Eurasian Chem.-Technol. J. 26 (2024) 211–224

https://doi.org/10.18321.ectj1645

Vapor-Liquid-Liquid Equilibrium of Methanol, Cyclohexane, and Hexane Systems at 0.1 MPa: Binary and Ternary Phase Behavior Analysis

Q.F. Gillani[1], P. Askar[1], A. Ospanova[1], M.A. Jamali[1], N. Nuraje[1,2]*

[1]Department of Chemical and Materials Engineering, School of Engineering and Digital Sciences,
Nazarbayev University, Astana, 010000, Republic of Kazakhstan
[2]Renewable Energy Lab, National Laboratory Astana, Nazarbayev University, Astana, 010000, Republic of Kazakhstan

Article info

Received:
16 July 2024

Received in revised form:
29 August 2024

Accepted:
53 October 2024

Keywords:
Vapor-Liquid-Liquid Equilibrium (VLLE)
Liquid-Liquid Equilibrium (LLE)
Binary systems
Ternary systems
Methanol
Cyclohexane
n-hexane
Universal Quasi-Chemical (UNIQUAC)
Non-Random Two-Liquid (NRTL)
Phase behavior

Abstract

This study presents an evaluation of the liquid-liquid equilibria (LLE) for both binary and ternary systems involving methanol, cyclohexane, and *n*-hexane at a pressure of 1 MPa. The investigation encompasses a comprehensive analysis of phase behavior, including thermodynamic modeling, and graphical representations. The binary system of methanol and cyclohexane is examined extensively to understand their phase equilibrium at varying temperatures, with a focus on the T-xx diagram, activity coefficient calculations, and vapor-liquid equilibrium (VLE) analyses. Furthermore, the ternary system incorporating *n*-hexane alongside methanol and cyclohexane is investigated to explore the intricacies of multicomponent phase behavior. Through the utilization of thermodynamic models such as the Non-Random Two-Liquid (NRTL) model and Universal Quasi-Chemical (UNIQUAC) model, key insights into the phase compositions, distribution coefficients, azeotropes, and residue curves are elucidated. The findings from this study provide valuable insights into the thermodynamic interactions within these systems, offering essential guidance for process design and optimization in various industrial applications.

1. Introduction

The exploration of the liquid-liquid equilibria (LLE), in two component and three component systems is crucial, in a range of applications, including chemical production, extraction and separation methods [1–3]. It's important to study how the different components behave and are distributed in these systems to improve process design, purity of products and reduce harm. This research specifically looks at analyzing the (liquid + liquid) equilibrium, in a mixture of methanol and cyclohexane as in a ternary system with methanol, cyclohexane and *n*-hexane, under a pressure of 0.1 MPa.

Methanol, cyclohexane and *n*-hexane are commonly used in a range of industries, for different purposes. Methanol, known as an alcohol plays a role in various chemical reactions and is essential for making formaldehyde, acetic acid and biodiesel [4]. Cyclohexane, a type of hydrocarbon is widely utilized as a solvent, in the pharmaceutical, chemical and manufacturing industries because of its lack of polarity and its capability to dissolve substances [3, 5, 6]. Likewise, *n*-hexane, a hydrocarbon compound is mainly used as an extraction solvent in sectors like food processing and pharmaceuticals due, to its solubility properties [7, 8].

In the study of vapor-liquid-liquid equilibrium (VLLE), the interactions between the components of a mixture play a crucial role in determining the phase behavior. Binary mixtures comprise two components, while ternary mixtures involve three components,

---

*Corresponding author.
E-mail address: nurxat.nuraje@nu.edu.kz

such as methanol, cyclohexane, and hexane. The vapor-liquid equilibrium (VLE) data for these mixtures is influenced by various factors, including the relative volatility and the activity coefficients of the components, which dictate their tendency to partition between the vapor and liquid phases [9, 10]. For binary mixtures, the mole fractions of the components can be denoted as x1 for component 1 and x2 for component 2, with the relationship x1 + x2 = 1 [11]. In ternary mixtures, this relationship extends to include a third component, represented as x1 + x2 + x3 = 1. The relative volatility, denoted by α, quantifies the ease of separation of the components based on their respective vapor-liquid distribution ratios, K values. A relative volatility of less than 1.05 indicates that large-scale distillation processes are not workable [11, 12].

The study of the equilibrium, between two liquids in these setups, at 1 MPa involves goals. Initially, it seeks to describe the phase interactions observed when combining methanol and cyclohexane in ratios clarifying how the components are distributed among the liquid phases that coexist [4, 13]. The addition of *n*-hexane, to the system allows for an exploration of how a third component affects equilibrium conditions and phase compositions [14]. Through an analysis of this system we can understand better the solubility interactions between methanol, cyclohexane and *n*-hexane which can aid in optimizing extraction and separation processes for purposes. Previous studies have shown that the Non-Random Two-Liquid (NRTL) and Universal Quasi-Chemical (UNIQUAC) models are effective in correlating data and exhibit temperature interaction parameters [15, 16]. Research conducted by Hiroyuki Matsuda et al. has highlighted the determination of cloud points for mixtures like Methanol + Cyclohexane using laser scattering techniques uncovering critical solution temperatures (UCST) and variations in mole fractions, at different temperature levels [6]. Utilizing Aspen allows for collecting data over a range of temperatures and pressures. Our study began by analyzing the system of cyclohexane and methanol followed by studying diagrams involving cyclohexane, *n*-hexane and methanol.

The results of this research have implications, for process design, environmental sustainability and product quality control. By examining the liquid equilibria in these systems we can develop strategies to improve process efficiency reduce solvent usage and minimize waste generation. Understanding phase behavior also helps industries implement quality control measures to produce high purity products with impurities or contaminants [17].

This research explores the (liquid + liquid) equilibrium, in the system of (methanol + cyclohexane) and the ternary system of (methanol + cyclohexane + *n*-hexane) at 0.1 MPa using Aspen Plus V8.2 software. The reliable correlations discovered in this study can greatly benefit the field of chemical engineering and process optimization by enhancing our knowledge of phase behavior within these systems. This study sets the stage for creating environmentally friendly industrial processes with a wide range of applications, across various industries [18].

2. Experimental

The regression of binary liquid-liquid equilibria (LLE) data to obtain values of the parameters in activity models is considered separately from the regression of vapor-liquid equilibrium (VLE) data since it can be a little more difficult to implement correctly, and the results from the various models can be much more different from is the case for VLE [19]. This is because in VLE the equality of the fugacities of each species in each phase leads to Eq. 1.

$$f_i^L = x_1\gamma_1 P^{vap} = f_i^V = y_1 P \text{ or } \gamma_1 = YiPi/P \qquad \text{Eq. (1)}$$

so that the ratio of the mole fractions in the two phases results from the combined effects of the activity coefficient in the liquid phase and the ratio of the vapor pressure to the total pressure. However, in LLE the equality of fugacity of each species in each phase leads to

$$f_i^I = x^I{}_1\gamma^I{}_1 P^{vap} = f_i^{II} = x^{II}{}_1\gamma^{II}{}_1 P^{vap} \qquad \text{Eq. (2)}$$

so that the ratio of the species mole fractions in the two phases in LLE depends completely on the ratio of activity coefficients. As a result, the calculation of LLE is very sensitive to the thermodynamic models used, the values of the activity coefficients, and their accuracy over the whole concentration range [20].

The problem formulation for VLLE of nc components is presented below. The governing mass balances and summation equations for

$$F = V + L_1 + L_2 \qquad \text{Eq. (3)}$$

$$z_i F = y_i V + x_i^{L1} L_1 + x_i^{L2} L_2 \qquad \text{Eq. (4)}$$

The superscripts, L_1 and L_2, on x_i refer to liquid phases 1 and 2, respectively. The phase number (L_1 or L_2) arbitrary to distinguish the two liquid phases that may coexist [15].

Performing LLE calculations presents a challenge in chemical process simulation, particularly when using Aspen Plus, a software tool. Unlike VLE calculations, which typically yield results with models, the selected model and activity coefficient values highly influenced LLE calculations. This increased sensitivity is due to the reliance of LLE on the ratio of activity coefficients in each phase without considering factors, like vapor pressure [2]. Therefore, choosing the elements is crucial for LLE predictions. It's important to mention that certain thermodynamic models like UNIQUAC and NRTL are suggested for LLE calculations in Aspen Plus. Although the Wilson model is present in the software, it's not advisable for LLE simulations as it struggles to predict this type of equilibrium. Before diving into the methods, it's essential to give an outline of the models used to confirm data.

2.1 Non-Random Two Liquid Model (NRTL)

The NRTL model, created by Renon and Prausnitz in 1968, is an approach used to expect phase equilibria in systems involving liquid-liquid and vapor liquid-liquid phases. This model suggests that molecules within a solution exhibit interactions than random distribution, impacting the system's thermodynamic properties. Through activity coefficients, the NRTL model describes these interactions at a level highlighting the random nature of the mixture. By incorporating temperature factors, this equation adjusts for changes in these interactions with varying temperatures [21]. This model has found extensive application in various industrial sectors, including petrochemical, pharmaceutical, and chemical engineering, due to its ability to accurately predict phase behavior and mixture properties in complex systems.

2.2 Universal Quasi-Chemical Model (UNIQUAC)

The UNIQUAC model, developed by Fredenslund, Jones and Prausnitz in 1975, is an approach used to predict the phase behavior of liquid-liquid and vapor liquid systems. Unlike the NRTL model that highlights random molecular distribution UNIQUAC focuses on how molecules interact uniquely within a mixture. This model considers segment activity coefficients based on factors, like size and shape to describe the interactions between different molecules in the mixture [22]. The UNIQUAC formula includes parameters that adjust based on temperature variations to reflect how interactions change with temperature. This model is commonly used in chemical engineering and process improvement to make forecasts about phase behavior and mixture characteristics across industrial sectors, from petrochemicals to pharmaceuticals.

3. Methodology

The process of analyzing liquid-liquid equilibria (LLE) data using Aspen Plus starts with setting up the details. This includes giving it a title, choosing the units (like METCBAR in metric) and specifying the components involved, which are methanol and cyclohexane in this case. After that, a suitable thermodynamic model is chosen, followed by setting up the LLE simulation in Aspen Plus with the UNIQUAC model selected from the Properties menu. The parameters for the UNIQUAC model are taken from Aspens data bank as an estimate. Then experimental data is incorporated into Aspen Plus by creating a dataset within the Properties menu. The experimental data is sourced from places like the NIST Thermodynamic Data Engine (TDE) for regression analysis. This involves selecting interaction parameters considering temperature ranges and running regression analysis to get results. Finally, plotting data using the T-xx phase equilibrium option within Aspen Plus provides results. Further exploration of a system involving a component, like *n*-hexane is conducted through software simulations to thoroughly analyze mixture properties focusing on both binary and ternary stages initially.

The process and order of simulation runs carried out using Aspen are explained in Fig. 1. It described two parallel simulation pathways: the binary system (methanol-cyclohexane) and the ternary system (methanol-cyclohexane-n-hexane), differentiating between VLE in the binary system and LLE in the ternary system.

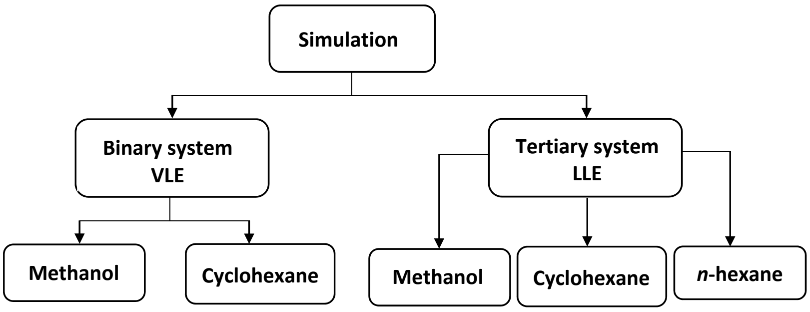

Fig. 1. The methodological framework and sequence of simulation runs conducted through Aspen Plus.

4. Results and discussion

4.1 Phase behavior analysis for binary LLE system

In Fig. 2 the T-xx diagram displays an overview of how the methanol and cyclohexane system behaves, under temperature and composition settings. Known as a tool in chemical engineering, this diagram showcases the relationship between temperature and the amount of methanol present in the mixture.

The distinct curves show when boiling begins for each liquid as the amount of the component is gradually changed. A significant point is the area where both liquid and vapor exist together, giving details about the system's phase balance. The detailed representation of boiling patterns offers insights into how methanol and cyclohexane mix highlighting their limited ability to dissolve in each other [13].

Table 1 displays temperature compositions for the methanol cyclohexane system in the first and second liquid phases. In Table 1, the columns labeled "Methanol (X_1)" and "Cyclohexane ($Y_1 = 1-X_1$)" represent the mole fractions of methanol and cyclohexane in one of the two coexisting liquid phases at equilibrium across different temperatures. The "Methanol (X_1)" column indicates the mole fraction of methanol in the liquid phase, while "Cyclohexane ($Y_1 = 1-X_1$)" shows the corresponding mole fraction of cyclohexane, calculated as the complement of X_1 since the system comprises only these two components. These values describe how the composition of methanol and cyclohexane in one of the liquid phases varies with temperature under liquid-liquid equilibrium conditions at a pressure of 0.1 MPa. The data shows the proportions of methanol and cyclohexane in each phase as temperatures vary.

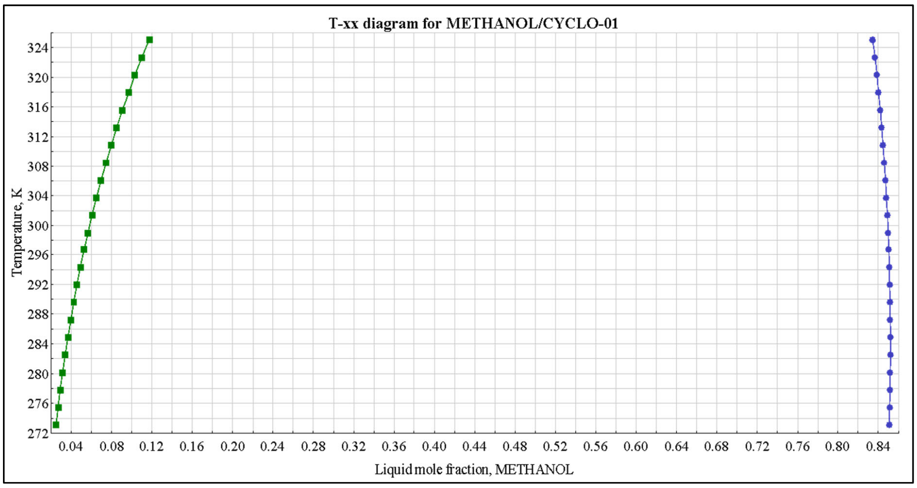

Fig. 2. The T-xx diagram depicts the phase behavior of the methanol-cyclohexane binary system across varying temperature and composition conditions. The green curve represents the liquid phase boundary, while the blue curve represents the vapor phase boundary.

Table 1. (Liquid + liquid) equilibrium data for {Methanol (1) + cyclohexane (2)} at P = 0.1 MPa at various temperatures

Temperature (K)	Methanol (X_1)	Cyclohexane ($Y_1 = 1-X_1$)	Methanol (X_2)	Cyclohexane ($Y_2 = 1-X_2$)
279.2963	0.0458805	0.9541194	0.890896	0.109104
285.2111	0.0598004	0.9401995	0.873694	0.126306
291.1259	0.0779784	0.9220215	0.852789	0.147211
296.0549	0.0974996	0.9025003	0.831622	0.168378
301.9697	0.1282284	0.8717716	0.799898	0.200102
307.8845	0.1708141	0.8291859	0.75786	0.24214
313.7993	0.2337563	0.7662437	0.69723	0.30277
318.7283	0.3215956	0.6784044	0.613158	0.386842
321.2544	0.4233778	0.5766222	0.519994	0.480006
321.5625	0.4752949	0.5247051	0.475295	0.524705

As the temperature rises, there is a change in phase compositions. At lower temperatures, the data indicates that the methanol-rich phase (Phase 2) has a much higher methanol mole fraction (e.g., X_2 = 0.890896 at 279.3 K) compared to the cyclohexane-rich phase (Phase 1, where X_1 = 0.0458805). Thus, methanol is more concentrated in the second liquid phase, while cyclohexane is more prevalent in the first liquid phase. As the temperature increases, the methanol content in both phases increases. This results in a gradual shift towards more balanced compositions between the two phases, with a significant increase in methanol concentration in the cyclohexane-rich phase (e.g., X_1 = 0.475 at 321.5625 K. This shift also emphasizes how sensitive the system is to temperature changes and underscores why understanding phase behavior is crucial for optimizing processes and industrial applications.

This information serves as a foundation, for designing and optimizing separation processes in distillation applications focused on separating methanol and cyclohexane components. By utilizing the insights provided by this data engineers can develop distillation techniques tailored to composition and temperature conditions encountered in real world scenarios.

4.2 Gibbs free energy for binary system LLE

Figure 3 show the Gibbs free energy values for methanol mole fractions at a steady temperature of 25 °C (298 K) in the binary LLE setup involving methanol and cyclohexane. The Gibbs free energy (ΔG) is a fundamental thermodynamic potential that quantifies the maximum reversible work a system can perform under constant temperature and pressure. It integrates the enthalpic (ΔH) and entropic (ΔS) contributions of the system, as expressed by the equation:

$$\Delta G = \Delta H - T\Delta S$$

This equation highlights the interplay between enthalpy, which relates to the heat exchange and molecular interactions, and entropy, which represents the system's degree of disorder. In phase equilibrium studies, the Gibbs free energy serves as a critical indicator of phase stability and the tendency of components to distribute themselves across phases [21].

In binary liquid systems like methanol and cyclohexane, phase behavior is strongly influenced by the chemical nature and interactions of the components. Methanol, being a polar and hydrogen-bonding molecule, contrasts with the non-polar, hydrophobic nature of cyclohexane. This fundamental difference leads to limited miscibility and the formation of distinct liquid phases. The Gibbs free energy curve reflects these interactions, showing how the system's energetics change as the methanol mole fraction varies [7].

Figure 3 illustrates the Gibbs free energy (ΔG) of mixing for varying methanol mole fractions at a steady temperature of 298 K in the binary LLE system involving methanol and cyclohexane. ΔG is a critical thermodynamic parameter that quantifies the energy change associated with mixing under constant temperature and pressure. Negative ΔG\Delta GΔG values indicate that mixing is thermodynamically favorable, while values closer to zero suggest reduced stability of the homogeneous phase.

At low methanol mole fractions, ΔG values are significantly negative, reflecting the stability of the cyclohexane-rich phase. This stability arises from minimal interactions between the non-polar cyclohexane and the relatively sparse polar methanol molecules. As the mole fraction of methanol increases, ΔG values become less negative, signaling a gradual reduction in thermodynamic favorability. This trend is attributed to the increasing presence of methanol molecules, which disrupt the cyclohexane matrix and introduce unfavorable polar–nonpolar interactions.

The Gibbs free energy curve (Fig. 3) exhibits a concave shape, with a pronounced minimum at a specific methanol mole fraction. This minimum corresponds to the most stable composition for the mixture, where the system achieves a balance between enthalpy (ΔH) and entropy (ΔS) contributions. Beyond this point, the increasing slope of the curve indicates a tendency toward phase separation, where

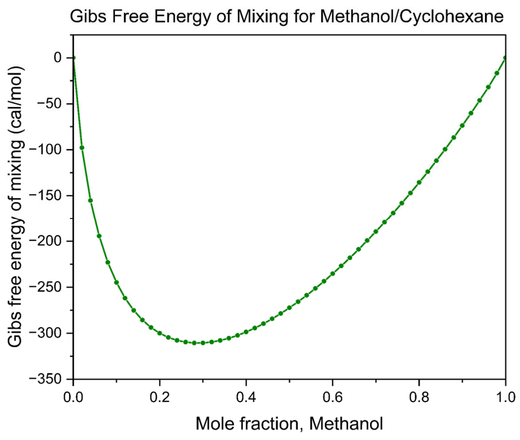

Fig. 3. Gibbs free energy of mixing versus mole fraction of methanol in methanol-cyclohexane binary mixture.

two distinct liquid phases form: one methanol-rich and the other cyclohexane-rich [14]. The observed trend highlights the critical role of molecular interactions in governing phase behavior. Negative ΔG values throughout the curve confirm that the mixture is thermodynamically stable overall, but the reduction in stability at higher methanol fractions suggests immiscibility, leading to liquid–liquid equilibrium (LLE). These insights are essential for understanding and predicting the phase behavior of the methanol-cyclohexane system in practical applications [1].

This behavior is typical in LLE systems, where the Gibbs free energy determines the equilibrium composition of each phase. At equilibrium, the chemical potentials of the components in each phase become equal, ensuring no net transfer of species between phases. Therefore, the observed trend of the Gibbs free energy offers a direct insight into how phase stability is controlled by the molecular interactions and energetic considerations within the mixture.

The behavior of the Gibbs free energy curve aids in predicting critical points, such as binodal and spinodal lines, which delineate regions of stability and instability in the phase diagram. The binodal line represents compositions where two phases coexist in equilibrium, while the spinodal line indicates where spontaneous phase separation occurs due to an unstable energy configuration. By interpreting the Gibbs free energy curve, one can gain essential insights into these phase boundaries, aiding in the accurate modeling of phase behavior in binary liquid systems like methanol-cyclohexane.

Plotting the Gibbs free energy as a function of methanol mole fraction offers a visual representation of how different compositions influence the thermodynamic stability of the system. This plot not only illustrates the stable and unstable regions of the mixture but also highlights the compositions where phase transitions occur, providing valuable information for understanding and predicting the behavior of liquid-liquid equilibrium systems.

4.3 VLE behaviour of methanol and cyclohexane

Figure 4 illustrates the vapor-liquid equilibrium (VLE) between methanol and cyclohexane through two distinct curves: the bubble point curve (blue) and the dew point curve (green). The x-axis represents the mole fraction of methanol in the liquid phase, while the y-axis indicates the temperature in degrees Kelvin. The bubble point curve shows the temperatures at which the first vapor bubble forms as the liquid mixture is heated, while the dew point curve represents the temperatures at which the first liquid droplet condenses as the vapor mixture cools. The area between these two curves defines the two-phase region where both liquid and vapor coexist, while the regions outside indicate either liquid (below the bubble point curve) or vapor (above the dew point curve) phases.

The T-xy chart derived from studying the VLE of methanol and cyclohexane illustrates the makeup of the liquid and vapor phases under temperatures and pressures. In Fig. 4 the analysis of the methanol cyclohexane blend, on the T-xy diagram provides insights. Firstly, it shows that methanol and cyclohexane mix in both liquid and vapor phases at all temperatures indicating a solution with no separation between phases. Secondly Fig. 4 displays a deviation from Raoults Law as methanols vapor pressure differs from expected values below and above the line. This divergence points to unique interactions between molecules in the mixture compared to their forms. Moreover, each components volatility is influenced by its concentration; methanol is more volatile in low methanol mixes while cyclohexane becomes more volatile in high methanol blends. These observations are key for understanding distillation processes by helping predict vapor composition based on liquid mixtures composition and temperature. Additionally, the absence of a point on the diagram indicates that there are no boiling compositions for this blend at the specified pressure implying consistent variations, between vapor and liquid compositions throughout distillation.

The T-xy chart explains how the methanol cyclohexane mixture behaves, in ways that are not ideal offering insights, into its phase properties and distillation behavior.

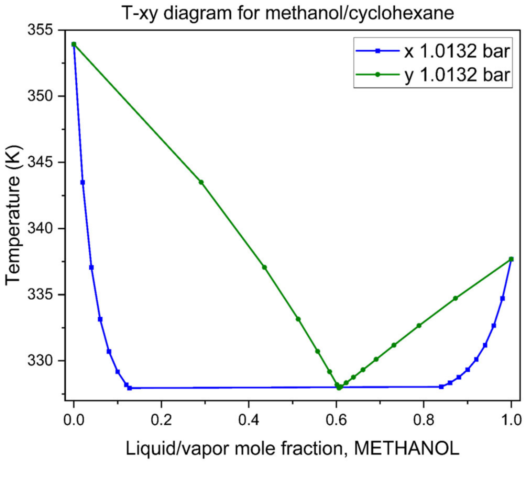

Fig. 4. VLE analysis of methanol and cyclohexane.

4.4 Activity coefficient calculated in both liquid phases

The examination of how the solubility of methanol and cyclohexane changes with temperature in various environments shows distinct patterns. Methanol becomes less soluble as the temperature increases, moving towards non-ideal behavior, while cyclohexane's solubility remains relatively stable or experiences minor fluctuations. This variation is particularly evident in the VLE phase. These findings emphasize how temperature affects the solubility of methanol and cyclohexane, with methanol becoming less soluble at higher temperatures and cyclohexane maintaining a consistent solubility pattern. Understanding these dynamics is essential for processes that involve extraction and separation, as temperature changes can significantly influence phase equilibrium and product purity.

The activity coefficient (γ) is a measure of the deviation of a component's behavior from ideality in a mixture. It reflects how the actual concentration of a component differs from its concentration in an ideal solution. A high activity coefficient ($\gamma >> 1$) indicates strong deviations from ideal behavior, suggesting that the interactions between molecules of the component and the solvent are unfavorable compared to the interactions in a pure state. Conversely, a low activity coefficient (γ close to 1) suggests that the component behaves nearly ideally, with minimal deviation from its behavior as a pure substance.

Relation to Solubility:

In the context of methanol and cyclohexane, the activity coefficients provide insights into the solubility patterns observed at different temperatures:

- ***High Activity Coefficients (Methanol):*** The activity coefficient values for methanol in the first liquid phase increase significantly as the temperature decreases (e.g., from 6.212 at 333 K to 35.866 at 273 K). These high values indicate that methanol exhibits significant non-ideality and is less soluble in cyclohexane. Methanol, being a polar substance, experiences weak interactions with the non-polar cyclohexane molecules, leading to its reduced solubility. The high activity coefficients suggest that methanol is more "active" in the mixture compared to its ideal state, meaning it tends to escape the phase and form a separate phase (or vaporize), leading to phase separation.
- ***Low Activity Coefficients (Cyclohexane):*** On the other hand, cyclohexane maintains relatively low activity coefficient values (ranging from 1.072 at 333 K to 1.006 at 273 K) in the methanol-rich phase. These low values imply that cyclohexane behaves nearly ideally, as its non-polar nature aligns well with itself even when present in a mixture with methanol. The low activity coefficients reflect minimal deviation from its pure-state behavior, indicating that cyclohexane remains stable and soluble across a range of temperatures, hence maintaining a consistent solubility pattern.

The variation in activity coefficients between methanol and cyclohexane emphasizes the disparity in their molecular interactions and solubility behavior. Methanol, with its polar nature, experiences unfavorable interactions in a cyclohexane-rich environment, leading to a higher activity coefficient and reduced solubility. In contrast, cyclohexane's low activity coefficient indicates it maintains stability and solubility due to its compatibility with itself, even within the methanol-rich phase.

Understanding these activity coefficients is crucial for designing and optimizing separation processes like distillation, where temperature manipulation directly affects the VLE and phase distribution. As the activity coefficients change with temperature, the solubility behavior of methanol and cyclohexane can be controlled to achieve the desired purity and yield.

Figure 5 illustrates the activity coefficients calculated for both liquid phases during the VLE analysis of methanol and cyclohexane. Table 2 further details these values at different temperatures and shows the trend of increasing activity coefficients for methanol and stable, low values for cyclohexane. This data underscores the temperature-dependent non-ideality of methanol and the relatively ideal behavior of cyclohexane, aligning with the solubility observations.

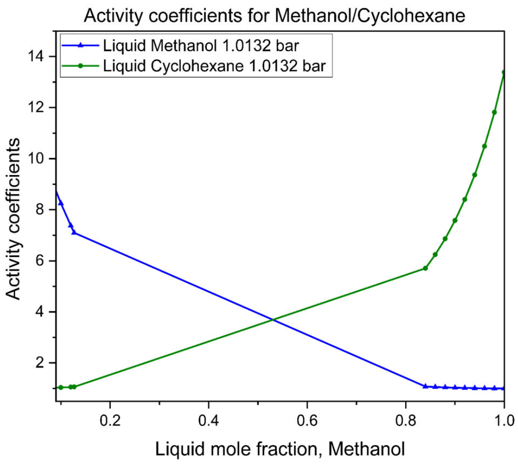

Fig. 5. Activity coefficient calculated in both liquid phases during VLE analysis of methanol and cyclohexane.

Table 2. Activity coefficient calculated in both liquid phases during VLE analysis of methanol and cyclohexane at 0.1 MPa

Sr. No	Temperature (K)	γ_1 in first liquid phase	γ_1 in second liquid phase	γ_2 in first liquid phase	γ_2 in second liquid phase
		Methanol	Cyclohexane	Methanol	Cyclohexane
1	333	6.212199	1.072762	1.089136	5.281945
2	328	7.087775	1.060445	1.083176	5.503851
3	323	8.10136	1.050219	1.078134	5.708242
4	318	9.279903	1.041687	1.073897	5.89297
5	313	10.65472	1.034558	1.070324	6.05772
6	308	12.26431	1.028593	1.067317	6.201802
7	303	14.15575	1.023602	1.064803	6.324629
8	298	16.38697	1.019427	1.062722	6.425731
9	293	19.029	1.015941	1.061017	6.505145
10	288	22.17197	1.013031	1.059677	6.561847
11	283	25.92651	1.010609	1.058662	6.596246
12	278	30.43237	1.008598	1.057949	6.608468
13	273	35.86621	1.006935	1.057525	6.598794

Figure 5 illustrates the activity coefficients of methanol and cyclohexane in both liquid phases over a range of temperatures. The activity coefficient (γ) quantifies the deviation from ideal behavior, where a value of 1 represents ideality, and values significantly greater or less than 1 indicate non-ideal interactions.

In the methanol-rich phase, the activity coefficient of methanol (γ_1) exhibits a steep increase at lower temperatures, indicating significant non-ideality and reduced solubility of methanol in cyclohexane due to unfavorable interactions between polar (methanol) and non-polar (cyclohexane) molecules. This trend diminishes with increasing temperature, suggesting that temperature mitigates these unfavorable interactions.

Conversely, cyclohexane's activity coefficient (γ_2) in the methanol-rich phase remains close to 1, reflecting near-ideal behavior. This is consistent with the minimal interaction of cyclohexane molecules in a methanol-rich environment, aligning with cyclohexane's non-polar nature and reduced solubility.

In the cyclohexane-rich phase, methanol's activity coefficient (γ_1) decreases slightly at higher temperatures, indicating a marginal improvement in its compatibility with cyclohexane. Cyclohexane's activity coefficient (γ_2) in this phase remains low across the temperature range, showcasing its stability and compatibility within its dominant phase.

4.5 K-values for methanol/cyclohexane binary VLE interaction

Figure 6 shows that the binary VLE analysis of methanol and cyclohexane using the Aspen plus NRTL model provides crucial information regarding the phase behavior and distribution of components in the system. The data includes pressure (P), mole fraction of methanol, total temperature (T), and total K values for methanol and cyclohexane. The K values represent the equilibrium distribution coefficients, indicating the relative concentrations of each component in the liquid phases [2].

Observing the trend in K values with varying mole fractions of methanol reveals insights into the system's phase equilibrium and selectivity towards different components. At lower methanol mole fractions, the K values for methanol are higher, indicating a preference for methanol in one of the liquid phases. Conversely, as the mole fraction of methanol increases, the K values for cyclohexane become relatively higher, suggesting a shift towards cyclohexane-rich phases.

This graph is essential for understanding the distribution of components in liquid-liquid systems and can optimize separation processes and design efficient extraction units in chemical engineering applications. It provides valuable input for thermodynamic modeling and simulation studies aimed at predicting phase equilibria under various operating conditions.

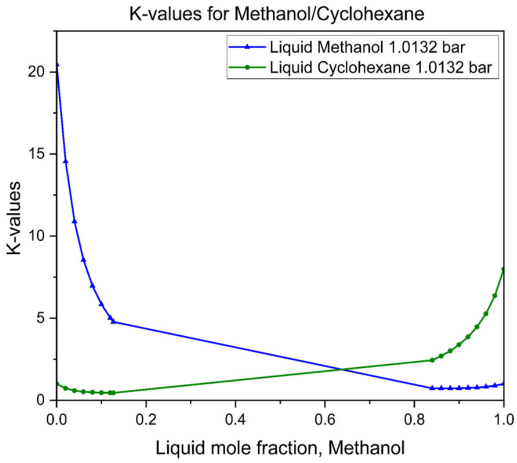

Fig. 6. Binary VLE analysis of methanol and cyclohexane using the Aspen Plus NRTL Model: k values obtained.

4.6 Vapor-liquid-liquid equilibrium (VLLE)

Vapor-liquid-liquid equilibrium (VLLE) calculations play a critical role in understanding and predicting the behavior of multi-phase systems, particularly when three components interact to form vapor and two immiscible liquid phases. Unlike simpler binary systems, VLLE predominantly involves ternary systems, which offer more flexibility in determining the equilibrium state and composition of each phase. This preference aligns with the principles outlined by the Gibbs phase rule, which governs the number of degrees of freedom (DF) in a system. The degrees of freedom in non-reacting systems are determined by the equation:

$$DF = C - P + 2$$

where: C represents the number of components; P signifies the number of phases [23].

For example, in a binary system with three phases (liquid, liquid, and vapor), the equation yields only one degree of freedom (C=2, P=3). This limited degree of freedom makes it challenging to identify the specific temperature-pressure point where all three phases coexist simultaneously. However, in a ternary system (C=3), there are two degrees of freedom. This additional degree of freedom simplifies the process of pinpointing the VLLE state at various compositions through the use of a ternary diagram, enabling a comprehensive view of the equilibrium behavior at different conditions.

VLLE calculations are essential in chemical engineering as they provide detailed insights into the distribution of components across vapor and two liquid phases, which is crucial for designing efficient separation processes like distillation and liquid-liquid extraction. They help engineers optimize process parameters by identifying the specific conditions for phase coexistence, enhancing separation efficiency and product purity. VLLE data also play a critical role in validating and refining thermodynamic models such as NRTL and UNIQUAC, ensuring accurate predictions in complex mixtures. Furthermore, these calculations offer valuable understanding of intricate phase behaviors, such as azeotrope formation and partial miscibility, helping to develop effective separation strategies. Overall, VLLE calculations are fundamental for accurately predicting equilibrium states and optimizing separation processes, contributing to safety, efficiency, and economic feasibility in chemical engineering applications [24].

4.7 Residue curves

The LLE behavior of a ternary system comprising methanol, n-hexane, and cyclohexane at a pressure of 0.1 MPa and a temperature of 273 K, modeled using the NRTL approach is depicted through Fig. 7.

This graphical representation illustrates the composition of two coexisting liquid phases at equilibrium, shedding light on the distribution of components within the system. Each curved line, termed as residue curves, delineates the composition of the solvent-rich phase (raffinate) as a function of the solute-rich phase (extract) composition.

Upon examination of the diagram it becomes evident that there are curves labeled from Curve 1.0 to Curve 17.0 each representing different compositions, at equilibrium between the two liquid phases. Although the tie lines connecting these equilibrium compositions are not shown we can infer their presence to gain an understanding of the phase behavior. The region enclosed by these curves indicates conditions where the mixture separates into phases while the area outside represents a single phase region with complete uniformity [25].

Upon analyzing the diagram, it is clear that methanol tends to partition into the extract phase as seen by the decrease in fractions of n hexane and cyclohexane in the raffinate phase with increasing methanol concentration. This observation highlights methanols attraction towards the solute phase, which influences phase equilibrium behavior.

Considering how varying process parameters like pressure and temperature can impact the LLE behavior of this mixture is crucial. While this study maintained pressure at 0.1 MPa and temperature at 273 K consistently any changes in these parameters could have an effect on phase behavior.

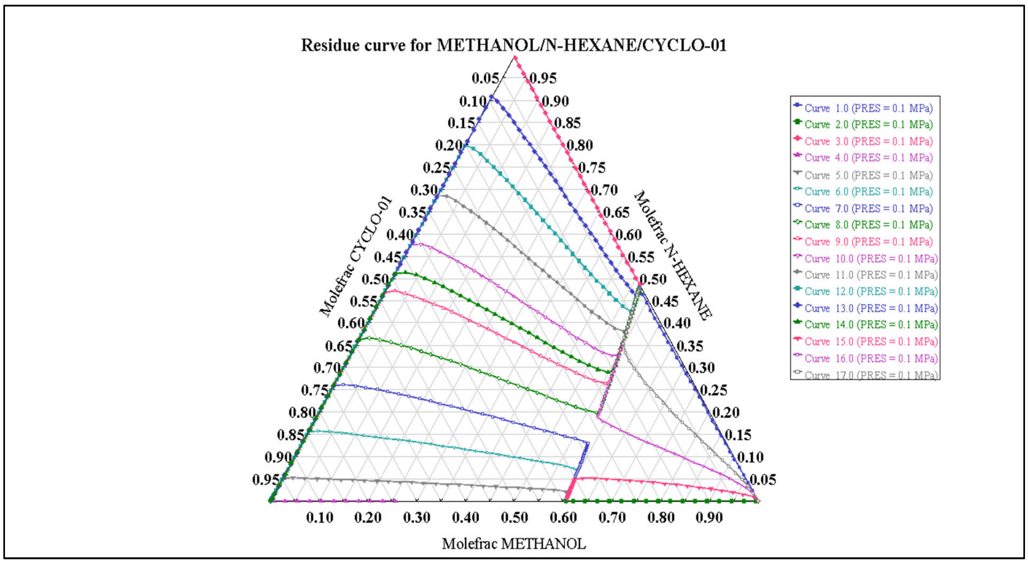

Fig. 7. Residue diagram of LLE behavior of a ternary system comprising methanol, *n*-hexane, and cyclohexane at a pressure of 0.1 MPa and a temperature of 273 K.

The residue curve map provides insights into how methanol, *n*-hexane and cyclohexane behave in LLE systems and serves as a tool for optimizing process design, in chemical engineering applications [26].

4.8 Equilibrium composition analysis

The equilibrium composition analysis for the ternary LLE system involving methanol, n-hexane, and cyclohexane modeled using the NRTL model. The Table 3 displays the mole fractions of each component in two liquid phases (Liquid1 and Liquid2) across ten different equilibrium states.

In the First Phase of Liquid, the mole fraction of methanol gradually decreases from approximately 0.016 to 0.077 as the system progresses from Case 1 to Case 10. This decrease correlates with an increase in the mole fraction of cyclohexane, which starts at around 0.984 in Case 1 and decreases to 0 in Case 10.

In the second phase of the liquid, a similar trend is observed, albeit with different magnitudes. Methanol's mole fraction in the second phase of liquid starts at 0.536 in Case 1 and increases to 0.905 in Case 10. In the second phase of liquid, the mole fraction of *n*-hexane decreases from approximately 0.464 in Case 1 to 0 in Case 10. Meanwhile, cyclohexane's mole fraction in the second phase of liquid starts at 0.4636 in Case 1 and also decreases progressively, reaching 0 by Case 10. This reflects the decreasing presence of these components in the second liquid phase as methanol becomes increasingly dominant [27]. The data illustrates the dynamic nature of the ternary LLE system, indicating shifts in equilibrium compositions between the two liquid phases as the relative proportions of methanol, n-hexane, and cyclohexane change. This information is crucial for designing separation processes and understanding the behavior of these components in liquid-liquid systems.

4.9 Phase envelop composition analysis

In this research we used Aspen to study the composition of phase envelopes and examine how a mixture of cyclohexene, *n*-hexane and methanol behaves for LLE under pressure and temperature settings. By setting the pressure at 0.1 MPa and the temperature, at 273 K we applied the NRTL model to predict how the components are distributed in the system. The mole fraction data provided in Table 4 displays the compositions of methanol, *n*-hexane and cyclohexene along the phase envelope. This analysis helped us understand how the mixture transitions between phase and two phase states and revealed the compositions of phases that coexist in equilibrium. Such studies play a role in chemical engineering by helping design and optimizing separation processes providing insights into managing complex interactions within multicomponent systems [28]. Figure 8 shows a diagram illustrating how a system containing methanol, *n*-hexane and cyclohexane behaves regarding LLE under a pressure of 0.1 MPa and a temperature of 273 K using the NRTL model. Similarly, Fig. 9 presents a diagram using the UNIQUAC model for this system under similar conditions.

Table 3. Mole fractions of each component in two liquid phases (Liquid1 and Liquid2) across ten different equilibrium states

Number of iteration	Mole fractions in first liquid phase			Mole fractions in second liquid phase		
	methanol	*n*-hexane	cyclohexane	methanol	*n*-hexane	cyclohexane
1	0.0162551	0	0.9837448	0.5363701	0	0.4636299
2	0.0290537	0.0832141	0.8877322	0.5810676	0.0289025	0.3900298
3	0.0439087	0.1672862	0.7888051	0.6608919	0.0478967	0.2912113
4	0.057233	0.2516324	0.6911345	0.7556613	0.0545746	0.189764
5	0.0672522	0.3410651	0.5916826	0.812876	0.0597245	0.1273995
6	0.0738118	0.437835	0.4883531	0.8448267	0.0661863	0.0889869
7	0.0775006	0.5430838	0.3794156	0.8659548	0.0731697	0.0608754
8	0.0789673	0.6580601	0.2629725	0.8817116	0.080323	0.0379653
9	0.0787003	0.7841582	0.1371415	0.8944252	0.087526	0.0180487
10	0.0770453	0.9229547	0	0.9052531	0.0947468	0

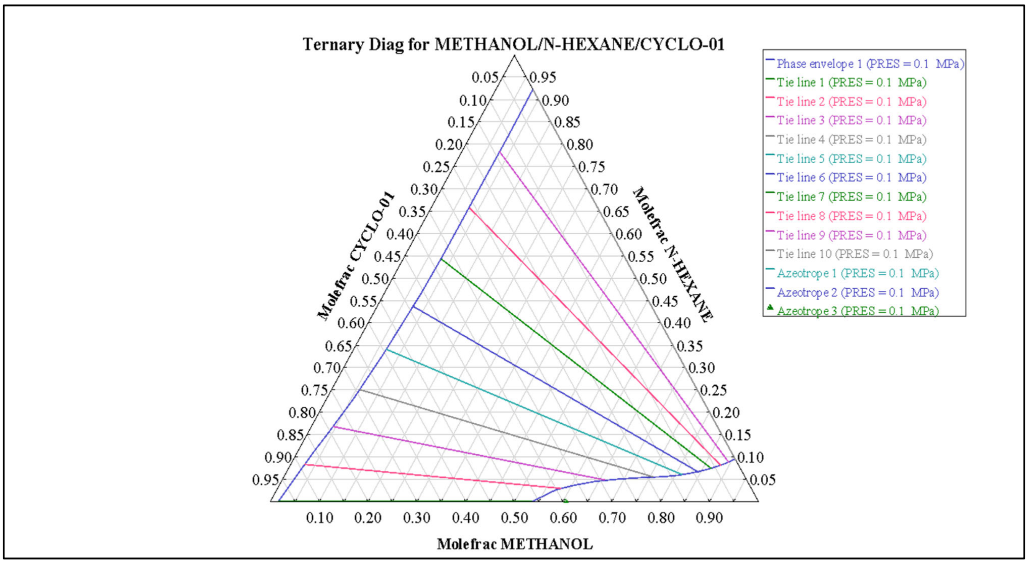

Fig. 8. Ternary diagram for methanol/cyclohexane/hexane system using NRTL Model

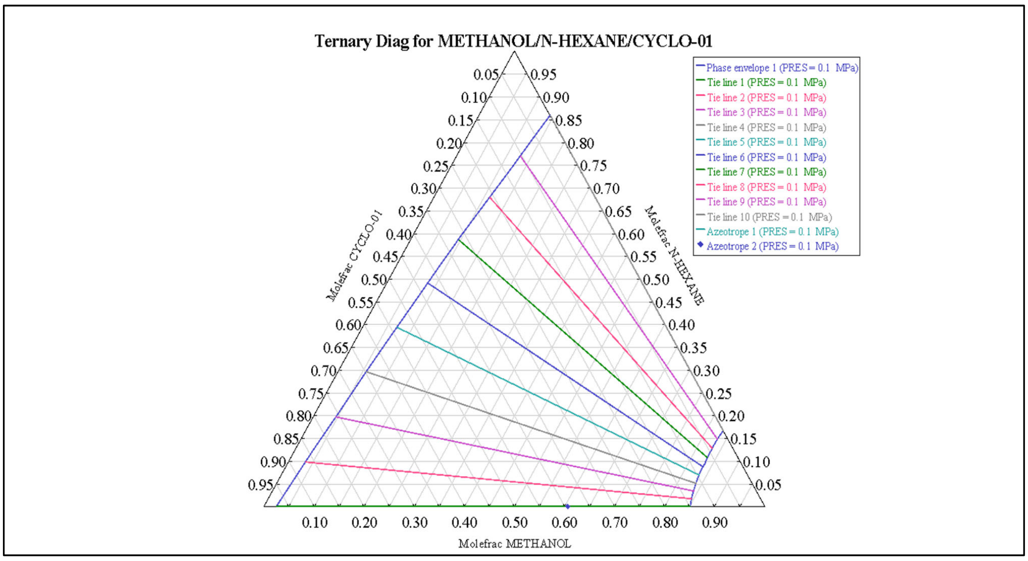

Fig. 9. Ternary diagram for methanol/cyclohexane/hexane system using UNIQUAC Model.

Table 4. Mole fractions of methanol, *n*-hexane, and cyclohexane, at 273 K and 0.1 MPa

Sr No.	Mole fraction of methanol	Mole fraction of *n*-hexane	Mole fraction of cyclohexane
1	0.0163	0	0.9837
2	0.0266	0.0686	0.9048
3	0.0339	0.1112	0.8548
4	0.0411	0.1514	0.8075
5	0.0479	0.1907	0.7614
6	0.0543	0.2311	0.7146
7	0.0604	0.2762	0.6634
8	0.0663	0.3302	0.6035
9	0.0713	0.3946	0.5340
10	0.0752	0.4677	0.4571
...	...	...	...
31	0.5711	0.0244	0.4045
32	0.5364	0	0.4636

4.10 Azeotrope

Azeotropes represent a point in a binary or ternary phase diagram where the vapor and liquid phases have the same composition, resulting in a constant boiling point. This phenomenon arises when components of the mixture reach a specific ratio that creates equilibrium between the phases, which has significant implications for separation processes, particularly distillation. Azeotropes can be challenging because they create a barrier to achieving complete separation using simple distillation, as the mixture boils without changing composition [29]. This may necessitate alternative separation techniques, such as the use of entrainers (third components) or pressure-swing distillation, to break the azeotrope and achieve further separation.

On the other hand, azeotropes can also offer advantages in specific applications where maintaining a consistent composition is beneficial. For example, azeotropes can be used to create solvent mixtures with stable boiling points, which are advantageous in processes requiring precise temperature control [18]. Table 5 illustrates the ternary LLE behavior of methanol, *n*-hexane, and cyclohexane at different temperatures, highlighting azeotrope formation. As the table shows, the mixture's composition shifts at varying temperatures, revealing the presence of azeotropic points. These findings emphasize the complex thermodynamics involved in these systems, which is crucial for designing and optimizing separation processes in industries like pharmaceuticals, petrochemicals, and environmental engineering. Understanding and managing azeotropes help develop efficient strategies for overcoming separation challenges, enhancing process efficiency, and improving product purity [19]. Understanding the behavior of such systems facilitates the development of efficient separation strategies, ultimately enhancing process efficiency and product purity.

Table 5 presents the mole fractions of methanol, *n*-hexane, and cyclohexane at three distinct azeotropic compositions, corresponding to temperatures that differ by only 1 K. Despite this narrow temperature range, the mole fractions of the components exhibit substantial changes. For example, at 326.68 K, the mole fraction of methanol is 0.516, while at 327.36 K, it increases to 0.605, reflecting methanol's

Table 5. Ternary LLE behavior of methanol, *n*-hexane, and cyclohexane with azeotropes at different temperatures

Sr. No.	Mole fraction methanol	Mole fraction *n*-hexane	Mole fraction cyclohexane	Temperature (K)
1	0.516973	0.48302	0	326.6838
2	0.5848372	0.144049	0.2711138	327.5763
3	0.605765	0	0.394235	327.3617

increasing dominance in the system. Similarly, the mole fraction of cyclohexane decreases from 0.483 at 326.68 K to 0.394 at 327.36 K, indicating a reduced presence of cyclohexane in the mixture. These variations underscore the sensitivity of the azeotropic composition to minor temperature fluctuations. This sensitivity is significant for the design of separation processes, where precise temperature control is essential to optimize the recovery of components and maintain azeotropic stability.

5. Conclusion

This study provides a comprehensive evaluation of the vapor-liquid-liquid equilibrium (VLLE) and liquid-liquid equilibrium (LLE) behavior of the methanol, cyclohexane, and *n*-hexane ternary system at 0.1 MPa. Key findings include the identification of critical compositions and temperatures for binary and ternary mixtures. For example, in the binary system, the mole fraction of methanol in the methanol-rich phase increases from 0.045 at 279 K to 0.475 at 321 K, indicating a significant shift in component distribution with temperature. In the ternary system, the mole fractions of methanol and *n*-hexane in the first liquid phase varied from 0.016 to 0.077 and 0 to 0.923, respectively, across equilibrium states. Table 5 highlights the influence of minor temperature changes (1 K) on the azeotropic compositions, with methanol's mole fraction increasing by nearly 9%, demonstrating the sensitivity of the system to thermal conditions.

These results highlight the complex thermodynamic interactions within multicomponent systems and the importance of precise control over operating conditions in separation processes. While this study focuses primarily on the ternary mixture, future work could explore additional systems or incorporate experimental data to validate these findings further. The insights gained are instrumental for designing efficient and environmentally friendly separation processes in the chemical and pharmaceutical industries.

Acknowledgements

This work was supported by the Ministry of Science and Higher Education of the Republic of Kazakhstan under project No. BR21882439.

References

[1]. P. Alessi, M. Fermeglia, I. Kikic, *J. Chem. Eng. Data* 34 (1989) 236–240. DOI:10.1021/je00056a026

[2]. S. Li, X. Huang, Q. Huang, et al., *Fluid Phase Equilib*. 476 (2018) 103–111. DOI:10.1016/J.FLUID.2018.07.013

[3]. M. Ionita, S. Sima, M. Cismondi, C. Secuianu, *Rev. Roum. Chim*. 66 (2021). DOI:10.33224/rrch.2021.66.3.11

[4]. B. Coto, R. Wiesenberg, C. Pando, et al., *Berichte der Bunsengesellschaft für physikalische Chemie* 100 (1996) 482–489. DOI:10.1002/BBPC.19961000413

[5]. D.W. Green, R. H. Perry, "Perry's Chemical Engineers'" Handbook, 8th Ed., 2008. ISBN:978-0-07-159313-7.

[6]. H. Matsuda, K. Ochi, K. Kojima, *J. Chem. Eng. Data* 48 (2003) 184–189. DOI:10.1021/je020156+

[7]. L. Lepori, E. Matteoli, B. Marongiu, *Fluid Phase Equilib.* 42 (1988) 229–240. DOI:10.1016/0378-3812(88)80061-X

[8]. T. Yamaguchi, S. Chong, N. Yoshida, *J. Chem. Phys.* 158 (2023) 084502. DOI:10.1063/5.0142256

[9]. T. Ishikawa, B.C.-Y. Lu, *Fluid Phase Equilib*. 3 (1979) 23–34. DOI:10.1016/0378-3812(79)80025-4

[10]. H. Binous, K. Mejbri, A. Bellagi, *Comput. Appl. Eng. Educ.* 29 (2021) 1589–1601. DOI:10.1002/cae.22411

[11]. K. Kojima, H. Moon, K. Ochi, *Fluid Phase Equilib*. 56 (1990) 269–284. DOI:10.1016/0378-3812(90)85108-M

[12]. A. Gilani, J. Sardroodi, F. Verpoort, S. Rahmdel, *J. Mol. Liq*. 340 (2021) 117196. DOI:10.1016/J.MOLLIQ.2021.117196

[13]. J. Cai, J. Zhang, W. Song, *J. Chem. Eng. Data* 60 (2015) 976–982. DOI:10.1021/JE5010388

[14]. M. Li, Y. Yu, L. Zhang, J. Li, Y. Song, *J. Solution Chem.* 50 (2021) 1258–1284. DOI:10.1007/s10953-021-01116-0

[15]. I. Gascón, H. Artigas, P. Cea, et al., *Phys. Chem. Liq*. 41 (2003) 1–13. DOI:10.1080/00319100290032703

[16]. L. Zhang, Y. Yu, Z. Liao, et al., *J. Chem. Eng. Data* 65 (2020) 477–486. DOI:10.1021/acs.jced.9b00479

[17]. M. Góral, P. Oracz, S. Warycha, *Fluid Phase Equilib.* 135 (1997) 51–61. DOI:10.1016/S0378-3812(97)00065-4

[18]. M.A. Jamali, A. Bissenbay, N. Nuraje, *Eurasian Chem.-Technol J.* 25 (2023) 183–192. DOI:10.18321/ectj1521

[19]. P. Oracz, M. Góral, G. Wilczek-Vera, S. Warycha, *Fluid Phase Equilib*. 112 (1995) 291–306. DOI:10.1016/0378-3812(95)02801-K

[20]. G. Hradetzky, D. Lempe, *Fluid Phase Equilib.* 69 (1991) 285–301. DOI:10.1016/0378-3812(91)90040-E

[21]. H. Renon, J.M. Prausnitz, *Ind. Eng. Chem. Process Des. Dev*. 8 (1969) 413–419. DOI:10.1021/i260031a019

[22]. T.F. Anderson, J.M. Prausnitz, *Ind. Eng. Chem. Process Des. Dev.*, 17 (1978) 552–561. DOI:10.1021/i260068a028

[23]. Z. Zhang, P. Jia, D. Huang, et al., *J. Chem. Eng. Data* 58 (2013) 3054–3060. DOI:10.1021/JE4004993

[24]. J.-H. Oh, S.-J. Park, *J. Chem. Eng. Data* 50 (2005) 1564–1569. DOI:10.1021/JE050029O

[25]. M. Rolemberg, M. Krähenbühl, *J. Chem. Eng. Data* 46 (2001) 256–260. DOI: 10.1021/JE000059L

[26]. C. Lindemann, P. Duchet-Suchaux, A. Razzouk, et al., *J. Chem. Eng. Data* 61 (2016) 2412–2418. DOI: 10.1021/ACS.JCED.6B00022

[27]. Y. Tanaka, M. Kawakami, *Fluid Phase Equilib*. 125 (1996) 103–114. DOI:10.1016/S0378-3812(96)03108-1

[28]. M. Domínguez, S. Martín, H. Artigas, et al., *J. Chem. Eng. Data* 47 (2002) 405–410. DOI: 10.1021/JE0101707

[29]. B. Khalfaoui, A. Meniai, R. Borja, *Fluid Phase Equilib*. 127 (1997) 181–190. DOI:10.1016/S0378-3812(96)03129-9