene (2) at 101.3 kPa: (black filled square), liquid-phase and (black unfilled square), vapor-phase from this work; (pink sphere), liquid-phase and (pink circle), vapor-phase from literature;<sup>42</sup> (purple filled triangle), liquid-phase; (purple unfilled triangle), vapor-phase from the literature;<sup>29</sup> and (—), correlated by NRTL.



**Figure 2.**  $T$ – $xy$  diagram for methylcyclohexane (1) + toluene (2) at 53.3 and 101.3 kPa: (green sphere), liquid-phase and (green circle), vapor-phase at 53.3 kPa from literature;<sup>45</sup> (black filled square), liquid-phase and (black unfilled square), vapor-phase at 101.3 kPa from this work; (—), correlated by NRTL; and (---), UNIQUAC.

vapor phases on an entrainer-free basis, respectively.  $x_1$ ,  $x_2$ , and  $x_3$  denote the mole fractions of methylcyclohexane, toluene, and GVL in the liquid phase, respectively.  $y_1$ ,  $y_2$ , and  $y_3$  indicate the mole fractions of methylcyclohexane, toluene, and GVL in the vapor phase, respectively. Moreover, the VLE data of the pseudoternary mixture containing GVL with  $E/F = 2$  and  $E/F = 3$  at a pressure of 100 kPa were investigated, with the results listed in Table 5.

We also investigated the VLE for the pseudoternary mixture of methylcyclohexane (1) + toluene (2) containing NMP (3) with  $E/F = 1$  at a pressure of 100 kPa as a benchmark entrainer. The VLE data are provided as a pseudoternary mixture in Table 6. The VLE measurements for pseudoternary systems were performed at 100 kPa rather than 101.3 kPa due to the ambient pressure in our laboratory varying between 100 and 101.3 kPa. Therefore, the pressure of 100 kPa was selected, as it allows more accurate control of the pressure within the setup. In both pseudoternary mixtures, one liquid phase is observed throughout the entire composition range of methylcyclohexane at all investigated  $E/F$ s and temperature ranges.

The nonideality of the substance in the liquid phase for the pseudoternary mixture, as indicated by the activity coefficient of the component  $i$  ( $\gamma_i$ ), was determined using eq 1 with consideration of the ideal gas applied in the system since the VLE data were measured at the atmospheric and vacuum pressures. For the pseudoternary mixture, the relative volatility of methylcyclohexane to toluene ( $\alpha_{12}$ ) was determined by eq 3.

$$\alpha_{12} = \frac{y_1'/x_1'}{y_2'/x_2'} \quad (3)$$

where  $x_1'$  and  $x_2'$  denote the liquid-phase mole fractions of methylcyclohexane and toluene on an entrainer-free basis, respectively.  $y_1'$  and  $y_2'$  represent the vapor-phase mole fractions of methylcyclohexane and toluene on an entrainer-free basis, respectively.

As observed in Figure 3, reducing the pressure in the VLE significantly reduces the equilibrium temperature since the reduced pressure will decrease the boiling point of each compound.

Figure 4 indicates that increasing the amount of GVL with the  $E/F$  ratio at 2 and 3, while maintaining the pressure constant at 100 kPa, leads to an increase in the equilibrium temperature. The addition of a higher amount of GVL to the mixture results in a higher equilibrium temperature. GVL exhibits a higher affinity for toluene, resulting in reduced vaporization of toluene. As a result, a higher temperature is required to achieve vaporization for equilibrium, thereby raising the overall equilibrium temperature.

Figures 5 and 6 are used to visually demonstrate the influence of GVL on the separation of the mixture by presenting  $x'$ – $y'$  diagrams. The presence of GVL induces a significant rise in the relative volatility of methylcyclohexane to toluene compared to that of the mixture without GVL. Thus, the close-boiling behavior in the methylcyclohexane–toluene mixture was successfully eliminated.

The introduction of GVL into the mixture resulted in a change in the nonideality behavior of the mixture. It is confirmed by the increase in the activity coefficients of methylcyclohexane ( $\gamma_1$ ) and toluene ( $\gamma_2$ ), as listed in Tables 4 and 5, compared to the activity coefficients in the binary mixture depicted in Table 2. The increase in relative volatility

**Table 4. VLE Data for Methylcyclohexane (1) + Toluene (2) + Gamma-valerolactone (3) with E/F = 1 (Mass Basis) and Pressures at 50, 80, and 100 kPa<sup>a,b</sup>**

| T/K     | $x_1'$ | $x_1$ | $x_2$ | $x_3$ | $y_1'$ | $y_1$ | $y_2$ | $y_3$ | $\gamma_1$ | $\gamma_2$ | $\alpha_{12}$ |
|---------|--------|-------|-------|-------|--------|-------|-------|-------|------------|------------|---------------|
| 50 kPa  |        |       |       |       |        |       |       |       |            |            |               |
| 372.75  | 0.000  | 0.000 | 0.523 | 0.477 | 0.000  | 0.000 | 0.994 | 0.006 |            | 1.299      |               |
| 368.43  | 0.080  | 0.041 | 0.477 | 0.482 | 0.233  | 0.232 | 0.763 | 0.005 | 3.262      | 1.250      | 3.50          |
| 365.26  | 0.184  | 0.098 | 0.434 | 0.468 | 0.404  | 0.402 | 0.595 | 0.003 | 2.598      | 1.182      | 3.00          |
| 362.38  | 0.283  | 0.147 | 0.374 | 0.479 | 0.534  | 0.530 | 0.463 | 0.007 | 2.491      | 1.172      | 2.91          |
| 359.90  | 0.377  | 0.194 | 0.320 | 0.486 | 0.647  | 0.643 | 0.350 | 0.007 | 2.467      | 1.126      | 3.03          |
| 358.07  | 0.474  | 0.241 | 0.267 | 0.492 | 0.746  | 0.742 | 0.252 | 0.006 | 2.425      | 1.034      | 3.26          |
| 356.84  | 0.586  | 0.306 | 0.216 | 0.478 | 0.804  | 0.799 | 0.194 | 0.007 | 2.138      | 1.027      | 2.90          |
| 355.79  | 0.687  | 0.348 | 0.158 | 0.494 | 0.862  | 0.856 | 0.137 | 0.007 | 2.082      | 1.023      | 2.83          |
| 354.83  | 0.801  | 0.416 | 0.104 | 0.480 | 0.915  | 0.909 | 0.084 | 0.007 | 1.907      | 0.988      | 2.68          |
| 354.14  | 0.897  | 0.443 | 0.050 | 0.507 | 0.964  | 0.962 | 0.036 | 0.002 | 1.936      | 0.895      | 3.06          |
| 353.84  | 1.000  | 0.508 | 0.000 | 0.492 | 1.000  | 0.998 | 0.000 | 0.002 | 1.771      |            |               |
| 80 kPa  |        |       |       |       |        |       |       |       |            |            |               |
| 388.60  | 0.000  | 0.000 | 0.519 | 0.481 | 0.000  | 0.000 | 0.989 | 0.011 |            | 1.318      |               |
| 384.56  | 0.082  | 0.043 | 0.475 | 0.482 | 0.215  | 0.213 | 0.777 | 0.010 | 2.922      | 1.266      | 3.05          |
| 381.29  | 0.181  | 0.095 | 0.433 | 0.472 | 0.384  | 0.383 | 0.607 | 0.010 | 2.596      | 1.192      | 2.82          |
| 378.71  | 0.281  | 0.146 | 0.373 | 0.481 | 0.512  | 0.506 | 0.482 | 0.012 | 2.392      | 1.185      | 2.68          |
| 376.52  | 0.367  | 0.183 | 0.316 | 0.501 | 0.619  | 0.612 | 0.376 | 0.012 | 2.451      | 1.163      | 2.80          |
| 374.08  | 0.475  | 0.240 | 0.265 | 0.495 | 0.713  | 0.706 | 0.283 | 0.011 | 2.308      | 1.126      | 2.75          |
| 372.07  | 0.576  | 0.292 | 0.214 | 0.494 | 0.784  | 0.777 | 0.214 | 0.009 | 2.212      | 1.114      | 2.67          |
| 370.73  | 0.673  | 0.339 | 0.164 | 0.497 | 0.848  | 0.838 | 0.151 | 0.011 | 2.135      | 1.069      | 2.70          |
| 369.29  | 0.783  | 0.397 | 0.110 | 0.493 | 0.909  | 0.900 | 0.091 | 0.009 | 2.041      | 1.002      | 2.76          |
| 368.53  | 0.897  | 0.444 | 0.051 | 0.505 | 0.960  | 0.948 | 0.040 | 0.012 | 1.965      | 0.966      | 2.74          |
| 367.71  | 1.000  | 0.501 | 0.000 | 0.499 | 1.000  | 0.988 | 0.000 | 0.012 | 1.856      |            |               |
| 100 kPa |        |       |       |       |        |       |       |       |            |            |               |
| 396.48  | 0.000  | 0.000 | 0.521 | 0.479 | 0.000  | 0.000 | 0.983 | 0.017 |            | 1.318      |               |
| 392.70  | 0.082  | 0.042 | 0.470 | 0.488 | 0.205  | 0.202 | 0.783 | 0.015 | 2.878      | 1.287      | 2.88          |
| 389.67  | 0.180  | 0.095 | 0.431 | 0.474 | 0.374  | 0.369 | 0.617 | 0.014 | 2.496      | 1.202      | 2.72          |
| 387.03  | 0.275  | 0.142 | 0.374 | 0.484 | 0.497  | 0.491 | 0.496 | 0.013 | 2.390      | 1.198      | 2.60          |
| 384.45  | 0.383  | 0.199 | 0.321 | 0.480 | 0.610  | 0.603 | 0.386 | 0.011 | 2.242      | 1.166      | 2.52          |
| 382.24  | 0.468  | 0.230 | 0.262 | 0.508 | 0.701  | 0.691 | 0.295 | 0.014 | 2.357      | 1.164      | 2.66          |
| 380.75  | 0.581  | 0.295 | 0.213 | 0.492 | 0.772  | 0.761 | 0.225 | 0.014 | 2.107      | 1.137      | 2.44          |
| 379.72  | 0.666  | 0.334 | 0.167 | 0.499 | 0.842  | 0.830 | 0.156 | 0.014 | 2.086      | 1.038      | 2.67          |
| 378.43  | 0.790  | 0.388 | 0.103 | 0.509 | 0.902  | 0.889 | 0.096 | 0.015 | 1.993      | 1.082      | 2.45          |
| 377.63  | 0.893  | 0.452 | 0.054 | 0.494 | 0.956  | 0.943 | 0.044 | 0.013 | 1.854      | 0.963      | 2.57          |
| 377.27  | 1.000  | 0.503 | 0.000 | 0.497 | 1.000  | 0.985 | 0.000 | 0.015 | 1.758      |            |               |

<sup>a</sup> $T$  is the equilibrium temperature;  $x_1'$  is a liquid-phase mole fraction of methylcyclohexane on a GVL-free basis;  $x_1$ ,  $x_2$ , and  $x_3$  are liquid-phase mole fractions of methylcyclohexane, toluene, and GVL, respectively;  $y_1'$  is a vapor-phase mole fraction of methylcyclohexane on a GVL-free basis;  $y_1$ ,  $y_2$ , and  $y_3$  are vapor-phase mole fractions of methylcyclohexane, toluene, and GVL, respectively;  $\gamma_1$  is the activity coefficient of methylcyclohexane;  $\gamma_2$  is the activity coefficient of toluene; and  $\alpha_{12}$  is the relative volatility of methylcyclohexane to toluene. <sup>b</sup>Expanded combined uncertainties  $U$  with  $k = 2$  are  $U(T) = 0.4$  K,  $U(P) = 0.23$  kPa, and  $U(x_i) = U(y_i) = 0.006$ .

can be attributed to the stronger molecular interaction between GVL and toluene, as opposed to the GVL and methylcyclohexane interaction. This is mainly because GVL is a polar entrainer, while toluene is comparatively less nonpolar than methylcyclohexane. Consequently, GVL is expected to have more affinity toward toluene compared to methylcyclohexane. Accordingly, the interaction between methylcyclohexane and toluene can be minimized.

The results in Tables 4 and 5 show that the presence of GVL in the mixture provides lower activity coefficients for toluene ( $\gamma_2$ ) compared to those of methylcyclohexane ( $\gamma_1$ ). This implies that GVL has a stronger interaction with toluene than with methylcyclohexane. As a result, methylcyclohexane has a higher vaporization efficiency, making it easier to separate from the mixture. An investigation was conducted to examine the impact of pressure on relative volatility. Figure 5 illustrates that reducing the pressure from 100 to 80 and 50 kPa leads to an

increase in relative volatility. The reduction in pressure will amplify the nonideality of the mixture, thus leading to an increase in relative volatility. Nevertheless, the rise in relative volatility is merely modest. It can be observed that interactions between GVL and toluene do not significantly increase when the pressure is dropped to 80 and 50 kPa. This study also investigated the effect of the amount of GVL on the relative volatility, as depicted in Figure 6. Similarly to the pressure effect, increasing the E/F ratio to 2 and 3 has a slight effect on enhancing the relative volatility. This indicates that increasing the amount of GVL in E/F ratios 2 and 3 did not result in a significant increase in the interaction between GVL and toluene compared to that observed in E/F = 1.

Introducing NMP to the methylcyclohexane-toluene mixture with E/F = 1 at a pressure of 100 kPa induces an increase in the equilibrium temperature compared to that of the binary mixture, as shown in Figure 7.

**Table 5. VLE Data for Methylcyclohexane (1) + Toluene (2) + Gamma-valerolactone (3) with E/F = 2 and 3 (Mass Basis) and Pressure at 100 kPa<sup>a,b</sup>**

| T/K     | $x_1'$ | $x_1$ | $x_2$ | $x_3$ | $y_1'$ | $y_1$ | $y_2$ | $y_3$ | $\gamma_1$ | $\gamma_2$ | $\alpha_{12}$ |
|---------|--------|-------|-------|-------|--------|-------|-------|-------|------------|------------|---------------|
| E/F = 2 |        |       |       |       |        |       |       |       |            |            |               |
| 405.28  | 0.000  | 0.000 | 0.346 | 0.654 | 0.000  | 0.000 | 0.970 | 0.030 |            | 1.560      |               |
| 399.63  | 0.078  | 0.027 | 0.323 | 0.650 | 0.204  | 0.198 | 0.774 | 0.028 | 3.701      | 1.540      | 3.01          |
| 396.20  | 0.152  | 0.053 | 0.296 | 0.651 | 0.329  | 0.319 | 0.649 | 0.032 | 3.301      | 1.543      | 2.75          |
| 392.31  | 0.268  | 0.094 | 0.258 | 0.648 | 0.518  | 0.508 | 0.472 | 0.020 | 3.268      | 1.426      | 2.95          |
| 389.01  | 0.370  | 0.129 | 0.219 | 0.652 | 0.657  | 0.643 | 0.336 | 0.021 | 3.277      | 1.311      | 3.26          |
| 386.78  | 0.455  | 0.155 | 0.185 | 0.660 | 0.718  | 0.702 | 0.276 | 0.022 | 3.152      | 1.356      | 3.04          |
| 384.48  | 0.567  | 0.190 | 0.145 | 0.665 | 0.799  | 0.785 | 0.197 | 0.018 | 3.054      | 1.318      | 3.03          |
| 382.62  | 0.677  | 0.228 | 0.109 | 0.663 | 0.867  | 0.852 | 0.131 | 0.017 | 2.902      | 1.229      | 3.11          |
| 381.33  | 0.769  | 0.257 | 0.077 | 0.666 | 0.918  | 0.901 | 0.081 | 0.018 | 2.819      | 1.112      | 3.34          |
| 379.77  | 0.890  | 0.296 | 0.036 | 0.668 | 0.967  | 0.953 | 0.032 | 0.015 | 2.700      | 0.992      | 3.62          |
| 378.84  | 1.000  | 0.340 | 0.000 | 0.660 | 1.000  | 0.986 | 0.000 | 0.014 | 2.493      |            |               |
| E/F = 3 |        |       |       |       |        |       |       |       |            |            |               |
| 417.51  | 0.000  | 0.000 | 0.270 | 0.730 | 0.000  | 0.000 | 0.949 | 0.051 |            | 1.453      |               |
| 414.94  | 0.063  | 0.017 | 0.250 | 0.733 | 0.149  | 0.142 | 0.808 | 0.050 | 2.935      | 1.422      | 2.61          |
| 412.08  | 0.108  | 0.030 | 0.248 | 0.722 | 0.301  | 0.288 | 0.670 | 0.042 | 3.634      | 1.272      | 3.54          |
| 408.02  | 0.237  | 0.064 | 0.207 | 0.729 | 0.446  | 0.428 | 0.531 | 0.041 | 2.771      | 1.334      | 2.60          |
| 403.72  | 0.330  | 0.086 | 0.176 | 0.738 | 0.565  | 0.548 | 0.421 | 0.031 | 2.919      | 1.386      | 2.65          |
| 400.48  | 0.436  | 0.114 | 0.147 | 0.739 | 0.670  | 0.653 | 0.322 | 0.025 | 2.832      | 1.378      | 2.62          |
| 395.46  | 0.567  | 0.146 | 0.111 | 0.743 | 0.814  | 0.794 | 0.181 | 0.025 | 3.041      | 1.168      | 3.35          |
| 391.68  | 0.671  | 0.171 | 0.084 | 0.745 | 0.872  | 0.860 | 0.125 | 0.015 | 3.087      | 1.182      | 3.35          |
| 388.62  | 0.779  | 0.200 | 0.057 | 0.743 | 0.924  | 0.906 | 0.074 | 0.020 | 3.006      | 1.120      | 3.45          |
| 385.51  | 0.893  | 0.222 | 0.027 | 0.751 | 0.973  | 0.955 | 0.026 | 0.019 | 3.094      | 0.922      | 4.38          |
| 384.58  | 1.000  | 0.254 | 0.000 | 0.746 | 1.000  | 0.981 | 0.000 | 0.019 | 2.849      |            |               |

<sup>a</sup>T is the equilibrium temperature;  $x_1'$  is a liquid-phase mole fraction of methylcyclohexane on a GVL-free basis;  $x_1$ ,  $x_2$ , and  $x_3$  are liquid-phase mole fractions of methylcyclohexane, toluene, and GVL, respectively;  $y_1'$  is a vapor-phase mole fraction of methylcyclohexane on a GVL-free basis;  $y_1$ ,  $y_2$ , and  $y_3$  are vapor-phase mole fractions of methylcyclohexane, toluene, and GVL, respectively;  $\gamma_1$  is the activity coefficient of methylcyclohexane;  $\gamma_2$  is the activity coefficient of toluene;  $\alpha_{12}$  is the relative volatility of methylcyclohexane to toluene. <sup>b</sup>Expanded combined uncertainties  $U$  with  $k = 2$  are  $U(T) = 0.4$  K,  $U(P) = 0.23$  kPa, and  $U(x_1) = U(y_1) = 0.006$ .

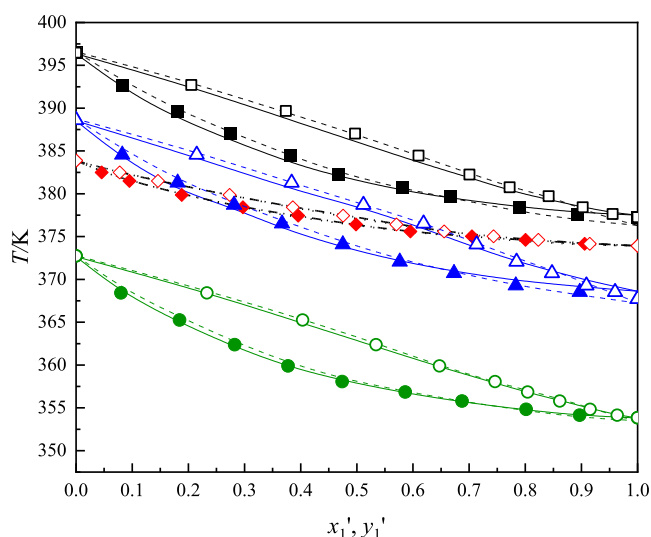
**Table 6. VLE Data for Methylcyclohexane (1) + Toluene (2) + 1-Methylpyrrolidin-2-one (3) with E/F = 1 (Mass Basis) and Pressure at 100 kPa<sup>a,b</sup>**

| T/K    | $x_1'$ | $x_1$ | $x_2$ | $x_3$ | $y_1'$ | $y_1$ | $y_2$ | $y_3$ | $\gamma_1$ | $\gamma_2$ | $\alpha_{12}$ |
|--------|--------|-------|-------|-------|--------|-------|-------|-------|------------|------------|---------------|
| 399.15 | 0.000  | 0.000 | 0.513 | 0.487 | 0.000  | 0.000 | 0.986 | 0.014 |            | 1.251      |               |
| 395.29 | 0.091  | 0.050 | 0.487 | 0.463 | 0.216  | 0.213 | 0.773 | 0.014 | 2.418      | 1.142      | 2.74          |
| 393.85 | 0.133  | 0.070 | 0.452 | 0.478 | 0.297  | 0.294 | 0.695 | 0.011 | 2.438      | 1.152      | 2.75          |
| 392.62 | 0.179  | 0.096 | 0.438 | 0.466 | 0.377  | 0.373 | 0.616 | 0.011 | 2.323      | 1.089      | 2.78          |
| 391.02 | 0.232  | 0.124 | 0.407 | 0.469 | 0.447  | 0.439 | 0.543 | 0.018 | 2.205      | 1.079      | 2.67          |
| 389.79 | 0.280  | 0.148 | 0.376 | 0.476 | 0.510  | 0.507 | 0.486 | 0.007 | 2.205      | 1.083      | 2.68          |
| 388.43 | 0.329  | 0.175 | 0.353 | 0.472 | 0.561  | 0.555 | 0.435 | 0.010 | 2.111      | 1.070      | 2.60          |
| 387.30 | 0.372  | 0.193 | 0.322 | 0.485 | 0.617  | 0.611 | 0.380 | 0.009 | 2.169      | 1.058      | 2.71          |
| 386.36 | 0.421  | 0.219 | 0.296 | 0.485 | 0.656  | 0.648 | 0.340 | 0.012 | 2.084      | 1.056      | 2.62          |
| 385.43 | 0.482  | 0.251 | 0.265 | 0.484 | 0.707  | 0.700 | 0.290 | 0.010 | 2.012      | 1.032      | 2.60          |
| 384.52 | 0.527  | 0.272 | 0.240 | 0.488 | 0.742  | 0.735 | 0.255 | 0.010 | 1.994      | 1.030      | 2.59          |
| 383.83 | 0.588  | 0.311 | 0.214 | 0.475 | 0.781  | 0.776 | 0.217 | 0.007 | 1.873      | 1.005      | 2.50          |
| 383.23 | 0.629  | 0.323 | 0.185 | 0.492 | 0.812  | 0.798 | 0.189 | 0.013 | 1.889      | 1.024      | 2.55          |
| 382.34 | 0.692  | 0.360 | 0.156 | 0.484 | 0.851  | 0.836 | 0.146 | 0.018 | 1.817      | 0.967      | 2.56          |
| 381.33 | 0.793  | 0.414 | 0.103 | 0.483 | 0.904  | 0.892 | 0.094 | 0.014 | 1.732      | 0.964      | 2.47          |
| 380.48 | 0.893  | 0.465 | 0.051 | 0.484 | 0.954  | 0.940 | 0.045 | 0.015 | 1.664      | 0.956      | 2.51          |
| 379.52 | 1.000  | 0.506 | 0.000 | 0.494 | 1.000  | 0.986 | 0.000 | 0.014 | 1.646      |            |               |

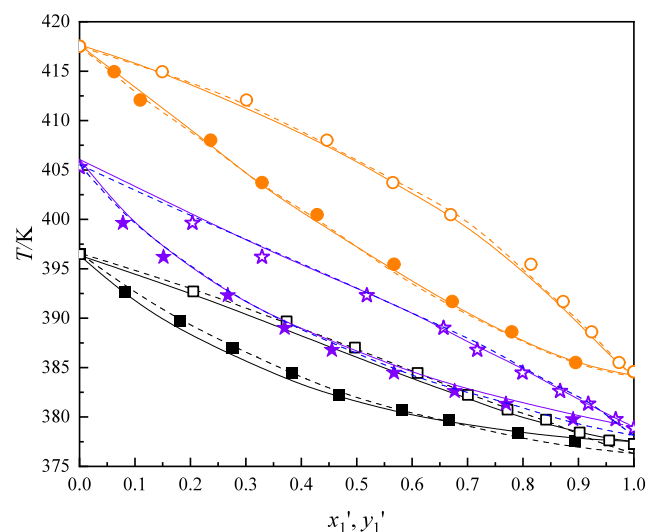
<sup>a</sup>T is the equilibrium temperature;  $x_1'$  is a liquid-phase mole fraction of methylcyclohexane on an NMP-free basis;  $x_1$ ,  $x_2$ , and  $x_3$  are liquid-phase mole fractions of methylcyclohexane, toluene, and NMP, respectively;  $y_1'$  is a vapor-phase mole fraction of methylcyclohexane on a NMP-free basis;  $y_1$ ,  $y_2$ , and  $y_3$  are vapor-phase mole fractions of methylcyclohexane, toluene, and NMP, respectively;  $\gamma_1$  is the activity coefficient of methylcyclohexane;  $\gamma_2$  is the activity coefficient of toluene; and  $\alpha_{12}$  is the relative volatility of methylcyclohexane to toluene. <sup>b</sup>Expanded combined uncertainties  $U$  with  $k = 2$  are  $U(T) = 0.4$  K,  $U(P) = 0.23$  kPa, and  $U(x_1) = U(y_1) = 0.006$ .

The interaction between NMP and toluene decreases the toluene vaporization. Consequently, an increased temperature must be attained to reach equilibrium, thus elevating the entire

equilibrium temperature. Figure 8 demonstrates that NMP effectively enhanced the relative volatility of methylcyclohex-



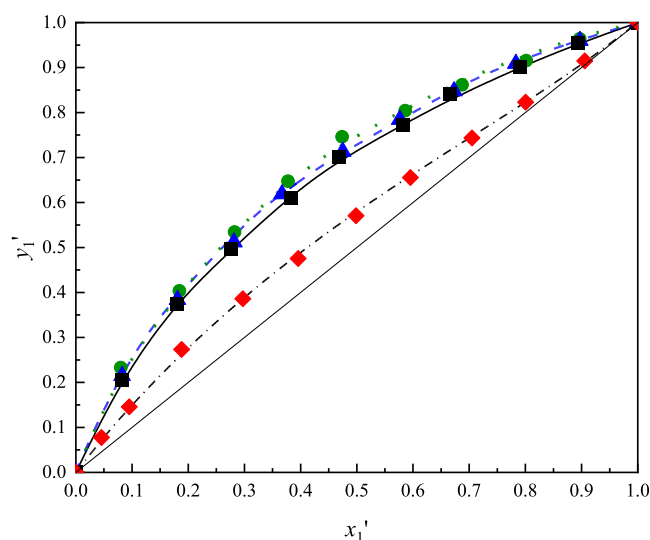
**Figure 3.**  $T$ - $x'$ - $y'$  diagram for methylcyclohexane (1) + toluene (2) + gamma-valerolactone (3) with  $E/F = 1$ : (black filled square),  $x'_1$  and (□),  $y'_1$  experimental at 100 kPa; (red filled diamond),  $x'_1$  and (red unfilled diamond),  $y'_1$  experimental at 101.3 kPa (no entrainer); (blue filled triangle),  $x'_1$  and (blue unfilled triangle),  $y'_1$  experimental at 80 kPa; (green sphere),  $x'_1$  and (green circle),  $y'_1$  experimental at 50 kPa; (—), correlated by NRTL; and (---), UNIQUAC: black, blue, and green line for the pressure of 100, 80, and 50 kPa, respectively; and correlated by (---), NRTL; and (..), UNIQUAC for no entrainer.



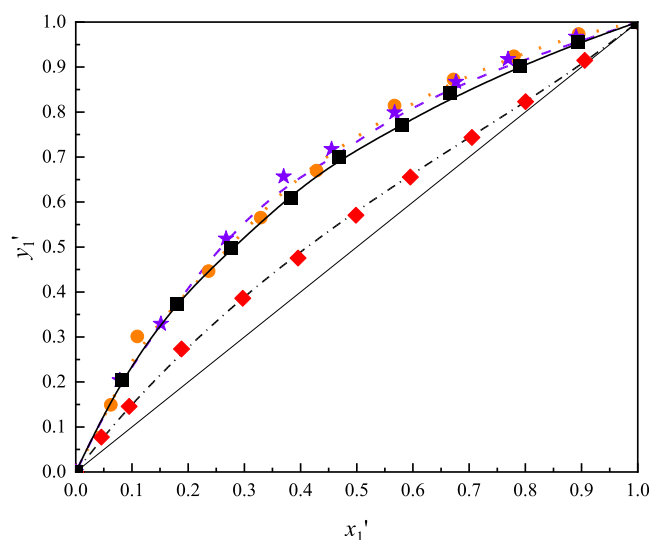
**Figure 4.**  $T$ - $x'$ - $y'$  diagram for methylcyclohexane (1) + toluene (2) + gamma-valerolactone (3) at 100 kPa with  $E/F = 1$ : (black filled square),  $x'_1$  and (unfilled square),  $y'_1$  experimental;  $E/F = 2$ : (purple filled star),  $x'_1$  and (purple unfilled star),  $y'_1$  experimental;  $E/F = 3$ : (orange sphere),  $x'_1$  and (orange circle),  $y'_1$  experimental; (—), correlated by NRTL; and (---), UNIQUAC: black, purple, and orange line for  $E/F = 1, 2$ , and  $3$ , respectively.

ane to toluene, resulting in the elimination of close-boiling behavior.

This can be described as NMP acting as a polar entrainer that exhibits more interaction with toluene than with methylcyclohexane. According to Table 6, the presence of NMP in the mixture induces this nonideal behavior, which is confirmed by the increased activity coefficients for both methylcyclohexane ( $\gamma_1$ ) and toluene ( $\gamma_2$ ) compared to the activity coefficients in their binary mixture, which are

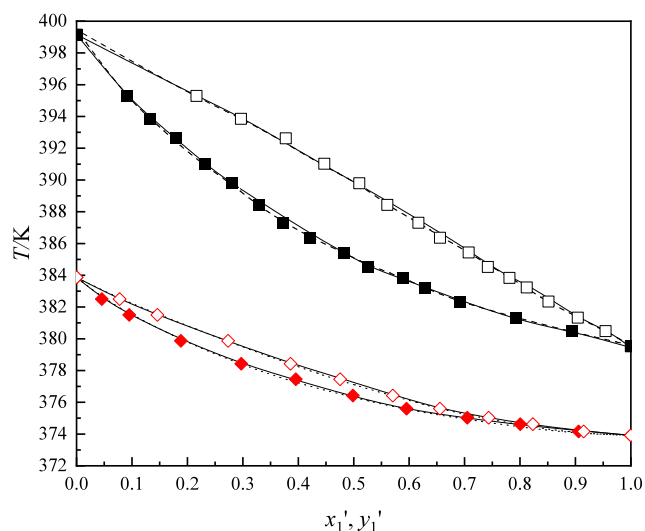


**Figure 5.**  $x'$ - $y'$  diagram for methylcyclohexane (1) + toluene (2) + gamma-valerolactone (3) with  $E/F = 1$ : (square), experimental at 100 kPa; (triangle), 80 kPa; (circle), 50 kPa; (diamond), no entrainer at 101.3 kPa; (—), correlated by NRTL at 100 kPa; (---), 80 kPa; and (..), 50 kPa; and (---), correlated by NRTL for no entrainer.

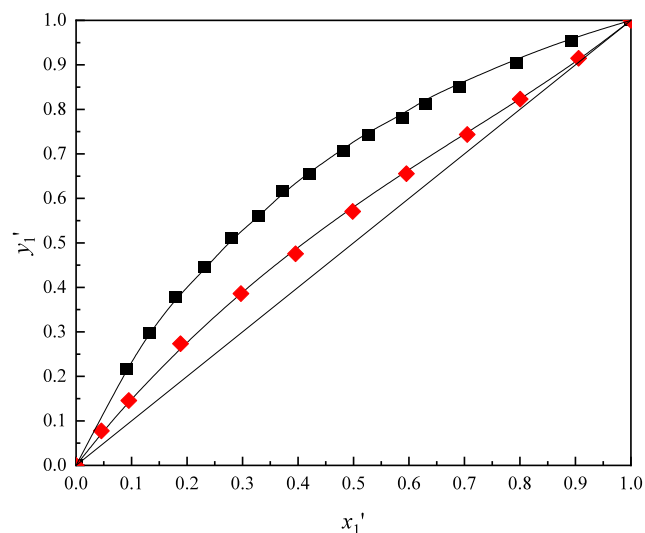


**Figure 6.**  $x'$ - $y'$  diagram for methylcyclohexane (1) + toluene (2) + gamma-valerolactone (3) at 100 kPa:  $E/F = 1$ : (square);  $E/F = 2$ : (star);  $E/F = 3$ : (circle); (diamond), no entrainer at 101.3 kPa; correlated by NRTL for  $E/F = 1$ : (—);  $E/F = 2$ : (---);  $E/F = 3$ : (..); and (---), correlated by NRTL for no entrainer.

presented in Table 2. The addition of NMP to the mixture produces lower activity coefficients of toluene ( $\gamma_2$ ) than methylcyclohexane ( $\gamma_1$ ), indicating that NMP has more interaction with toluene than with methylcyclohexane. As a result, the interaction between toluene and methylcyclohexane decreases, leading to a more facile vaporization of methylcyclohexane. This implies that easier separation of methylcyclohexane from toluene will be attained. The binary end points of our works were compared with the data from the literature, as presented in Figures S4–S7 of the Supporting Information. Overall, the experimental data from our study align well with the literature values.<sup>46–50</sup> For the toluene (1) + gamma-valerolactone (2), Figure S4 indicates that the experimental data from this work are in good agreement



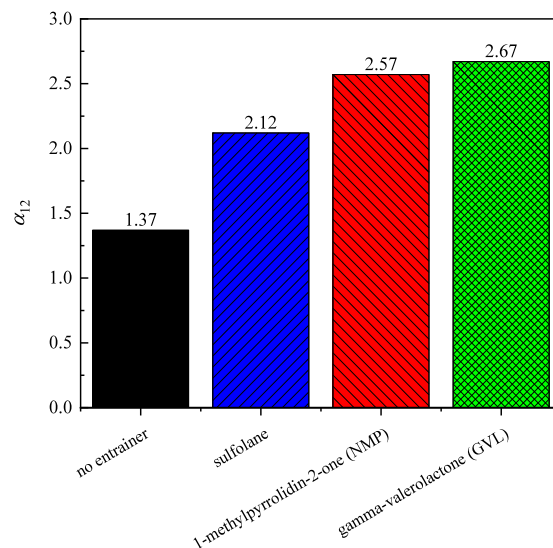
**Figure 7.**  $T$ - $x'$ - $y'$  diagram for methylcyclohexane (1) + toluene (2) + 1-methylpyrrolidin-2-one (3) at 100 kPa and  $E/F = 1$ : (square),  $x_1'$ ; ( $\square$ ),  $y_1'$  experimental; (diamond),  $x_1$  and ( $\diamond$ ),  $y_1$  experimental at 101.3 kPa (no entrainer); (—), correlated by NRTL; and (---), UNIQUAC.



**Figure 8.**  $x'$ - $y'$  diagram for methylcyclohexane (1) + toluene (2) + 1-methylpyrrolidin-2-one (3) at 100 kPa: (square),  $E/F = 1$ ; (diamond), no entrainer at 101.3 kPa; (—), correlated by NRTL.

with the literature values.<sup>46</sup> At a pressure of 100 kPa, the vapor phase composition of toluene is slightly higher than the values reported in the literature.<sup>46</sup> In the case of the toluene (1) + 1-methylpyrrolidin-2-one (2) mixture, the VLE data from this work align closely with the VLE data from Zaretskii et al.<sup>48</sup> and show a slightly higher vapor phase composition of toluene compared to the data from Gupta and Rawat,<sup>47</sup> as illustrated in Figure S5. For the 1-methylpyrrolidin-2-one (1) + toluene (2) and 1-methylpyrrolidin-2-one (1) + methylcyclohexane (2) mixtures, the phase boundary pressures observed in this study are consistent with the trend outlined in the literature.<sup>49,50</sup> This is further supported by the phase boundary pressure profile, as illustrated in Figures S6 and S7, predicted by the UNIQUAC-Hayden O'Connell (HOC) model from Aspen Plus since the experimental data for the investigated temperature are unavailable in the existing literature.

In addition, the relative volatility performance of GVL was compared to those of NMP and sulfolane, which acted as benchmark entrainers. The comparison was performed at a mole fraction of methylcyclohexane of 0.5, an  $E/F$  of 1, and a pressure of 100 kPa. The relative volatility of the mixture with no entrainer and with the addition of GVL and NMP entrainers, respectively, was obtained from this work. While the relative volatility with the addition of sulfolane entrainer was taken from the literature.<sup>19</sup> As illustrated in Figure 9, the GVL



**Figure 9.** Relative volatility of methylcyclohexane (1) + toluene (2) ( $\alpha_{12}$ ) with no entrainer, and with entrainers of sulfolane and 1-methylpyrrolidin-2-one as benchmark entrainers, and gamma-valerolactone as a biobased entrainer at  $x_1' = 0.5$ ,  $E/F = 1$ , and a pressure of 100 kPa. The experiment was conducted in duplo, and the deviation of the relative volatility was 0.02. The relative volatility data for sulfolane was taken from the literature.<sup>19</sup>

outperforms both benchmark entrainers in terms of relative volatility performance. Thus, GVL shows great potential and serves as an effective biobased entrainer to substitute NMP or sulfolane in the separation of methylcyclohexane from toluene.

**3.2. Thermodynamic Consistency Tests.** The reliability of the VLE data for both binary and pseudoternary mixtures was tested using the Van Ness,<sup>35</sup> which is based on the Gibbs–Duhem equation. The Van Ness test is expressed in eqs 4 and 5.

$$\Delta P = \frac{1}{n_p} \times \sum_{i=1}^{n_p} \Delta P_i = \frac{1}{n_p} \times \sum_{i=1}^{n_p} 100 \left| \frac{P_i^{\text{cal}} - P_i^{\text{exp}}}{P_i^{\text{exp}}} \right| \quad (4)$$

$$\Delta y = \frac{1}{n_p} \times \sum_{i=1}^{n_p} \Delta y_i = \frac{1}{n_p} \times \sum_{i=1}^{n_p} 100 |y_i^{\text{cal}} - y_i^{\text{exp}}| \quad (5)$$

where  $n_p$  is the number of experimental data points,  $P$  stands for pressure,  $y$  denotes a vapor-phase mole fraction, and the superscripts cal and exp represent the calculated values from the model and the experimental value, respectively. The calculated value for this test was obtained from the NRTL correlation. The experimental data point is considered to meet the Van Ness test criteria and is therefore considered consistent if the values are  $\Delta P < 1$  and  $\Delta y < 1$ . According to Table 7, the VLE data for the investigated binary and pseudoternary mixtures have the values of  $\Delta P$  and  $\Delta y$  less than

Table 7. Results of Thermodynamic Consistency Tests<sup>a,b</sup>

| mixture                                       | Van Ness   |            | Fredenslund |               | results    |
|-----------------------------------------------|------------|------------|-------------|---------------|------------|
|                                               | $\Delta y$ | $\Delta P$ | AAD $y$     | AAD $P$ (kPa) |            |
| methylcyclohexane (1) + toluene (2)           | 0.3        | 0.6        | 0.003       | 0.56          | consistent |
| methylcyclohexane (1) + toluene (2) + GVL (3) | 0.6        | 0.9        | 0.006       | 0.92          | consistent |
| methylcyclohexane (1) + toluene (2) + NMP (3) | 0.3        | 0.2        | 0.003       | 0.23          | consistent |

$$^a \Delta y = \frac{1}{n_p} \times \sum_{i=1}^{n_p} \Delta y_i = \frac{1}{n_p} \times \sum_{i=1}^{n_p} 100 |y_i^{\text{cal}} - y_i^{\text{exp}}| < 1; \quad \Delta P = \frac{1}{n_p} \times \sum_{i=1}^{n_p} \Delta P_i = \frac{1}{n_p} \times \sum_{i=1}^{n_p} 100 \left| \frac{P_i^{\text{cal}} - P_i^{\text{exp}}}{P_i^{\text{exp}}} \right| < 1 \quad ^b \text{ A A D}$$

$$y = \frac{1}{n_p} \left\{ \sum_{i=1}^{n_p} |y_{i,\text{exp}} - y_{i,\text{cal}}| \right\} \leq 0.01; \quad \text{AAD } P = \frac{1}{n_p} \left\{ \sum_{i=1}^{n_p} |P_{i,\text{exp}} - P_{i,\text{cal}}| \right\}$$

1. Moreover, the residual distribution of  $\ln(\gamma_1/\gamma_2)$  should behave randomly to satisfy the Van Ness test. The residual distribution of  $\ln(\gamma_1/\gamma_2)$  for each mixture, as shown in Figures S8–S10 in the Supporting Information, confirms their random distribution. The results indicate that the VLE data from our work are thermodynamically consistent.

The VLE data was also tested according to the criterion from Fredenslund<sup>36</sup> which compared the experimental and calculated values of vapor-phase mole fraction, as provided in eq 6.

$$\frac{1}{n_p} \left\{ \sum_{i=1}^{n_p} |y_{i,\text{exp}} - y_{i,\text{cal}}| \right\} \leq 0.01 \quad (6)$$

Based on Fredenslund's criterion, the VLE data are considered consistent if the average absolute value of the vapor-phase mole fraction between the experimental and calculated values is less than 0.01. For the binary mixture of methylcyclohexane (1) + toluene (2) at 101.3 kPa, the Legendre polynomial equation in Fredenslund's test was used to calculate the excess Gibbs energy, as shown in eqs 7 and 8.

$$\frac{g^E}{RT} = x_1(1 - x_1) \sum_{k=1}^n a_k L_k(x_1) \quad (7)$$

where

$$L_k(x_1) = [(2k - 1)(2x_1 - 1)L_{k-1}(x_1) - (k - 1)L_{k-2}(x_1)] / k \quad (8)$$

The method uses the objective function (OF) as depicted in eq 9.

$$\text{OF} = \sum_{i=1}^N (P_i^{\text{calc}} - P_i^{\text{exp}})^2 \quad (9)$$

where the number of the data is signified by  $N$ ; the calculated and experimental values for the pressure are represented as  $P^{\text{cal}}$  and  $P^{\text{exp}}$ , respectively. The obtained excess Gibbs energy allows for the calculation of the activity coefficient and the vapor-phase mole fraction. For the pseudoternary mixtures, the calculated value of the vapor-phase mole fraction was obtained from the NRTL correlation. The NRTL model incorporates temperature-dependent binary interaction parameters that provide a more accurate description for the VLE data containing an entrainer, wherein the liquid mixture exhibits nonideal behavior. Conversely, the Legendre polynomial equation and its parameters are mathematical approximations that do not explicitly consider the interaction among the components in a complex mixture. This prevents the equation from accurately describing the pseudoternary mixture that exhibits nonideal behavior. Thus, in the pseudoternary

mixtures, the NRTL model is selected as it can more precisely represent the excess Gibbs energy to predict the vapor-phase mole fraction compared to the Legendre polynomial equation. As suggested by Wisniak,<sup>51</sup> the criterion from Fredenslund should be complemented by a residual distribution analysis between the experimental and calculated values of vapor-phase mole fraction or other variables, such as pressure, which should be random and close to the value of zero.<sup>51–53</sup> The use of Fredenslund's criterion utilizing the calculated values of vapor-phase mole fraction obtained from the activity coefficient model, such as NRTL, complemented by residual distribution analysis as a thermodynamic consistency test, has been implemented in the existing literature.<sup>52–54</sup> In this work, the criterion from Fredenslund along with additional criteria proposed by Wisniak,<sup>51</sup> was employed to evaluate the reliability of the VLE data for the pseudoternary mixtures. These criteria provide an adequate framework for examining thermodynamic consistency. Table 7 shows that the experimental VLE data of the investigated mixtures passed the thermodynamic consistency test since the average absolute deviation of the vapor-phase mole fraction is less than 0.01. Figures S11–S13 in the Supporting Information, respectively, present the residual plots of vapor-phase mole fractions for the binary mixture and the pseudoternary mixtures. It indicates that the values are less than 0.01 in all composition ranges.

Moreover, the residual distribution and the average absolute deviation of the calculated and measured pressure are random and close to zero, respectively. The graphical representation of the pressure residual distribution can be seen in Figures S14–S16 in the Supporting Information. These results indicate that the experimental value of the VLE data for the investigated mixtures is reliable.

**3.3. Correlation for the VLE Data.** Two thermodynamic models, namely, NRTL and UNIQUAC, were chosen to correlate the VLE data. These thermodynamic models often provide a good agreement with the experimental data, making them favored choices among researchers for correlating the VLE data containing entrainers.<sup>55–61</sup> The NRTL formula is provided in eq 10 as follows:

$$\ln \gamma_i = \frac{\sum_{j=1}^{n_c} x_j \tau_{ji} G_{ji}}{\sum_{k=1}^{n_c} x_k G_{ki}} + \sum_{j=1}^{n_c} \frac{x_j G_{ij}}{\sum_{k=1}^{n_c} x_k G_{kj}} \left( \tau_{ij} - \frac{\sum_{m=1}^{n_c} x_m \tau_{mj} G_{mj}}{\sum_{k=1}^{n_c} x_k G_{kj}} \right) \quad (10)$$

where  $\gamma_i$  and  $n_c$  is the activity coefficient of component  $i$  and the number of components, respectively. The parameters in the NRTL model are formulated in eq 11 as follows:

$$G_{ij} = \exp(-C_{ij}\tau_{ij}); \tau_{ij} = A_{ij} + B_{ij}/T; \tau_{ii} = 0; G_{ii} = 1 \quad (11)$$

where  $C_{ij}$  represents the nonrandomness constant in the binary component interaction of  $ij$ .

For the UNIQUAC model, the formula is expressed in eq 12.

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_{j=1}^{n_c} x_j l_j - q_i \ln \left( \sum_{j=1}^{n_c} \theta_j \tau_{ji} \right) + q_i - q_i \sum_{j=1}^{n_c} \frac{\theta_j \tau_{ij}}{\sum_{k=1}^{n_c} \theta_k \tau_{kj}} \quad (12)$$

where  $\theta_i$  and  $\Phi_i$  indicate the average of area and volume fractions of component  $i$ , respectively;  $r_i$  and  $q_i$  correspond to the parameters of volume and surface area of component  $i$ , respectively; and  $z$  denotes the number of lattice coordination. The parameters  $r_i$  and  $q_i$  are retrieved from the Aspen Plus physical property databank and provided in Table 8. The parameters in the UNIQUAC model are expressed in eq 13.

$$\begin{aligned} \tau_{ij} &= \exp(A_{ij} + B_{ij}/T); l_i \\ &= \frac{z}{2}(r_i - q_i) - (r_i - 1); \Phi_i \\ &= \frac{r_i x_i}{\sum_{j=1}^{n_c} r_j x_j}; \theta_i \\ &= \frac{x_i q_i}{\sum_{j=1}^{n_c} x_j q_j}; z \\ &= 10 \end{aligned} \quad (13)$$

**Table 8. Parameters of Pure Components for  $r_i$  and  $q_i$  in UNIQUAC Model<sup>a,b</sup>**

| component                | $r_i$ | $q_i$ |
|--------------------------|-------|-------|
| methylcyclohexane        | 4.64  | 3.55  |
| toluene                  | 3.92  | 2.97  |
| gamma-valerolactone      | 3.71  | 3.04  |
| 1-methylpyrrolidin-2-one | 3.98  | 3.20  |

<sup>a</sup> $r_i$  is the volume parameter of component  $i$ ;  $q_i$  is the surface area parameter of component  $i$ . <sup>b</sup>Taken from the Aspen Plus physical property databank.

The binary interaction parameters (BIPs) for the methylcyclohexane-toluene pair were determined from the regression of the VLE data for the binary mixture of methylcyclohexane and toluene at two different pressures: 101.3 kPa (this work) and 53.3 kPa (literature<sup>45</sup>). These BIPs are subsequently employed in the regression of pseudoternary mixtures of methylcyclohexane and toluene with the addition of GVL and NMP, respectively, in which the VLE data for methylcyclohexane (1) + toluene (2) + GVL (3) was measured from 50 to 100 kPa. Thus, the regression was performed on the binary mixture under both normal and low pressures in order to encompass the temperature range within the investigated pseudoternary mixture of methylcyclohexane (1) + toluene (2) + GVL (3). In the NRTL model, the nonrandomness parameter ( $C_{ij}$ ) for the binary and pseudoternary mixtures regression were assigned a value of 0.3. The algorithm with the maximum likelihood concept proposed by Britt and Luecke<sup>62</sup>

was employed to minimize the objective function in order to determine the BIPs. The objective function (OF) formula is shown in eq 14.

$$\text{OF} = \sum_{k=1}^{n_p} \left\{ \left| \frac{P_k^{\text{cal}} - P_k^{\text{exp}}}{\sigma_P} \right|^2 + \left| \frac{T_k^{\text{cal}} - T_k^{\text{exp}}}{\sigma_T} \right|^2 + \left| \frac{x_{1,k}^{\text{cal}} - x_{1,k}^{\text{exp}}}{\sigma_x} \right|^2 + \left| \frac{y_{1,k}^{\text{cal}} - y_{1,k}^{\text{exp}}}{\sigma_y} \right|^2 \right\} \quad (14)$$

where  $n_p$  represents the number of data points and  $\sigma$  defines the standard deviation of the data. The optimal values of the BIPs for all pairs in the NRTL and UNIQUAC models are reported in Table 9.

The average absolute deviation between the experimental and regression values is provided in Table 10. Both models give a satisfactory fit to the experimental data for the regression of the binary mixture of methylcyclohexane (1) + toluene (2), as illustrated in Figure 2. This is also confirmed by the small deviation between the experimental and regression results presented in Table 10.

For the pseudoternary mixture of methylcyclohexane (1) + toluene (2) + GVL (3), the VLE data with  $E/F = 1$  at the pressures of 50, 80, and 100 kPa and  $E/F = 2$  and 3 at the pressure of 100 kPa were correlated together as one regression in order to achieve more accurate BIPs to represent the experimental VLE data. The NRTL and UNIQUAC models provided satisfactory results. However, the NRTL model performed better than the UNIQUAC model in representing the experimental VLE data for the regression of the pseudoternary mixture comprising GVL, as indicated by the smaller average absolute deviation listed in Table 10. Moreover, the graphical depiction in Figures 3 and 4 illustrates that the correlation results obtained from the NRTL model exhibit a better agreement with the experimental data compared to the regression results obtained from the UNIQUAC model. This suggests that the NRTL model provides a good quantitative correlation in the pseudoternary mixture of methylcyclohexane and toluene containing GVL. Hence, the NRTL model can be employed for modeling the extractive distillation process for the pseudoternary mixture of methylcyclohexane and toluene with the GVL as an entrainer. Figures 5 and 6 display the  $x'$ - $y'$  diagram, where only the regression result from the NRTL model is provided and compared with the experimental value with a good agreement.

In the regression of pseudoternary mixtures of methylcyclohexane and toluene containing NMP, the NRTL and UNIQUAC models both yield good regression results. The NRTL model yields a slightly better accuracy for correlating the experimental data compared to that of the UNIQUAC model, as shown by the average absolute deviation listed in Table 10 and represented in Figure 7. However, the deviation between the NRTL and UNIQUAC models is not significant. Therefore, both models are recommended to be applied for process modeling in extractive distillation. The NRTL regression results are further deployed to show an  $x'$ - $y'$  diagram between the experimental and regression values for a mixture of methylcyclohexane and toluene with the addition of NMP, as illustrated in Figure 8.

**Table 9. Binary Interaction Parameters of the NRTL and UNIQUAC Models for Methylcyclohexane (1) + Toluene (2) + Gamma-valerolactone (3) and Methylcyclohexane (1) + Toluene (2) + 1-Methylpyrrolidin-2-one (3)<sup>a</sup>**

| <i>i</i> component                 | <i>j</i> component           | $A_{ij}$ | $A_{ji}$ | $B_{ij}/K$ | $B_{ji}/K$ | $C_{ij}$ |
|------------------------------------|------------------------------|----------|----------|------------|------------|----------|
| NRTL <sup>b</sup>                  |                              |          |          |            |            |          |
| methylcyclohexane <sup>d</sup> (1) | toluene (2)                  | −1.018   | 2.709    | 792.083    | −1248.381  | 0.30     |
| methylcyclohexane (1)              | gamma-valerolactone (2)      | 3.396    | −8.614   | −672.438   | 3617.877   | 0.30     |
| toluene (1)                        | gamma-valerolactone (2)      | 0.208    | −1.592   | 5066.002   | 703.426    | 0.30     |
| methylcyclohexane (1)              | 1-methylpyrrolidin-2-one (2) | −3.548   | 4.113    | 1979.856   | 394.855    | 0.30     |
| toluene (1)                        | 1-methylpyrrolidin-2-one (2) | 13.533   | 13.858   | −5223.890  | −3020.539  | 0.30     |
| UNIQUAC <sup>c</sup>               |                              |          |          |            |            |          |
| methylcyclohexane <sup>d</sup> (1) | toluene (2)                  | 0.324    | −0.769   | −363.296   | 446.877    |          |
| methylcyclohexane (1)              | gamma-valerolactone (2)      | −1.991   | 1.183    | 341.007    | −387.553   |          |
| toluene (1)                        | gamma-valerolactone (2)      | −1.219   | 0.318    | 155.438    | −15.592    |          |
| methylcyclohexane (1)              | 1-methylpyrrolidin-2-one (2) | 8.904    | −14.505  | −3571.259  | 5452.163   |          |
| toluene (1)                        | 1-methylpyrrolidin-2-one (2) | −0.647   | −5.553   | 403.434    | 1791.435   |          |

<sup>a</sup> $A_{ij}$ ,  $A_{ji}$ ,  $B_{ij}$ , and  $B_{ji}$  are unsymmetrical parameters;  $C_{ij}$  is the nonrandomness constant. <sup>b</sup>NRTL Model:  $\tau_{ij} = A_{ij} + B_{ij}/T$  <sup>c</sup>UNIQUAC Model:  $\tau_{ij} = \exp(A_{ij} + B_{ij}/T)$  <sup>d</sup>The binary interaction parameters of methylcyclohexane (1)–toluene (2) pair were obtained from the correlation based on the combination of the binary VLE data measured in this work and literature.<sup>45</sup>

**Table 10. Average Absolute Deviation (AAD) from the Correlated Results Using NRTL and UNIQUAC Models<sup>a</sup>**

|                                                                    | AAD <sup>b</sup> |         |        |       |
|--------------------------------------------------------------------|------------------|---------|--------|-------|
|                                                                    | $T/K$            | $P/kPa$ | $x_1'$ | $y_1$ |
| methylcyclohexane (1) + toluene (2)                                |                  |         |        |       |
| NRTL                                                               | 0.02             | 0.56    | 0.003  | 0.003 |
| UNIQUAC                                                            | 0.03             | 0.45    | 0.004  | 0.004 |
| methylcyclohexane (1) + toluene (2) + gamma-valerolactone (3)      |                  |         |        |       |
| NRTL                                                               | 0.36             | 0.92    | 0.002  | 0.006 |
| UNIQUAC                                                            | 0.31             | 2.13    | 0.003  | 0.009 |
| methylcyclohexane (1) + toluene (2) + 1-methylpyrrolidin-2-one (3) |                  |         |        |       |
| NRTL                                                               | 0.07             | 0.23    | 0.001  | 0.003 |
| UNIQUAC                                                            | 0.09             | 0.31    | 0.001  | 0.001 |

<sup>a</sup> $T$  is the temperature;  $P$  is the pressure;  $x_1'$  is a liquid-phase mole fraction of methylcyclohexane on an entrainer-free basis;  $y_1$  is a vapor-phase mole fraction of methylcyclohexane. <sup>b</sup>Average absolute deviation (AAD)  $\Delta M = \frac{1}{n} \sum |M_{\text{exp}} - M_{\text{cal}}|$ , where  $n$  is total of data points;  $M$  denotes for  $T$ ,  $P$ ,  $x_1'$ , and  $y_1$ , respectively.

#### 4. CONCLUSIONS

In this work, isobaric VLE data were measured using a Fischer Labodest VLE602 ebulliometer for the binary mixture of methylcyclohexane (1) + toluene (2) and the pseudoternary mixtures of methylcyclohexane (1) + toluene (2) containing the entrainers of GVL and NMP. All of the experimental VLE data were thermodynamically consistent, having successfully passed the Van Ness and Fredenslund tests. Based on the results, introducing GVL and NMP into the mixture is capable of eliminating a close-boiling behavior, as revealed by a significant increase in the relative volatility. With the addition of GVL, reducing the pressure yields a slight increase in the relative volatility of methylcyclohexane to toluene. Similar behavior occurs when the amount of GVL added to the mixture increases; the relative volatility is also enhanced but only modestly. According to the relative volatility performance, GVL outperforms benchmark entrainers such as NMP and sulfolane, indicating that GVL is a promising and effective biobased alternative to conventional organic entrainers in the separation of methylcyclohexane from toluene through extractive distillation.

The data correlation was implemented to acquire the optimized binary interaction parameters. The NRTL and

UNIQUAC models were employed to establish correlations for the VLE data of binary and pseudoternary mixtures. Both models were able to accurately fit the VLE data of the binary mixture. For the pseudoternary mixture containing GVL, the NRTL model demonstrated better agreement with the experimental values than the UNIQUAC model. In the pseudoternary mixture involving NMP, the UNIQUAC and NRTL models both yielded an accurate correlation of the experimental data.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jced.4c00509>.

Comparison between experimental and literature values for the VLE data ( $x$ – $y$ ) of methylcyclohexane + toluene binary mixture; ( $T$ – $xy$ ) of toluene (1) + gamma-valerolactone (2), and toluene (1) + 1-methylpyrrolidin-2-one (2) binary mixtures, ( $x$ – $P$ ) of 1-methylpyrrolidin-2-one (1) + toluene (2), and 1-methylpyrrolidin-2-one (1) + methylcyclohexane (2) binary mixtures; comparison between experimental and literature vapor pressure data for pure compound of methylcyclohexane and toluene; residual distribution of vapor composition; residual distribution of pressure; residual distribution of  $\ln(\gamma_1/\gamma_2)$ ; and uncertainty calculations (PDF)

#### ■ AUTHOR INFORMATION

##### Corresponding Author

Dhoni Hartanto – Department of Chemical Engineering, Delft University of Technology, Delft 2629 HZ, The Netherlands; Department of Chemical Engineering, Faculty of Engineering, Universitas Negeri Semarang, Semarang 50229, Indonesia; [orcid.org/0000-0003-4127-5361](https://orcid.org/0000-0003-4127-5361); Email: [dhoni.hartanto@mail.unnes.ac.id](mailto:dhoni.hartanto@mail.unnes.ac.id)

##### Authors

Boelo Schuur – Sustainable Process Technology, Faculty of Science and Technology, University of Twente, Enschede 7500 AE, The Netherlands; [orcid.org/0000-0001-5169-4311](https://orcid.org/0000-0001-5169-4311)  
Tim Schuttevaer – Sustainable Process Technology, Faculty of Science and Technology, University of Twente, Enschede 7500 AE, The Netherlands

Anton A. Kiss – Department of Chemical Engineering, Delft University of Technology, Delft 2629 HZ, The Netherlands  
André B. de Haan – Department of Chemical Engineering, Delft University of Technology, Delft 2629 HZ, The Netherlands

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acs.jced.4c00509>

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors express their gratitude to the Indonesia Endowment Fund for Education (LPDP), Indonesia Ministry of Finance for providing Dhoni Hartanto with a PhD Scholarship through grant number SKPB-1597/LPDP/LPDP.3/2024.

## REFERENCES

- (1) Rico-Ramírez, V.; Diwekar, U. *Distillation, Multicomponent Distillation*; Academic Press: Oxford, 2000; pp. 1071–1081.
- (2) Kiss, A. A.; Lange, J.-P.; Schuur, B.; Brilman, D. W. F.; van der Ham, A. G. J.; Kersten, S. R. A. Separation Technology—Making a Difference in Biorefineries. *Biomass and Bioenergy* **2016**, *95*, 296–309.
- (3) Kiss, A. Design, Control and Economics of Distillation. In *Advanced Distillation Technologies*; Wiley, 2013; pp. 37–65.
- (4) Sherwood, J.; Farmer, T. J.; Clark, J. H. Catalyst: Possible Consequences of the N-Methyl Pyrrolidone REACH Restriction. *Chem.* **2018**, *4* (9), 2010–2012.
- (5) Kirman, C. R.; Sonawane, B. R.; Seed, J. G.; Azu, N. O.; Barranco, W. T.; Hamilton, W. R.; Stedeford, T. J.; Hays, S. M. An Evaluation of Reproductive Toxicity Studies and Data Interpretation of N-Methylpyrrolidone for Risk Assessment: An Expert Panel Review. *Regul. Toxicol. Pharmacol.* **2023**, *138*, No. 105337.
- (6) Qu, Y.; Qiu, Z.; Xue, K.; Zhou, M.; Dong, Z.; Hu, R.; Zhu, Z.; Wang, Y.; Zhong, L.; Qi, J. Experimental and Mechanism Exploration on the Separation of Methanol-Containing Azeotropic Compounds from Biodiesel by Phosphate Esters Ionic Liquids. *Fuel* **2024**, *355*, No. 129450.
- (7) Lei, Z.; Dai, C.; Zhu, J.; Chen, B. Extractive Distillation with Ionic Liquids: A Review. *AIChE J.* **2014**, *60* (9), 3312–3329.
- (8) Zhang, W.; Zhao, W.; Ren, S.; Hou, Y.; Wu, W. Highly Efficient Separation of Benzene + Cyclohexane Mixtures by Extraction Combined Extractive Distillation Using Imidazolium-Based Dicationic Ionic Liquids. *Green Chem. Eng.* **2023**, *4* (3), 312–323.
- (9) Malik, H.; Khan, H. W.; Hassan Shah, M. U.; Ahmad, M. I.; Khan, I.; Al-Kahtani, A. A.; Sillanpää, M. Screening of Ionic Liquids as Green Entrainers for Ethanol Water Separation by Extractive Distillation: COSMO-RS Prediction and Aspen plus Simulation. *Chemosphere* **2023**, *311*, No. 136901.
- (10) Shen, T.; Teng, L.; Hu, Y.; Shen, W. Systematic Screening Procedure and Innovative Energy-Saving Design for Ionic Liquid-Based Extractive Distillation Process. *Front. Chem. Sci. Eng.* **2023**, *17* (1), 34–45.
- (11) Zhao, Q.; Zhou, M.; Cheng, H.; Ruan, J.; Wang, Y.; Zhu, Z.; Cui, P.; Wang, Y.; Yang, J. Process Design and Multi-Objective Optimization for Separation of Isopropyl Acetate/Isopropanol/Water by Extractive Distillation Using Ionic Liquid Mixed Solvents. *Fuel* **2023**, *349*, No. 128730.
- (12) Hartanto, D.; Gupta, B. S.; Taha, M.; Lee, M.-J. Isobaric Vapour–Liquid Equilibrium of (Tert-Butanol+water) System with Biological Buffer TRIS at 101.3 kPa. *J. Chem. Thermodyn.* **2016**, *98*, 159–164.
- (13) Qi, J.; Qu, Y.; Zhou, M.; Su, Z.; Zhang, X.; Wei, R.; Xue, K.; Zhu, Z.; Meng, F.; Wang, Y. Phase Behavior and Molecular Insights on the Separation of Dimethyl Carbonate and Methanol Azeotrope by Extractive Distillation Using Deep Eutectic Solvents. *Sep. Purif. Technol.* **2023**, *305*, No. 122489.
- (14) Neubauer, M.; Wallek, T.; Lux, S. Deep Eutectic Solvents as Entrainers in Extractive Distillation—A Review. *Chem. Eng. Res. Des.* **2022**, *184*, 402–418.
- (15) Han, D.; Chen, Y.; Dong, M. Process Evaluation for the Separation of Acetonitrile-Water Using Extractive Distillation with Deep Eutectic Solvents as Entrainers. *Comput. Chem. Eng.* **2022**, *164*, No. 107865.
- (16) Wang, X.; Xu, H.; Zou, Y.; Hu, W.; Wang, L. Mechanistic Insight into Separation of Benzene and Cyclohexane by Extractive Distillation Using Deep Eutectic Solvent as Entrainer. *J. Mol. Liq.* **2022**, *368*, No. 120780.
- (17) Muqet, M. A.; Vellore, S.; Aniya, V.; Satyavathi, B.; Thella, P. K. Extractive Distillation of Ethyl Acetate-Ethanol-Water Ternary System Using Deep Eutectic Solvent (DES): A Techno Economic and Energy Assessment. *Chem. Eng. Process. - Process Intensif.* **2022**, *175*, No. 108913.
- (18) Sharma, B.; Singh, N.; Kushwaha, J. P. Natural Deep Eutectic Solvent-Mediated Extractive Distillation for Separation of Acetonitrile + Water Azeotropic Mixture. *J. Chem. Eng. Data* **2020**, *65* (4), 1497–1505.
- (19) Brouwer, T.; Schuur, B. Bio-Based Solvents as Entrainers for Extractive Distillation in Aromatic/Aliphatic and Olefin/Paraffin Separation. *Green Chem.* **2020**, *22* (16), 5369–5375.
- (20) Brouwer, T.; Schuur, B. Biobased Entrainer Screening for Extractive Distillation of Acetone and Diisopropyl Ether. *Sep. Purif. Technol.* **2021**, *270*, No. 118749.
- (21) Ye, L.; Han, Y.; Feng, J.; Lu, X. A Review about GVL Production from Lignocellulose: Focusing on the Full Components Utilization. *Ind. Crops Prod.* **2020**, *144*, No. 112031.
- (22) Strappaveccia, G.; Luciani, L.; Bartollini, E.; Marrocchi, A.; Pizzo, F.; Vaccaro, L.  $\gamma$ -Valerolactone as an Alternative Biomass-Derived Medium for the Sonogashira Reaction. *Green Chem.* **2015**, *17* (2), 1071–1076.
- (23) Duereh, A.; Sato, Y.; Smith, R. L. J.; Inomata, H. Methodology for Replacing Dipolar Aprotic Solvents Used in API Processing with Safe Hydrogen-Bond Donor and Acceptor Solvent-Pair Mixtures. *Org. Process Res. Dev.* **2017**, *21* (1), 114–124.
- (24) Havasi, D.; Mizsey, P.; Mika, L. T. Vapor–Liquid Equilibrium Study of the Gamma-Valerolactone–Water Binary System. *J. Chem. Eng. Data* **2016**, *61* (4), 1502–1508.
- (25) Stull, D. R. Vapor Pressure of Pure Substances. Organic and Inorganic Compounds. *Ind. Eng. Chem.* **1947**, *39* (4), 517–550.
- (26) Alonso, D. M.; Wettstein, S. G.; Dumesic, J. A. Gamma-Valerolactone, a Sustainable Platform Molecule Derived from Lignocellulosic Biomass. *Green Chem.* **2013**, *15* (3), 584–595.
- (27) Wong, C. Y. Y.; Choi, A. W.-T.; Lui, M. Y.; Fridrich, B.; Horváth, A. K.; Mika, L. T.; Horváth, I. T. Stability of Gamma-Valerolactone under Neutral, Acidic, and Basic Conditions. *Struct. Chem.* **2017**, *28* (2), 423–429.
- (28) De Bruycker, R.; Carstensen, H.-H.; Simmie, J. M.; Van Geem, K. M.; Marin, G. B. Experimental and Computational Study of the Initial Decomposition of Gamma-Valerolactone. *Proc. Combust. Inst.* **2015**, *35* (1), 515–523.
- (29) Coca, J.; Pis, J. J. Effect of Morpholine on the Vapor-Liquid Equilibrium of the System Methylcyclohexane-Toluene. *J. Chem. Eng. Data* **1979**, *24* (2), 103–105.
- (30) Liebert, V.; Nebig, S.; Gmehling, J. Experimental and Predicted Phase Equilibria and Excess Properties for Systems with Ionic Liquids. *Fluid Phase Equilib.* **2008**, *268* (1), 14–20.
- (31) Gutierrez, J. P.; Meindersma, W.; de Haan, A. B. Ionic Liquid Selection and Performance Evaluation for The Separation Of Methylcyclohexane/Toluene by Extractive Distillation. In *Distillation absorption 2010: conference proceedings*; Technische Universiteit Eindhoven: Eindhoven, 2010.
- (32) Quijada-Maldonado, E.; Meindersma, G. W.; de Haan, A. B. Pilot Plant Study on the Extractive Distillation of Toluene–Methylcyclohexane Mixtures Using NMP and the Ionic Liquid [Hmim][TCB] as Solvents. *Sep. Purif. Technol.* **2016**, *166*, 196–204.

- (33) Anwani, S. S.; Shirsat, S. P. Extractive Distillation Simulation for the Separation of Methylcyclohexane and Toluene Mixture with Phenol as an Extractor Using Chemcad. In *Novel Water Treatment and Separation Methods: Simulation of Chemical Processes*; Bhanvase, B. A.; Ugwekar, R. P.; Mankar, R. B., Eds.; Apple Academic Press, Taylor & Francis Group: New York: United States, 2017.
- (34) Tiverios, P. G.; Van Brunt, V. Extractive Distillation Solvent Characterization and Shortcut Design Procedure for Methylcyclohexane–Toluene Mixtures. *Ind. Eng. Chem. Res.* **2000**, *39* (6), 1614–1623.
- (35) Van Ness, H. C. *Thermodynamics in the Treatment of Vapor/Liquid Equilibrium (VLE) Data*. **1995**, *67* (6), 859–872.
- (36) Fredenslund, A. *Vapor-Liquid Equilibria Using UNIFAC: A Group-Contribution Method*; Elsevier, 1977.
- (37) Renon, H.; Prausnitz, J. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14* (1), 135–144.
- (38) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21* (1), 116–128.
- (39) Keestra, H.; Brouwer, T.; Schuur, B.; Lange, J.-P. Entrainer Selection for the Extractive Distillation of Acrylic Acid and Propionic Acid. *Chem. Eng. Res. Des.* **2023**, *192*, 653–663.
- (40) Taylor, B. N.; Kuyatt, C. E. *NIST Technical Note 1297 Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST, 1994.
- (41) Working Group 1 of the Joint Committee for Guides in Metrology (JCGM/WG 1). *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement*; ISO: Geneva, **2008**; Vol. 50, p. 134.
- (42) Quiggle, D.; Fenske, M. R. Vapor–Liquid Equilibria of Methylcyclohexane–Toluene Mixtures. *J. Am. Chem. Soc.* **1937**, *59* (10), 1829–1832.
- (43) Yaws, C. L.; Yang, H. C. To Estimate Vapor Pressure Easily. Antoine Coefficients Relate Vapor Pressure to Temperature for Almost 700 Major Organic Compounds. *Hydrocarb. Process.* **1989**, *68* (10), 65–68.
- (44) Willingham, C. B.; Taylor, W. J.; Pignocco, J. M.; Rossini, F. D. Vapor Pressures and Boiling Points of Some Paraffin, Alkylcyclopentane, Alkylcyclohexane, and Alkylbenzene Hydrocarbons. *J. Res. Natl. Bur. Stand. (1934)* **1945**, *35* (3), 219–244.
- (45) Weber, J. H. Vapor-Liquid Equilibria for System Methylcyclohexane–Toluene at Subatmospheric Pressures. *Ind. Eng. Chem.* **1955**, *47* (3), 454–457.
- (46) Al-Lami, M.; Havasi, D.; Koczka, K.; Mika, L. T. Isobaric Vapor–Liquid Equilibria for Binary Mixtures of Gamma-Valerolactone + Toluene. *J. Chem. Eng. Data* **2021**, *66* (1), 568–574.
- (47) Gupta, S. K.; Rawat, B. S. Isobaric Binary and Ternary Vapor–Liquid Equilibria of N-Methylpyrrolidone with Water and Toluene at 760 mmHg. *J. Chem. Eng. Data* **1992**, *37* (2), 139–140.
- (48) Zaretskii, M. I.; Kogan, V. B.; Kononov, N. F.; MiroshniChenko, A. A.; Usyushkina, I. V.; Podolyak, V. G. Liquid–Vapor Equilibrium in Systems Formed by Aromatic Hydrocarbons and Thiophene with Some Polar Solvents. *J. Appl. Chem. USSR* **1974**, *47* (9), 2142–2145.
- (49) Gierycz, P.; Rogalski, M.; Malanowski, S. Vapour–Liquid Equilibria in Binary Systems Formed by N-Methylpyrrolidone with Hydrocarbons and Hydroxyl Derivatives. *Fluid Phase Equilib.* **1985**, *22* (1), 107–122.
- (50) Linek, J.; Wichterle, I.; Marsh, K. N. Vapor–Liquid Equilibria for N-Methyl-2-Pyrrolidone + Benzene, + Toluene, + Heptane, and + Methylcyclohexane. *J. Chem. Eng. Data* **1996**, *41* (6), 1212–1218.
- (51) Wisniak, J.; Ortega, J.; Fernández, L. A Fresh Look at the Thermodynamic Consistency of Vapour-Liquid Equilibria Data. *J. Chem. Thermodyn.* **2017**, *105*, 385–395.
- (52) Huo, B.; Qiu, X.; Zhang, H.; Zhang, Y.; Yang, J.; Zhu, Z.; Wang, Y.; Gao, J. Isobaric Vapor–Liquid Equilibrium of Isoamyl Alcohol, Cyclohexane, n-Hexane, and the n-Heptane + Isoamyl Butyrate Binary System at 101.3 KPa. *J. Chem. Eng. Data* **2021**, *66* (12), 4476–4483.
- (53) Zhou, M.; Hu, R.; Qiu, Z.; Jiao, M.; Zhu, Z.; Wang, Y.; Cui, P.; Yang, J. Isobaric Vapor–Liquid Equilibrium of Ethyl Acetate + 1-Hexanol, Methanol + 1-Hexanol, and n-Heptane + Cyclohexanol Binary System at 101.3 KPa. *J. Chem. Eng. Data* **2023**, *68* (8), 2014–2022.
- (54) Wang, L.; Zhao, H.; Han, L.; Wang, Y.; Xin, J. Isobaric Vapor–Liquid Equilibrium of Binary Mixtures of 2-Methylpentanedioic Acid Dimethyl Ester and Dimethyl Adipate at 101.3, 50.0, 30.0, and 10.0 KPa. *J. Chem. Eng. Data* **2024**, *69* (4), 1613–1620.
- (55) Li, F.; Li, M.; Guo, J.; Hu, X.; Zhu, J.; Li, Q.; Zhao, H. Isobaric Vapor–Liquid Equilibrium Experiment of N-Propanol and N-Propyl Acetate at 101.3 KPa. *J. Chem. Eng. Data* **2023**, *68* (2), 358–365.
- (56) Cao, M.; Tian, H.; Li, M. Vapor–Liquid Equilibrium Data Determination and Model Correlation for 1-Octene + 1,4-Dioxane, 2-Octanol + 1,4-Dioxane, 1-Octene + Isophorone, and 2-Octanol + Isophorone Systems at 101.3 KPa. *J. Chem. Eng. Data* **2023**, *68* (9), 2275–2282.
- (57) Lei, Z.; Arlt, W.; Wasserscheid, P. Selection of Entrainers in the 1-Hexene/n-Hexane System with a Limited Solubility. *Fluid Phase Equilib.* **2007**, *260* (1), 29–35.
- (58) Zhang, Z.; Zhang, Z.; Dong, B.; Chen, J.; Xin, H.; Zhang, Q. Vapor-Liquid Equilibrium Experiment and Model Prediction for Separating Ethyl Propionate and Ethanol Using Ionic Liquids with Acetate Anion. *J. Mol. Liq.* **2020**, *318*, No. 113688.
- (59) Yang, C.; Zeng, H.; Yin, X.; Ma, S.; Sun, F.; Li, Y.; Li, J. Measurement of (Vapor+liquid) Equilibrium for the Systems {methanol+dimethyl Carbonate} and {methanol+dimethyl Carbonate+tetramethylammonium Bicarbonate} at P = (34.43, 67.74)KPa. *J. Chem. Thermodyn.* **2012**, *53*, 158–166.
- (60) Zhang, Y.; Wang, Z.; Xu, X.; Gao, J.; Xu, D.; Zhang, L.; Wang, Y. Entrainers Selection and Vapour-Liquid Equilibrium Measurements for Separating Azeotropic Mixtures (Ethanol + n-Hexane/Cyclohexane) by Extractive Distillation. *J. Chem. Thermodyn.* **2020**, *144*, No. 106070.
- (61) He, S.; Fan, W.; Huang, H.; Gao, J.; Xu, D.; Ma, Y.; Zhang, L.; Wang, Y. Separation of the Azeotropic Mixture Methanol and Toluene Using Extractive Distillation: Entrainer Determination, Vapor–Liquid Equilibrium Measurement, and Modeling. *ACS Omega* **2021**, *6* (50), 34736–34743.
- (62) Britt, H. I.; Luecke, R. H. The Estimation of Parameters in Nonlinear, Implicit Models. *Technometrics* **1973**, *15* (2), 233–247.