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Dhoni Hartanto,* Boelo Schuur, Matthijs Ammerlaan, Anton A. Kiss, and André B. de Haan

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ABSTRACT: In this work, dimethyl isosorbide (DMI) and 1-butylpyrrolidin-2-one (NBP), as biobased and greener organic solvents, were used for the first time as entrainers in extractive distillation to separate a close-boiling mixture of methylcyclohexane and toluene. Vapor−liquid equilibrium (VLE) data were collected for pseudoternary mixtures consisting of methylcyclohexane and toluene in the presence of DMI and NBP at various entrainer-to-feed ratios (E/F) and pressures. The VLE measurements were conducted by using a Fischer Labodest VLE602 ebulliometer, and the thermodynamic consistency of the data was verified by using the Van Ness test. Both DMI and NBP

were found to increase the relative volatility of methylcyclohexane to toluene, successfully eliminating close-boiling behavior. Compared to benchmark entrainers, both outperformed 1-methylpyrrolidin-2-one (NMP) and sulfolane under certain conditions. In comparison with other green entrainers, DMI and NBP showed similar performance to gamma-valerolactone (GVL) and Cyrene under specific conditions. The VLE data were accurately correlated by using the nonrandom two-liquid (NRTL) model.
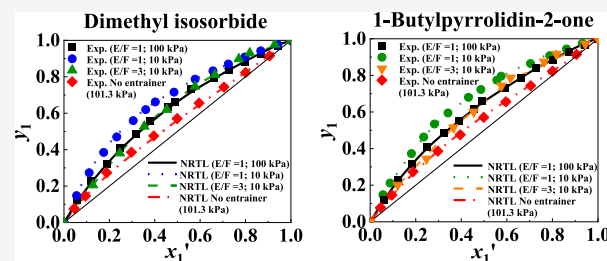
1. INTRODUCTION

Methylcyclohexane and toluene are a binary hydrocarbon mixture with close-boiling behavior. Methylcyclohexane (T_b = 374.15 K[1]) and toluene (T_b = 383.15 K[2]) exhibit a narrow boiling point difference. This is further reflected in their VLE profile,[3] where the vapor and liquid phase compositions are closely aligned. These characteristics make it challenging to separate the mixture into high-purity products using conventional separation technologies, such as conventional distillation. Therefore, it is necessary to separate this close-boiling mixture using advanced separation technology to achieve the desired specification of high-purity methylcyclohexane and toluene, respectively. Methylcyclohexane has been used in a wide range of applications, such as fuel additives to improve combustion performance, chemical intermediates, hydrogen carriers, and industrial separation processes as an extraction solvent.[4−7] Toluene also has a broad range of applications, such as fuel, hydrogen carriers, and extraction solvents.[8−10]

Separation processes in the chemical industry extensively utilize distillation because of its effectiveness in managing diverse feed flow rates and concentrations, favorable mass transfer, suitability for application in complicated mixtures, and capability to provide a high-purity final product.[11−13] Worldwide, there are currently more than 100,000 operating distillation columns, which account for over 50% of the total plant cost.[14,15] Nevertheless, distillation, as an established

technology, involves significant energy and water usage, which leads to high costs and a carbon footprint. Additionally, the use of conventional distillation, particularly in challenging separations that encompass azeotropes as well as mixtures with close-boiling behavior, is costly due to high energy and water consumption. Moreover, it can result in significant CO_2 emissions. Therefore, intensified distillation technology is utilized for azeotrope and close-boiling mixture separation. Extractive distillation is a frequently employed intensified distillation process that addresses separation challenges by increasing the relative volatility of the mixture. An entrainer with low volatility and high thermal stability is introduced to the mixture to interact with one of the compounds and, therefore, ease the separation of the to-be-separated compound. As a result of the improved separation, it is possible to reduce energy and water consumption, cost, and CO_2 emissions.

Selecting an appropriate entrainer is of utmost importance, as it will affect the effectiveness of extractive distillation.

Conventional solvents, such as NMP, are widely used as entrainers in extractive distillation. Regrettably, NMP is classified as a carcinogenic and reprotoxic substance, which will limit its future industrial use according to regulations from the U.S. Environmental Protection Agency (EPA) and the European Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH).[16−20] Hence, the utilization of substitute entrainers has gained significant attention in order to advance the sustainability of the extractive distillation process by reducing energy and water requirements and alleviating the negative environmental effects of conventional entrainers. Ionic liquids,[21,22] deep eutectic solvents,[23,24] natural deep eutectic solvents,[25,26] biological buffers,[27,28] and biobased solvents[29,30] are among the prospective entrainers that have been extensively studied.

Despite the increasing emphasis on green solvents, certain promising greener alternative entrainers, such as DMI as a biobased solvent and NBP, also known as TamiSolve NxG, as a greener organic solvent, remain largely unexplored as entrainers in extractive distillation. The absence of experimental VLE data and binary interaction parameters (BIPs) for methylcyclohexane and toluene in the presence of DMI and NBP limits the development of accurate and reliable extractive distillation processes. Given their potential as greener entrainers, employing these solvents could lead to more sustainable and environmentally friendly extractive distillation. This work aims to fill these important VLE data and knowledge gap.

Our previous study indicated that both solvents show favorable relative volatility for separating methylcyclohexane from toluene. This conclusion is based on prediction results obtained from group contribution methods and unimolecular quantum chemical calculations.[26] Regarding its greener properties, DMI can be readily synthesized from isosorbide, which is a product derived from sorbitol. DMI can also be directly produced from d-sorbitol.[31] Sorbitol, as one of the sugar alcohols, can naturally be found in fruits and plants.[32] In addition, it is commercially manufactured through the hydrogenation of glucose or sucrose.[33] DMI exhibits environmentally favorable characteristics, including nontoxicity, biodegradability, high-water solubility, and sustainability.[34] DMI was also listed among the top ten biobased solvents.[35] The toxicity of DMI is significantly lower than that of NMP. The acute oral toxicity values in rats, expressed as LD50 (lethal dose for 50% of the population), are 6530.8 mg/kg body weight for DMI and 4150 mg/kg body weight for NMP. A higher LD50 value indicates lower toxicity. Additionally, DMI is categorized as very slightly irritating to the skin and eyes and nonirritating to ears. Some reports have also shown that DMI is nongenotoxic, as it was found not to be mutagenic to both mammalian cells and bacteria. Furthermore, DMI is classified as nonreprotoxic, with no observed harmful effects on maternal health and embryo-fetal development.[36−39]

Furthermore, DMI possesses advantageous properties, such as being noncorrosive and nonflammable and having a high boiling point (T_b = 513.15 K at 101.3 kPa), low vapor pressure (0.11 kPa at 293.15 K), and a high decomposition temperature (>513.15 K).[37,40] DMI has a higher hydrogen bonding potential (Hansen solubility parameters (HSPs) for hydrogen bonding (δ_h) = 7.5 MPa$^{1/2}$) compared to NMP (δ_h = 7.2 MPa$^{1/2}$),[41,42] which makes it a promising entrainer candidate for extractive distillation. NBP is another highly promising, environmentally friendly entrainer. NBP is a high-boiling-point

organic and polar aprotic solvent (T_b = 514.15 K at 101.3 kPa) with good thermal and chemical stability (temperature decomposition is above 514.15 K), high water solubility, and low vapor pressure (0.013 kPa at 298.15 K) and is a noncorrosive solvent.[43,44] NBP has promising polarity (HSPs for polarity (δ_p) = 8.2 MPa$^{1/2}$), which is slightly lower compared to the polarity of NMP (δ_p = 12.3 MPa$^{1/2}$).[42,43] According to the European Chemical Agency (ECHA) and Economic Co-operation and Development (OECD) test method, NBP is classified as an inherently biodegradable solvent with low hazard potential and nonmutagenic properties and does not have reprotoxicity[45,46] as conventional solvents such as NMP, which is categorized as a reprotoxic solvent reported by OECD.[47] NBP demonstrates lower toxicity on fetal development compared to NMP, as evidenced by its higher value of no observed adverse effect level (NOAEL) for over 500 mg/kg body weight/day, in contrast to NMP's NOAEL of 160 mg/kg body weight/day.[38,48] These NOAEL values represent the highest dose of a substance that does not cause any harmful effects on fetal development. This indicates that a higher NOAEL value reflects lower toxicity. Therefore, NBP can be considered a greener solvent than NMP. Despite these advantages of DMI and NBP over conventional solvents, they have not been examined for use as entrainers in extractive distillation processes through VLE data measurements. Therefore, DMI and NBP were selected as entrainers in this study.

In addition, the effective design of extractive distillation requires reliable VLE data as a thermodynamic package. Despite its importance, there are currently no available VLE data for the methylcyclohexane and toluene mixture in the presence of the entrainers DMI and NBP, respectively. Recently, researchers have examined VLE data for a methylcyclohexane and toluene mixture with the addition of entrainers such as sulfolane, Cyrene,[29] morpholine,[49] gamma-valerolactone (GVL), 1-methylpyrrolidin-2-one,[3] and the ionic liquid 1-hexyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide.[50] Several studies on the separation of a methylcyclohexane and toluene mixture using extractive distillation through process simulation and a pilot plant have been conducted using entrainers such as the ionic liquid 1-hexyl-3-methylimidazolium tetracyanoborate ([hmim][TCB]) and NMP,[51] ionic liquids of 1-hexyl-3-methylimidazolium tetracyanoborate and 1-butyl-3-methylimidazolium tetracyanoborate, NMP,[52] and phenol.[53] In addition, Tiverios and Van Brunt (2000) evaluated extractive distillation through process simulation to separate methylcyclohexane from toluene using several entrainers, such as propylene glycol, aniline, methyl n-amyl ketone, phenol, dimethylformamide (DMF), acetophenone, o-cresol, furfural, and cyclohexane.[54]

This work aimed to assess the effectiveness of DMI and NBP as entrainers in the separation of methylcyclohexane from toluene by using extractive distillation. This was achieved by performing VLE data measurements for the pseudoternary mixtures of methylcyclohexane and toluene in the presence of DMI and NBP. The relative volatility performance of DMI and NBP was compared to that of NMP and sulfolane as benchmark entrainers, as well as GVL and Cyrene as alternative green entrainers. The reliability of the VLE data was evaluated using the Van Ness thermodynamic consistency test.[55] Moreover, the NRTL model was implemented for the VLE data correlation in order to determine the optimum BIPs for the studied mixtures.

Table 1. Material Specifications

chemicals	CAS number	molecular weight (g/mol)	$T_{boiling}$ (K)^{a,b}	density (g/cm^3)^{a,c}	companies	purity (mass fraction)^a	method of purity analysis	method of purification
methylcyclohexane	108-87-2	98.19	374.15	0.770	Sigma-Aldrich	≥0.990	GC^d	none
toluene	108-88-3	92.14	383.15	0.865	Sigma-Aldrich	0.999	GC^d	none
dimethyl isosorbide	5306-85-4	174.19	513.15	1.167	Sigma-Aldrich	≥0.990	GC^d	none
1-butylpyrrolidin-2-one	3470-98-2	141.21	514.15	0.960	BioPSX	0.995	GC^d	none
acetone	67-64-1	58.08	329.15	0.791	Merck	≥0.998	GC^d	none

^{a}Specified by the companies. ^{b}At 101.3 kPa. ^{c}At 298.15 K and 101.3 kPa. ^{d}Gas chromatography (GC).

2. EXPERIMENTAL METHODS

2.1. Chemicals. Chemicals used in this study were acquired from commercial companies. The purity of the chemicals was determined by using gas chromatography (GC). All chemicals were used in their original form without undergoing any further purification procedures, as no notable contaminants were found. Table 1 provides detailed specifications of the chemicals.

2.2. Apparatus and Experimental Procedures. Isobaric vapor−liquid equilibrium measurements for the pseudoternary mixtures of methylcyclohexane and toluene containing DMI and NBP, respectively, were performed using an ebulliometer, Fischer Labodest VLE602, Germany. The uncertainty of the apparatus was ±0.01 K for temperature and ±0.01 kPa for pressure. The VLE data were experimentally obtained at pressures of 10.0 and 100.0 kPa. The pressure was regulated in a closed system with a vacuum pump (Pfeiffer DUO 3, Germany) and a pressure controller (Burkert 2871, Germany) connected to the setup. The target pressure was configured using an i-Fischer Unicontrol VLE. After the desired pressure was achieved, the pressure in the setup was maintained by a pressure controller. The mixtures were prepared using a digital analytical balance from Mettler Toledo AE200, United States, which has an uncertainty of 0.0001 g. Around 100 mL of a freshly prepared mixture was loaded into the setup to guarantee adequate circulation for the liquid and vapor phases. In order to ensure sufficient heating of the loaded mixture, a heating rod in the liquid chamber and a heating mantle in the vapor chamber were applied. In addition, a magnetic stirrer was used to properly mix the loaded mixture. Once the equilibrium was attained, which was defined by a constant temperature and pressure (±60 min), 0.1 mL of a liquid sample was collected by opening the valve from the liquid sampling port. For the vapor sample, a syringe was used to collect 0.1 mL of liquid droplets from the condensed vapor sample. A liquid and vapor sample were directly diluted in analytical-grade acetone for GC analysis to determine each sample's composition. The method used in this study was also previously employed in some works from literature.[3,29,30,56]

2.3. Sample Analytical Methods. A Thermo Scientific Trace 1300 Gas Chromatograph (GC) from Switzerland was used to determine the composition of the collected diluted liquid and vapor samples. The GC comprises two ovens that operate in parallel. The injection of samples was performed using a TriPlus 100 Liquid Autosampler (LS). An Agilent DB-1MS GC column with dimensions of 60 m in length, 0.25 mm in diameter, and a film thickness of 0.25 μm was used to analyze the diluted samples. The samples were injected into the Split/Splitless (SSL) injector by using a syringe with a

volume of 1 μL. The GC operated in a ramping temperature mode. A starting temperature of 30 °C was implemented, with the first ramp beginning at 10 °C/min and increasing to 45 °C immediately following the injection. The second ramp was set at 5 °C/min to 60 °C, followed by a subsequent ramp of 2.5 °C/min to 80 °C. Afterward, the fourth ramp increased at 5 °C/min to 95 °C. The final ramp in this method was 50 °C/min, reaching an endpoint temperature of 320 °C. The overall duration of the ramps was 21 min. The type of GC detector used was a flame ionization detector (FID), operated at 440 °C. The column operated at a flow rate of 2 mL/min, with a split flow rate of 300 mL/min and a splitting ratio of 150. A carrier gas pressurized at 213.2 kPa was used, consisting of an airflow rate of 350 mL/min, helium gas with a flow rate of 40 mL/min for makeup flow, and hydrogen gas with a flow rate of 50 mL/min.

Calibration was performed using standard mixtures of known composition. A regression equation was obtained by plotting GC area fractions against standard mole fractions, which was then used to determine the sample compositions from their measured area responses. The analysis to determine the composition of each sample was performed three times to ensure the elimination of any potential errors in the analytical approach. The average value from the triplicate analysis was calculated to obtain the final composition of the sample. The Joint Committee for Guides in Metrology (JCGM)[57] and the NIST Technical Note 1297[58] were used as a basis for the calculation of the standard uncertainty for a liquid- and a vapor-phase composition, as well as for temperature and pressure. The detailed standard uncertainty calculations are described (eqs S1−S3). Each table of the VLE data in Supporting Information includes the standard uncertainty values.

3. RESULTS AND DISCUSSION

3.1. Experimental Results. The reliability of the apparatus and methods employed in this study has been confirmed in our previous work.[3] As depicted in Figure S1, the VLE data for the binary mixture of methylcyclohexane and toluene at lower pressures of 26.7 and 53.3 kPa acquired from the literature[59] were used together with the VLE data at 101.3 kPa from our prior work[3] to obtain the BIPs of the methylcyclohexane−toluene pair. In addition, Figure S2 shows that the profile of close-boiling in the binary mixture of methylcyclohexane and toluene remains unaltered when the pressure is reduced from 101.3 kPa to 53.3 and 26.7 kPa.

In this work, the VLE data were measured for the pseudoternary mixtures of methylcyclohexane and toluene with entrainers DMI and NBP, respectively. For each

Table 2. The Extended Antoine and the NIST Wagner25 Parameters[a]

	Extended Antoine[b]								
Compound	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9
methylcyclohexane	85.776	−7080.8	0	0	−10.695	8.14×10^{-6}	2.0	146.58	572.10
toluene	70.037	−6729.8	0	0	−8.179	5.30×10^{-6}	2.0	178.18	591.75
1-butylpyrrolidin-2-one	44.387	−7118.4	0	0	−4.101	1.39×10^{-18}	6.0	496.64	756.51
	NIST Wagner25[c]								
	A_1	A_2	A_3	A_4	$\ln P_{ci}$	T_{ci}	T_{lower}	T_{upper}	
dimethyl isosorbide	−8.552	2.397	−4.204	−3.911	8.041	688	220	688	

[a]The extended Antoine and the NIST Wagner25 parameters were taken from the physical property databank of Aspen Plus.[60] [b]Equation of the extended Antoine: $\ln(P^s) = A_1 + A_2/(T + A_3) + A_4 T + A_5 \ln T + A_6 T^{A_7}$ for $A_8 \leq T \leq A_9$, where P^S is in kPa and T is in K. [c]Equation of the NIST Wagner25: $\ln(P^S) = \ln P_{ci} + \dfrac{A_1(1 - T_{ri}) + A_2(1 - T_{ri})^{1.5} + A_3(1 - T_{ri})^{2.5} + A_4(1 - T_{ri})^5}{T_{ri}}$ for $T_{lower} \leq T \leq T_{upper}$, where P^S is in kPa, T in K, and $T_{ri} = T/T_{ci}$.

pseudoternary mixture, entrainer-to-feed ratio (E/F) = 1 at pressures of 10.0 and 100.0 kPa and E/F = 3 at a pressure of 10.0 kPa were investigated. E/F is quantified as the mass ratio of the entrainer introduced to the binary mixture, calculated as the entrainer's mass divided by the binary mixture's mass. The VLE measurement was conducted at a pressure of 100.0 kPa instead of 101.3 kPa because the pressure in our laboratory fluctuated between 100.0 and 101.3 kPa. Consequently, a pressure of 100.0 kPa was selected, as it facilitated more precise pressure control in the setup. A pressure of 10.0 kPa was selected to obtain higher relative volatility in the pseudoternary mixtures. The experimental results for the pseudoternary mixture of methylcyclohexane and toluene involving the DMI entrainer with E/F = 1 at pressures of 10.0 and 100.0 kPa are depicted in Table S1, while those with E/F = 3 at a pressure of 10.0 kPa are provided in Table S2. The mole fraction of methylcyclohexane in the liquid phase on an excluded-entrainer basis and in the vapor phase was expressed by x_1' and y_1, respectively. The mole fractions in the liquid phase for methylcyclohexane, toluene, and the entrainer are represented as x_1, x_2, and x_3, respectively. In the vapor phase, the mole fractions for methylcyclohexane, toluene, and the entrainer are denoted as y_1, y_2, and y_3, respectively. The temperature at equilibrium, the activity coefficient of methylcyclohexane, the activity coefficient of toluene, and the relative volatility of methylcyclohexane to toluene are expressed by T, γ_1, γ_2, and α_{12}, respectively. As the entrainer was not observed in the vapor phase, its vapor-phase mole fraction is considered less than 0.0005. Therefore, in Tables S1−S4, the corresponding values (y_3) are reported as 0.000 for the sake of clarity and consistency.

The activity coefficient of component i in the pseudoternary mixtures, which is denoted as γ_i, was used to evaluate the nonideality of the component in the liquid phase, as shown in eq 1. The ideal gas assumption was considered to occur in the mixture since the VLE data were experimentally obtained at vacuum and atmospheric pressure.

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

where i stands for the component i, x represents the mole fraction in the liquid phase, y indicates the mole fraction in the vapor phase, and P and P_i^{sat} denote the total pressure and the saturated vapor pressure for component i, respectively. The extended Antoine and the NIST Wagner25 equations, with their corresponding parameters obtained from the physical properties of the Aspen Plus database, were utilized to

calculate the saturated vapor pressure of component i (P_i^{sat}), as shown in Table 2. The extended Antoine equation was used for methylcyclohexane, toluene, and NBP, while the NIST Wagner25 equation was used for DMI, as no extended Antoine parameters were available for DMI.

In order to assess the separation performance of the entrainer in the pseudoternary mixture, the relative volatility of methylcyclohexane to toluene (α_{12}) was evaluated using eq 2:

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

where x_1' and x_2' denote mole fractions of methylcyclohexane and toluene on an excluded-entrainer basis in the liquid phase.

Tables S3 and S4 present the experimental VLE data for the pseudoternary mixture of methylcyclohexane and toluene with the addition of NBP as an entrainer, with E/F = 1 at 10.0 and 100.0 kPa and with E/F = 3 at 10.0 kPa, respectively. The introduction of DMI into the mixture has effects similar to those observed with the addition of NBP. Figures 1 and 2
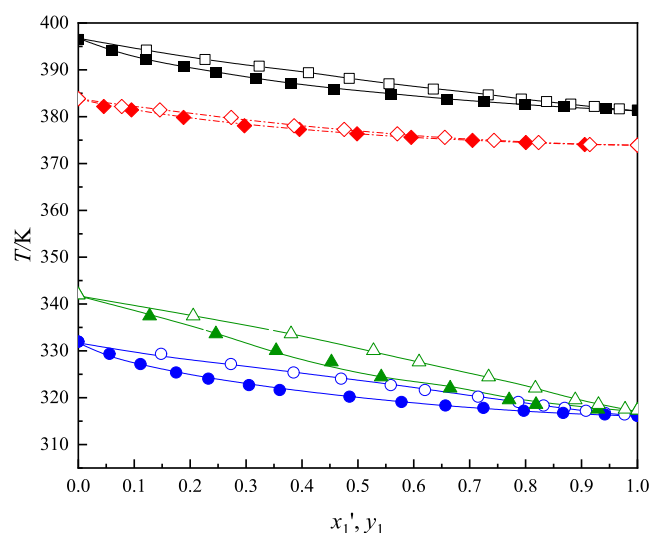

Figure 1. $T−x_1'−y_1$ diagrams of methylcyclohexane (1) + toluene (2) + dimethyl isosorbide (3), experimental for E/F = 1: (■), x_1' and (□), y_1 at 100.0 kPa; (blue ●), x_1' and (blue ○), y_1 at 10.0 kPa; E/F = 3: (green ▲), x_1' and (green △), y_1 at 10.0 kPa; no entrainer: (red ♦), x_1 and (red ◇), y_1 at 101.3 kPa;[3] and correlated by NRTL: (—), black and blue lines for E/F = 1 at 100.0 and 10.0 kPa, respectively; green line for E/F = 3 at 10.0 kPa; and (− · -), red line for no entrainer.

illustrate that adding DMI and NBP, respectively, at a pressure of 100.0 kPa with E/F = 1 increases the equilibrium temperature compared with the mixture without DMI and NBP.
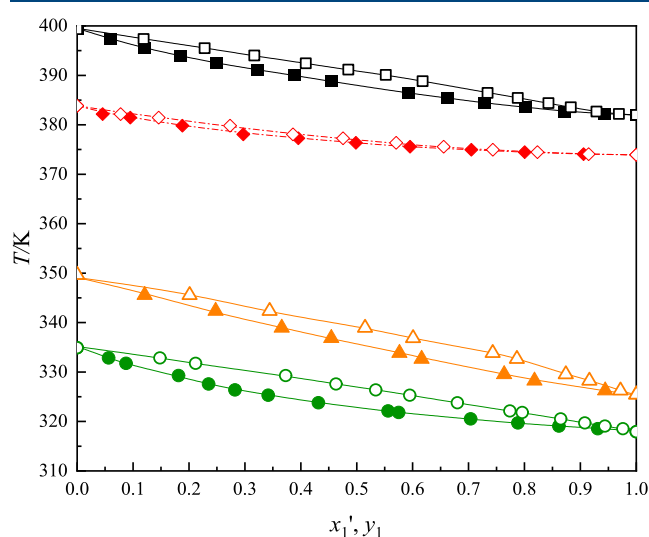

Figure 2. $T-x_1'-y_1$ diagrams of methylcyclohexane (1) + toluene (2) + 1-butylpyrrolidin-2-one (3), experimental for E/F = 1: (■), x_1' and (□), y_1 at 100.0 kPa; (green ●), x_1' and (green ○), y_1 at 10.0 kPa; E/F = 3: (yellow ▲), x_1' and (yellow △), y_1 at 10.0 kPa; no entrainer: (red ◆), x_1 and (red ◇), y_1 at 101.3 kPa;[3] and correlated by NRTL: (—), black and green lines for E/F = 1 at 100.0 and 10.0 kPa, respectively; orange line for E/F = 3 at 10.0 kPa; and (− · -), red line for no entrainer.

The presence of DMI and NBP demonstrates attraction toward toluene, leading to a decrease in toluene vaporization. As a result, an elevated temperature must be achieved to vaporize the mixture and attain equilibrium conditions. At E/F = 1, lowering the pressure from 100.0 to 10.0 kPa significantly reduces the equilibrium temperature. This occurs because reduced pressure lowers the boiling point of the components, enabling them to vaporize at a lower temperature. Therefore, the temperature needed to achieve equilibrium is decreased. At a pressure of 10.0 kPa, the addition of DMI and NBP, respectively, with E/F = 3 to the mixture shifts the equilibrium temperature higher than the addition of DMI and NBP with E/F = 1. Introducing larger amounts of DMI and NBP results in these entrainers predominating in the liquid composition. This considerably reduces the vaporization of both methylcyclohexane and toluene. Consequently, a higher temperature is required to vaporize both components and establish equilibrium, leading to an increase in the equilibrium temperature.

Graphical representations of $y-x'$ diagrams in Figures 3 and 4 illustrate the impact of DMI and NBP, respectively, on the methylcyclohexane–toluene separation. The addition of DMI and NBP to the mixture significantly increases the relative volatility of methylcyclohexane compared to the mixture, excluding these biobased and greener entrainers. As a result, the close-boiling profile is effectively removed from the methylcyclohexane–toluene mixture.

The presence of DMI and NBP in the methylcyclohexane–toluene mixture contributed to the change in nonideal characteristics. In contrast to the molecular interactions
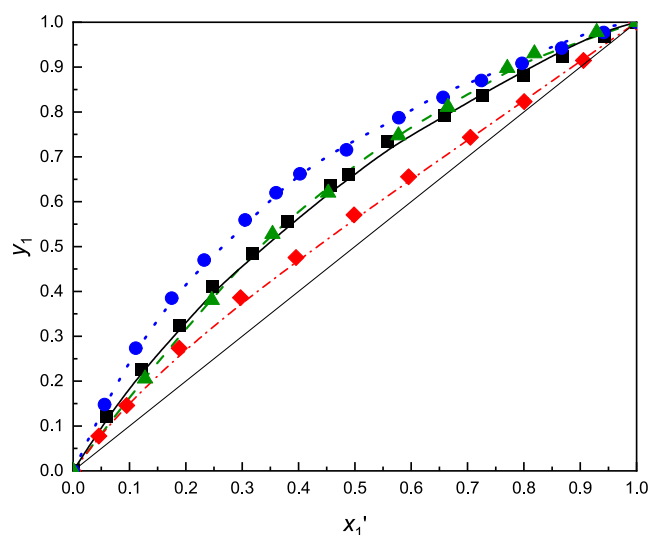

Figure 3. y_1-x_1' diagrams of methylcyclohexane (1) + toluene (2) + dimethyl isosorbide (3), experimental for E/F = 1: (■) at 100.0 kPa, and (blue ●) at 10.0 kPa; E/F = 3: (green ▲) at 10.0 kPa; no entrainer: (red ◆) at 101.3 kPa;[3] and correlated by NRTL: (—), black line for E/F = 1 at 100.0 kPa; (....), blue line for E/F = 1 at 10.0 kPa; (- - -), green line for E/F = 3 at 10.0 kPa; and (—· -), red line for no entrainer at 101.3 kPa.
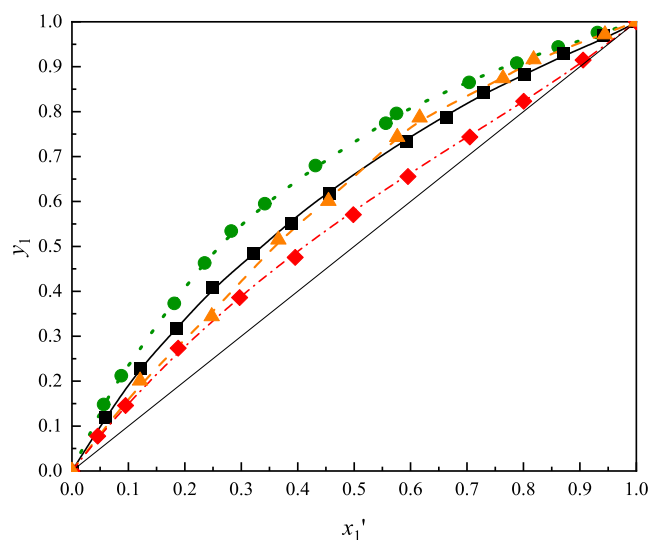

Figure 4. y_1-x_1' diagrams of methylcyclohexane (1) + toluene (2) + 1-butylpyrrolidin-2-one (3), experimental for E/F = 1: (■) at 100.0 kPa, and (green ●) at 10.0 kPa; E/F = 3: (yellow ▲) at 10.0 kPa; no entrainer: (red ◆) at 101.3 kPa;[3] and correlated by NRTL: (—), black line for E/F = 1 at 100.0 kPa; (....), green line for E/F = 1 at 10.0 kPa; (- - -), orange line for E/F = 3 at 10.0 kPa; and (—· -), red line for no entrainer at 101.3 kPa.

between DMI and NBP with methylcyclohexane, the interactions between DMI and NBP with toluene molecules are responsible for producing a higher relative volatility in the mixture. This is primarily because DMI and NBP act as polar entrainers, while toluene has a lower degree of nonpolarity in comparison to that of methylcyclohexane. Hence, DMI and NBP exhibit a higher affinity for toluene compared to methylcyclohexane. As a result, the addition of DMI and NBP can provide a minimum molecular interaction between methylcyclohexane and toluene. The data shown in Tables S1

and S2 for DMI and Tables S3 and S4 for NBP indicate that the introduction of DMI and NBP to the mixture leads to a higher activity coefficient of methylcyclohexane (γ_1) than toluene (γ_2). It can be inferred that DMI and NBP possess a more pronounced affinity for toluene compared to that for methylcyclohexane. Therefore, methylcyclohexane becomes more volatile, facilitating its separation from the mixture. The current work also examines the influence of pressure on relative volatility. Figures 3 and 4 confirm that reducing the pressure from 100.0 to 10.0 kPa at E/F = 1 induces an elevated relative volatility. As shown in Tables S1 and S3 for DMI and NBP, respectively, the activity coefficients of toluene (γ_2) at 10.0 kPa are lower than those at 100.0 kPa. This indicates that the interaction between DMI and NBP with toluene is stronger at 10.0 kPa compared to that at 100.0 kPa. These stronger interactions make it easier for methylcyclohexane to evaporate, and therefore, significant increases in relative volatility can be achieved.

Furthermore, this work also studied the quantitative impact of DMI and NBP on the relative volatility of the mixture. DMI and NBP with E/F = 3 were introduced into the mixture. The addition of entrainers at high E/F is reliable in industrial applications, particularly because entrainers are recycled within the extractive distillation process. Therefore, the entrainer consumption over time remains stable, requiring only a small amount of makeup entrainer rather than significant fresh entrainer input during continuous operation. Previous studies have also employed high E/F to achieve the desired separation performance.[54,61−66] In the separation of a methylcyclohexane−toluene mixture, the E/F values commonly used vary within the range of 0.7 to 18.8. For example, the E/F value for morpholine is 0.7,[49] while ILs have values between 3 and 18.8.[50,52] Additionally, some other organic entrainers, including acetophenone, methyl *n*-amyl ketone, cyclohexanone, *o*-cresol, dimethylformamide, phenol, propylene glycol, cyclohexane, and furfural, have E/F values ranging from 2.5 to 4.2.[54] At E/F = 1, the reduction in pressure from 100.0 to 10.0 kPa resulted in a significant increase in the relative volatility. Hence, the VLE measurements with the addition of DMI and NBP with E/F = 3 were performed at 10.0 kPa. Figures 3 and 4, however, illustrate that using a higher quantity of DMI and NBP, with E/F = 3 at 10.0 kPa, decreases the relative volatility compared to that at E/F = 1 and at 10.0 kPa. An increase in DMI and NBP quantity with E/F = 3 at 10.0 kPa leads to a higher equilibrium temperature in comparison to that at E/F = 1. This can be attributed to the increased temperature at E/F = 3, as already illustrated in Figures 1 and 2, which reduces the nonideality of the mixture. Table S2 shows that the activity coefficient of toluene at 10.0 kPa for E/F = 3 is higher than that at E/F = 1, as indicated in Table S1. This suggests a weaker interaction between DMI and toluene at a higher equilibrium temperature. A similar trend is observed for NBP, as presented in Table S4, where the activity coefficient of toluene at 10.0 kPa for E/F = 3 is higher than that for E/F = 1, as shown in Table S3. Therefore, at higher E/F ratios, the relative volatility of the mixture decreases again due to the weaker interactions between the entrainers and toluene. Consequently, the effectiveness of the methylcyclohexane−toluene separation is reduced. Furthermore, the molecular interactions between methylcyclohexane, toluene, and the entrainers have been studied in our previous work using COSMO−RS for unimolecular quantum chemical calculations.[26]

Additionally, the entrainers' effect on the separation of methylcyclohexane from toluene was compared using $y-x_1'$ diagrams in Figure 5. It reveals that the addition of DMI and
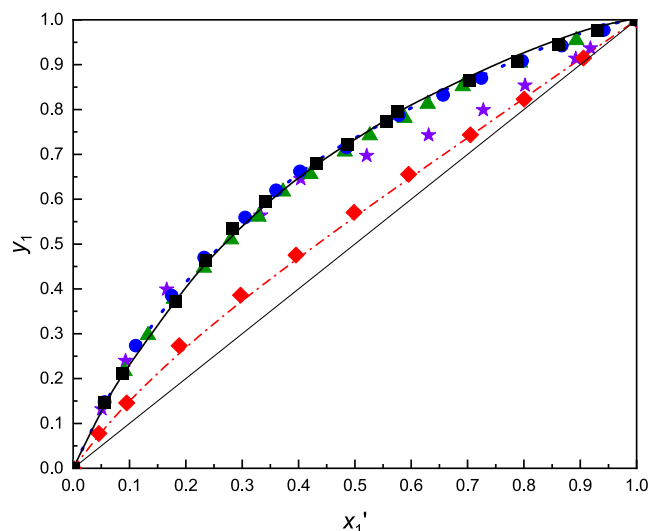

Figure 5. y_1-x_1' diagrams for the comparison of dimethyl isosorbide, 1-butylpyrrolidin-2-one, 1-methylpyrrolidin-2-one, and sulfolane in the methylcyclohexane (1) + toluene (2) mixture: (blue ●), dimethyl isosorbide with E/F = 1 at 10.0 kPa; (■), 1-butylpyrrolidin-2-one with E/F = 1 at 10.0 kPa; (green ▲), 1-methylpyrrolidin-2-one with E/F = 1 at 100.0 kPa (entrainer-free based on the vapor phase mole fraction);[3] (purple ★), sulfolane with E/F = 1 at 100.0 kPa;[29] no entrainer: (red ◆) at 101.3 kPa;[3] and correlated by NRTL: (....), blue line for dimethyl isosorbide with E/F = 1 at 10.0 kPa; (—), black line for 1-butylpyrrolidin-2-one with E/F = 1 at 10.0 kPa; and (− · -), red line for no entrainer at 101.3 kPa.

NBP, with E/F = 1 at 10.0 kPa, to the mixture results in a similar relative volatility performance for removing a close-boiling profile. The performance of both entrainers at E/F = 1 and 10.0 kPa in terms of relative volatility is slightly higher than that of the conventional entrainer NMP at E/F = 1 and 100.0 kPa across all methylcyclohexane composition ranges. This confirms their potential to replace the currently used NMP with more environmentally friendly, greener entrainers, provided that the right operating conditions are selected. In addition, in the methylcyclohexane-rich region, both entrainers at E/F = 1 and 10.0 kPa show significantly higher relative volatility performance than sulfolane, another conventional entrainer, at E/F = 1 and 100.0 kPa. Moreover, the relative volatility for the pseudoternary mixture methylcyclohexane (1) to toluene (2), in the presence of DMI and NBP at x_1' = 0.5 and E/F = 1, was compared with other green entrainers, such as GVL and Cyrene. Figure 6 illustrates that both DMI and NBP, at E/F = 1 and 10.0 kPa, demonstrate relative volatility similar to that of GVL and Cyrene at E/F = 1 and 100.0 kPa. These results show that, based on the relative volatility comparison, both DMI and NBP demonstrate noteworthy potential and could act as excellent biobased and greener organic entrainers, providing an alternative to NMP and sulfolane for the separation of methylcyclohexane from toluene via extractive distillation.

3.2. Test of Thermodynamic Consistency. The Van Ness thermodynamic consistency test[55] was performed to verify the consistency of the experimental VLE data for pseudoternary mixtures of methylcyclohexane and toluene
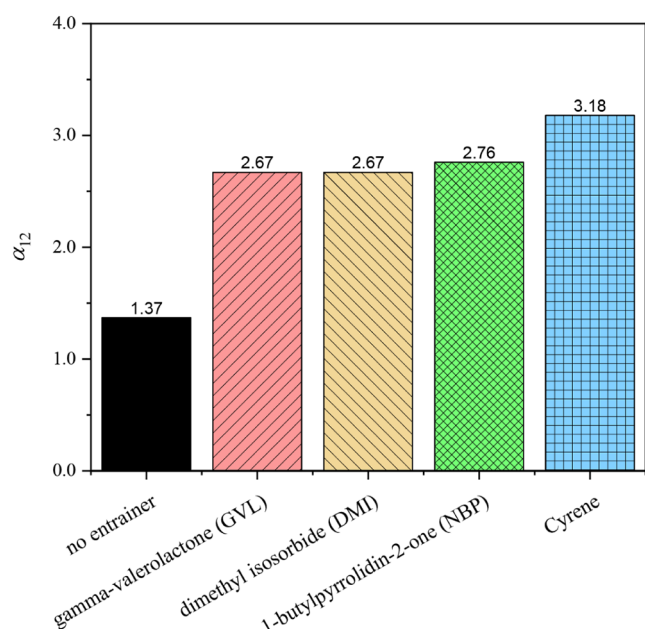
Figure 6. Comparison of the relative volatility (α_{12}) for methyl-cyclohexane (1) to toluene (2) at x_1' = 0.5, E/F = 1: with no entrainer and with the presence of biobased entrainers DMI, Cyrene, and GVL, as well as a greener entrainer NBP. Cyrene and GVL were evaluated at 100.0 kPa, while DMI and NBP were provided at 10.0 kPa. Experimental work was performed in duplicate with a relative volatility deviation of 0.07. Data for Cyrene were sourced from the literature,[29] while the binary mixture with no entrainer and with GVL was taken from our previous study.[3]

containing DMI and NBP. The Van Ness consistency test was calculated using eqs 3 and 4.

$$\Delta P = \frac{1}{n_p} \times \sum_{i=1}^{n_p} \Delta P_i = \frac{1}{n_p} \times \sum_{i=1}^{n_p} 100 \left| \frac{P_i^{cal} - P_i^{exp}}{P_i^{exp}} \right| \tag{3}$$

$$\Delta y = \frac{1}{n_p} \times \sum_{i=1}^{n_p} \Delta y_i = \frac{1}{n_p} \times \sum_{i=1}^{n_p} 100 |y_i^{cal} - y_i^{exp}| \tag{4}$$

where P stands for the pressure, y for the mole fraction in the vapor phase, n_p for the experimental data points, cal for the calculated values obtained from the correlation using the NRTL thermodynamic model, and exp for the experimental values. The experimental VLE data complies with the criteria of the Van Ness test if both values of ΔP and Δy are less than 1 and are thus regarded as consistent. In this work, the experimental VLE data for both pseudoternary mixtures satisfy the Van Ness test and are therefore considered consistent data, as the ΔP and Δy values are below 1, as depicted in Table 3.

In addition, the residual distribution of $\ln(\gamma_1/\gamma_2)$ is required to demonstrate randomness to comply with the Van Ness

Table 3. Thermodynamic Consistency Test

Mixture	Δy^a	ΔP^b	Test Results
methylcyclohexane (1) + toluene (2) + DMI (3)	0.4	0.5	Passed
methylcyclohexane (1) + toluene (2) + NBP (3)	0.1	0.5	Passed

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

test.[67] In this study, the residual distributions of $\ln(\gamma_1/\gamma_2)$ for DMI and NBP are illustrated in Figures S3−S5 and S6−S8, respectively, indicating their randomness. These results confirm that the VLE data measured in this study are consistent.

3.3. Data Correlation. In this study, the NRTL thermodynamic model was employed for VLE data correlation. The NRTL model frequently shows good results in the VLE data correlation for both binary and pseudoternary systems involving entrainers.[3,68−74] Additionally, our previous work showed that the NRTL model demonstrates better correlation than the UNIQUAC model.[3] The equation for the NRTL model is shown in eq 5:

$$\ln \gamma_i = \frac{\sum_{j=1}^{n_c} x_j \tau_{ji} G_{ji}}{\sum_{k=1}^{n_c} x_k G_{ki}} + \sum_{j=1}^{n_c} \frac{x_j G_{ij}}{\sum_{k=1}^{N} x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_{m=1}^{n_c} x_m \tau_{mj} G_{mj}}{\sum_{k=1}^{n_c} x_k G_{kj}} \right) \tag{5}$$

In eq 5, γ_i denotes the activity coefficient of component i and n_c represents the number of components. Furthermore, the parameters used in the NRTL model are defined in eqs 6−9.

$$G_{ij} = \exp(-C_{ij}\tau_{ij}) \tag{6}$$

$$\tau_{ij} = A_{ij} + B_{ij}/T \tag{7}$$

$$\tau_{ii} = 0 \tag{8}$$

$$G_{ii} = 1 \tag{9}$$

where C_{ij} is the nonrandomness constant in the binary interaction of components ij.

For the methylcyclohexane−toluene pair, the BIPs were regressed from the experimental VLE data for the binary mixture of methylcyclohexane and toluene at pressures of 101.3, 53.3, and 26.7 kPa. The experimental VLE data at 101.3 kPa were obtained from our previous work,[3] while those at 53.3 and 26.7 kPa were obtained from the literature.[59] The VLE data from these pressures were calculated together in a single correlation. The obtained BIPs were afterward used to perform the correlation for the pseudoternary mixtures of methylcyclohexane−toluene−DMI and methylcyclohexane−toluene−NBP, where the VLE for these systems was measured from 10.0 to 100.0 kPa. Therefore, the correlation for the binary mixture was conducted at normal and low pressures in order to approach the temperature range of the measured VLE data of both pseudoternary mixtures. In the binary mixture correlation, the parameter of nonrandomness (C_{ij}) for the NRTL model was selected with a value of 0.3. On the other hand, for the correlation of the pseudoternary mixtures, this parameter was not defined by a specific value to provide flexibility in the correlation, which yielded more accurate results. We initially examined the correlation of the pseudoternary mixtures by fixing the value at 0.3 for the methylcyclohexane−entrainer and toluene−entrainer pairs. However, the results were unsatisfactory. In strongly nonideal systems, this value can deviate from 0.3 to more accurately represent the system. Therefore, we decided to regress this parameter in order to achieve better correlation results. Furthermore, the parameters A_{ij} and A_{ji} were included in the regression rather than fixing them to 0. This method yielded more precise results. The maximum likelihood approach

Table 4. Values of Binary Interaction Parameters for the NRTL[a,b]

i component	j component	A_{ij}	A_{ji}	B_{ij}/K	B_{ji}/K	C_{ij}
[c]methylcyclohexane (1)	toluene (2)	−0.523	−0.811	−55.064	736.883	0.30
methylcyclohexane (1)	dimethyl isosorbide (3)	3.745	13.580	−1626.755	−2771.820	0.11
toluene (2)	dimethyl isosorbide (3)	5.206	−1.493	−2769.191	3938.608	0.11
methylcyclohexane (1)	1-butylpyrrolidin-2-one (3)	3.751	4.791	−2538.214	347.731	0.03
toluene (2)	1-butylpyrrolidin-2-one (3)	6.496	−13.495	−3624.621	7959.587	0.10

[a]Unsymmetrical parameters are denoted as A_{ij}, A_{ji}, B_{ij}, and B_{ji}; the nonrandomness constant is represented as C_{ij}. [b]NRTL: $\tau_{ij} = A_{ij} + B_{ij}/T$. [c]Experimental VLE data for a binary system of methylcyclohexane (1) and toluene (2) at 101.3 kPa from our previous work[3] and at 26.7 and 53.3 kPa from reference[59] were combined and used to obtain the BIPs of the methylcyclohexane and toluene pair.

provided by Britt and Luecke,[75] as shown in eq 10, was adopted for minimizing the objective function (OF) to obtain the BIPs.

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

(10)

Let n_p and σ denote the quantity of data points and the data standard deviation, respectively. The optimized BIP values for each pair are presented in Table 4, while the values of the root-mean-square deviation obtained from the comparison between the experimental results and the correlation values are provided in Table 5.

Table 5. Root-Mean-Square Deviation (RMSD) of the NRTL Model[a]

	RMSD[b]			
	T/K	P/kPa	x_1'	y_1
methylcyclohexane (1) + toluene (2)	0.02	0.31	0.005	0.005
methylcyclohexane (1) + toluene (2) + dimethyl isosorbide (3)	0.24	0.36	0.001	0.005
methylcyclohexane (1) + toluene (2) + 1-butylpyrrolidin-2-one (3)	0.15	0.36	0.001	0.002

[a]Temperature (T); pressure (P); mole fraction of methylcyclohexane in the liquid phase on an entrainer-free basis (x_1'); mole fraction of methylcyclohexane in the vapor phase (y_1). [b]RMSD: $\Delta M = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(M_{exp} - M_{cal})^2}$, where n represents the total number of data points; M stands for T, P, x_1', and y_1, respectively.

The correlation results from the NRTL model align well with the experimental data for the binary mixture of methylcyclohexane−toluene, as indicated in Figures S1 and S2. The NRTL model also provides good correlation results when implemented for the pseudoternary mixture of methylcyclohexane−toluene−DMI, as shown in Figures 1 and 3. Moreover, the model demonstrates satisfactory correlation for the pseudoternary mixture of methylcyclohexane−toluene−NBP, as depicted in Figures 2 and 4. The experimental VLE data for each pseudoternary mixture with E/F = 1 at 10.0 and 100.0 kPa and E/F = 3 at 10.0 kPa were regressed as a single correlation to attain more accurate BIPs that precisely describe the VLE data, encompassing various entrainer-to-feed ratios and pressures. The minimum RMSD in Table 5 also indicates a good correlation of the NRTL model. Therefore, the NRTL models, along with the obtained

optimum BIPs, are reliable for modeling the extractive distillation for separating methylcyclohexane from toluene using entrainers DMI and NBP, respectively.

4. CONCLUSIONS

The experimental VLE data for pseudoternary mixtures of methylcyclohexane + toluene + dimethyl isosorbide and methylcyclohexane + toluene +1-butylpyrrolidin-2-one were provided in this study. The VLE data were measured by using a Fischer Labodest VLE602 ebulliometer. According to the Van Ness thermodynamic consistency test, both pseudoternary mixtures were consistent.

This work revealed that the addition of DMI and NBP entrainers to the methylcyclohexane and toluene mixture can effectively eliminate a close-boiling profile, as the relative volatility is elevated significantly. For both pseudoternary mixtures, decreasing the pressure from 100.0 to 10.0 kPa at E/F = 1 leads to a significant increase in relative volatility. However, increasing the amount of DMI and NBP to E/F = 3 at 10.0 kPa results in a decrease in relative volatility compared to that observed with E/F = 1 at 10.0 kPa. The relative volatility performance of DMI and NBP was compared at E/F = 1 and 10.0 kPa. Both DMI and NBP demonstrate comparable relative volatility performance in mitigating close-boiling behavior. Moreover, both DMI and NBP at E/F = 1 and 10.0 kPa exhibit slightly higher relative volatility than NMP at E/F = 1 and 100.0 kPa across all composition ranges of methylcyclohexane and notably higher than sulfolane at E/F = 1 and 100.0 kPa in the methylcyclohexane-rich region. In comparison with other green entrainers, DMI and NBP at E/F = 1 and 10.0 kPa show relative volatility comparable to that of GVL and Cyrene at E/F = 1 and 100.0 kPa. Hence, DMI and NBP hold promise as biobased and greener entrainers to substitute conventional entrainers for extractive distillation, particularly in the separation of a close-boiling methylcyclohexane and toluene mixture.

The NRTL model was employed to correlate experimental VLE data for the binary mixture of methylcyclohexane−toluene and pseudoternary mixtures of methylcyclohexane−toluene containing DMI and NBP, respectively. The correlated results demonstrated satisfactory agreement with the experimental data. Furthermore, optimized binary interaction parameters for each pair were obtained. The NRTL model and the obtained binary interaction parameters can be properly used for the extractive distillation process modeling in the methylcyclohexane and toluene separation.

■ ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.5c01616.

Experimental VLE data; $T-xy$ and $x-y$ diagrams for the binary mixture of methylcyclohexane (1) + toluene (2) at different pressures; $\ln(\gamma_1/\gamma_2)$ residual distributions; uncertainty calculations (PDF)

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Notes

The authors declare no competing financial interest.

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