

Isobaric Vapor–Liquid Equilibrium for Binary System of *N*-Methyl-2-pyrrolidone + γ -Butyrolactone at 10.0, 20.0, and 101.3 kPa

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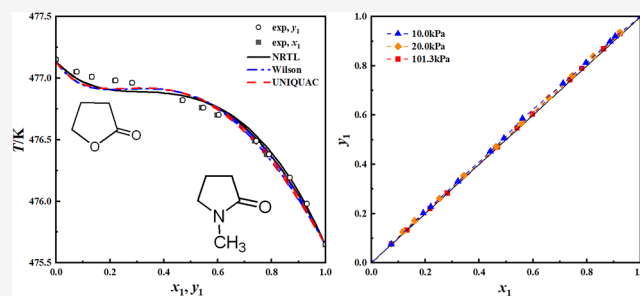


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ABSTRACT: The removal of γ -butyrolactone (GBL) from *N*-methyl-2-pyrrolidone (NMP) to produce electronic-grade NMP is a significant challenge to meet the rigorous purity standards of semiconductor manufacturing. Therefore, reliable thermodynamic data and models are essential for designing an intensified separation process. Herein, isobaric vapor–liquid equilibrium (VLE) data for the {NMP + GBL} binary system at 10.0, 20.0, and 101.3 kPa were determined by a Fischer Labodest VLE 602 ebulliometer. The results show that the {NMP + GBL} system is a close-boiling nonazeotropic mixture over the investigated pressure ranges. To verify the reliability of the experimental data, Herington area and Van Ness point tests used to determine the thermodynamic consistency of VLE data illustrate that all of the data have passed the test. In addition, the VLE data measured in the experiment are correlated with nonrandom two-liquid (NRTL), Wilson, and UNIQUAC activity coefficient models, and all three models show good agreement with the experimental data for this binary system. This study provides essential thermodynamic data and model parameters to support the development of purification processes for electronic-grade NMP.



1. INTRODUCTION

N-Methyl-2-pyrrolidone (NMP) is a strongly polar aprotic solvent with a high boiling point and excellent chemical stability.^{1,2} γ -Butyrolactone (GBL) is a cyclic ester known for its high solvency power and applications in pharmaceuticals, petrochemicals, and biodegradable polymers.³ Both NMP and GBL serve as excellent solvents in traditional industrial processes and have also gained importance in electronic materials manufacturing.^{3,4}

In traditional petrochemical processing, NMP acts as an effective extraction medium owing to its low volatility and strong affinity for aromatic compounds.^{5,6} In addition to its use in the surface treatment of textiles, resins, and plastics, NMP is also widely employed in pharmaceutical applications as a penetration enhancer and solubilizing agent.^{7,8} Within the pharmaceutical industry, NMP serves as a key solvent for drug extraction and crystallization, where it enhances solubility and permeability by acting as both cosolvent and complexing agent.⁹ Beyond these roles, NMP has become more and more important in advanced materials processing. It demonstrates exceptional capability in maintaining dispersions of nanomaterials such as graphene, single-walled carbon nanotubes, and other layered materials after their exfoliation.^{10–12} Furthermore, in photovoltaic (PV) module recycling, NMP emerges as a green alternative.¹³ Its structural similarity to 1,3-dimethylpropylene urea (DMPU) with carbonyl functionality, high boiling point, and chemical stability enables it to effectively dissolve ethylene-vinyl acetate (EVA) encapsulant

at temperatures below its boiling point.¹⁴ These attributes, together with its low cost and minimal environmental impact, make NMP a promising agent for improving the sustainability of PV module recycling.

Despite its widespread industrial utility, NMP has been classified as a substance of very high concern because of its reproductive toxicity. This classification has led to regulatory restrictions under frameworks such as the EU REACH regulation and the US EPA.^{15,16} These restrictions primarily target consumer products, including herbicides, pigments, and cosmetics, rather than prohibiting its use in enclosed industrial processes. Importantly, the unique physicochemical properties of NMP make it a solvent of great interest in industrial separation processes.¹⁷ These properties include its miscibility with both water and organic solvents, its high polarity, and its exceptional thermal stability. In recent studies, in the separation of ethyl acetate and *n*-heptane azeotrope, NMP has demonstrated superior extraction performance compared with several conventional solvents such as dimethyl sulfoxide, dimethylformamide, and ethylene glycol.¹⁸ With the develop-

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Table 1. Experimental Reagents Information

reagents	CAS no.	molecular weight (g·mol ⁻¹) ^a	boiling point (K) ^{a,b}	density (g·cm ⁻³) ^{a,c}	source	purity (in a mass fraction) ^a	water content (mass fraction, %) ^d	analysis ^e	purification
N-methyl-2-pyrrolidone	872-50-4	99.13	475.15	1.028	Aladdin	≥0.999	0.04	GC	none
γ-butyrolactone	96-48-0	86.09	477.15	1.120	Sigma-Aldrich	≥0.99	0.02	GC	none
isopropanol	67-63-0	60.10	355.15	0.785	Aladdin	≥0.999		GC	none
acetone	67-64-1	58.08	329.15	0.791	Aladdin	≥0.995		GC	none

^aSpecified by the commercial suppliers. ^bAt a pressure of 101.3 kPa. ^cAt a temperature of 298.15 K and a pressure of 101.3 kPa. ^dKarl Fischer (KF) titration. ^eGas chromatography (GC).

ment of the electronic industry, the market demand for high-quality NMP products will continue to grow.¹⁹

The critical importance of NMP is particularly evident in high-technology manufacturing sectors such as lithium-ion batteries and semiconductors, where stringent purity standards are essential.^{20,21} In lithium-ion battery production, the preparation of homogeneous and stable electrode slurries is crucial for controlled coating processes.^{22,23} NMP is a widely used solvent in cathode formulations due to its ability to dissolve the polyvinylidene fluoride (PVDF) binder, which is a fundamental component alongside active materials and conductive carbon black.²⁴ Despite ongoing efforts to identify alternatives, comprehensive assessments confirm that no fully mature substitute has yet been achieved for widespread industrial adoption. Consequently, NMP remains an industry benchmark for this function and continues to be the preferred solvent for cathode preparation, as emphasized in electrolyte and electrode designs for high-performance lithium-ion batteries.²⁵ This solvent capability, together with its excellent chemical and thermal stability, high boiling point, and low autoignition temperature, has established its global use in battery manufacture.^{26,27}

In the semiconductor industry, NMP is indispensable in photolithography processes.²⁸ Photoresist formulations comprise complex mixtures of polymeric resins, radiation-sensitive compounds, and solvents that must work together to delineate intricate circuit patterns. The subsequent photoresist stripping step requires complete and uniform removal of residual polymers without damaging the underlying wafer substrate.²⁹ Liquid NMP is used in formulations designed to remove both photoresists and bottom antireflective coatings (BARCs).³⁰ Although NMP is generally stable with slow oxidation rates in air and high hygroscopicity, its behavior under precision manufacturing conditions still requires careful consideration.³¹ Studies indicate that oxidation can occur in the presence of transition metals through catalytic mechanisms or under UV light with hydroxyl radical initiators.³⁰ The potential degradation pathways highlight the necessity for ultrahigh purity in electronic-grade NMP, as even trace impurities or degradation products can adversely affect semiconductor wafer surfaces, compromising device yield and reliability.³²

NMP is typically produced by the reaction of GBL with methylamine on an industrial scale.³³ This method is often preferred over alternative pathways, such as the catalytic hydrogenation of maleic anhydride or its derivatives, which typically requires high hydrogen pressures.² Consequently, GBL is not only a feedstock but also emerges as a primary impurity in the final NMP product. This presents a significant purification challenge, particularly for the semiconductor industry.^{34,35} Electronic-grade NMP, indispensable in semiconductor manufacturing, is subject to stringent industrial

specifications that require an organic purity of over 99.9%, alongside rigorous limitations on trace impurities to ensure safety and compatibility in advanced device manufacturing.^{36,37} The separation of NMP and GBL is difficult due to their pronounced chemical similarity and closely matched physical properties, most notably their nearly identical boiling points. This close-boiling behavior results in a relative volatility close to unity, rendering conventional separation techniques like standard extractive or azeotropic distillation highly inefficient for achieving the requisite ultrahigh purity.³⁸ While some studies have explored alternative separation strategies, the fundamental challenge persists.^{39–42} For example, Yin et al.⁴³ reported that perethylated pillar[5]arene (EtPS) achieves 99% selectivity for GBL over NMP through size-specific recognition. Despite such promising findings, the development of efficient and precise industrial-scale processes to remove trace GBL from NMP remains a critical pursuit for the production of electronic-grade solvents.^{44,45} This goal underscores the need for reliable thermodynamic data to guide the process design.

Vapor–liquid equilibrium (VLE) data are essential for designing distillation processes, as they describe the distribution of components between vapor and liquid phases.^{46–48} The experimental method employed for VLE measurements follows a well-established procedure that has been widely adopted and validated in previous studies.^{49,50} For example, Yan et al.⁵¹ measured the VLE for the {GBL + succinic anhydride} system at multiple pressures and verified its thermodynamic consistency. Li et al.⁵² determined the VLE for acetophenone and 1-phenylethanol at low pressures and correlated the data using the nonrandom two-liquid (NRTL) model. In another study, Rojas et al.⁵³ used VLE data to develop a pressure-swing distillation process for the isoamyl acetate and isoamyl alcohol system. Following these established methodologies, the measurement of VLE data to realize reliable thermodynamic models for the {NMP + GBL} system is a challenge that must be addressed to support process design.

In this paper, the isobaric VLE data for the {NMP + GBL} binary system were measured at 10.0, 20.0, and 101.3 kPa. For the measurements, a Fischer Labodest VLE 602 ebulliometer was used and widely employed in vapor–liquid equilibrium studies for its reliability and accuracy under various pressures.^{54,55} These measurements were conducted to systematically investigate the influence of pressure on the phase equilibrium behavior of the system. All experimental data passed the Herington area test⁵⁶ and the Van Ness point test⁵⁷ to ensure their thermodynamic consistency. In addition, NRTL,⁵⁸ Wilson,⁵⁹ and UNIQUAC models were used to correlate the experimental data, in order to provide reliable thermodynamic models and parameters for the simulation, design, and optimization of distillation processes.

2. EXPERIMENTAL SECTION

2.1. Materials

The chemicals used in this work were employed as supplied without further purification. Although the chemicals were used as received, their purities were verified by gas chromatography (GC) prior to the experiments. The impurity content in GBL was less than 0.01 mass fraction, and these impurities were structurally similar compounds with boiling points close to GBL. Given the low impurity levels and their similar physicochemical properties, the influence of such impurities on the measured equilibrium temperatures is negligible and within the experimental uncertainty. This is further supported by the satisfactory thermodynamic consistency of all measured VLE data. The mass fraction purities of the reagents were determined using an Agilent 8890 GC system, equipped with a flame ionization detector (FID) and a DM-624 ms capillary column (60 m $\times$ 320 μ m $\times$ 1.8 μ m). The water content of compounds was determined by coulometric Karl Fischer titration (KF). The CAS numbers, commercial sources, and purities of the reagents are summarized in Table 1.

2.2. Apparatus and Procedure

The VLE data for the {NMP + GBL} binary system were obtained using a Fischer Labodest VLE 602 ebulliometer (Germany). The accuracies of temperature and pressure, as specified by the manufacturer, were within ± 0.01 K and ± 0.01 kPa, respectively. The equilibrium temperature was recorded with a built-in thermocouple, and a schematic diagram of the experimental setup was provided in the work of Dias et al.⁶⁰ The Fischer Labodest VLE 602 ebulliometer employed is a well-established apparatus based on the Cottrell dynamic recirculation principle, which is widely recognized as one of the most reliable and accurate methods for isobaric VLE measurements at low to moderate pressures.^{61,62} Compared with static equilibrium cells, the dynamic recirculation design offers a relatively simple apparatus structure and straightforward operation, while rapidly providing complete VLE data that include both liquid and vapor-phase compositions.^{63,64} This feature enables fast attainment of phase equilibrium and effectively reduces the risk of thermal decomposition of the components, making it particularly suitable for high boiling, strongly polar systems such as NMP and GBL. The broad applicability and reliability of this apparatus for VLE measurements on challenging binary systems have been demonstrated in numerous recent studies, including the determination of VLE for the close-boiling mixture {methylcyclohexane + toluene},⁶⁵ the evaluation of greener entrainers for the {*n*-hexane + ethanol} azeotropic system,⁴⁸ and the measurement of the {ethanol + 3-methyl-1-butanol} system at multiple pressures.⁵⁵

The mass of each reagent was measured by a Sartorius BP210S electronic balance (Germany) with an accuracy of 0.0001 g. Approximately 95 mL of the prepared mixture was introduced into a 250 mL ebulliometer. System pressure was controlled by a Welch CRVpro6 vacuum pump, connected to an i-Fischer Unicontrol VLE digital interface, and maintained at the target value by adjusting a digital controller and a needle valve. All sampling and vent ports were sealed with caps fitted with silicone rubber septa and needle-valve stoppers to ensure system airtightness and prevent atmospheric contamination. Equilibrium conditions were achieved when the temperature and pressure in the setup remained constant within tolerances of 0.1 K and 0.03 kPa, respectively. The temperature stabilized within 20 min, and an additional 30 min was allowed before sampling to ensure that equilibrium conditions were fully established. The total duration for each experimental point was approximately 50 min. Heating was provided by an immersion heating rod in the liquid chamber, while an external thermal insulation jacket was used to minimize the heat loss. A magnetic stirrer was used to ensure a continuous and thorough mixing of the liquid phase. The produced vapor during boiling was condensed by a laboratory cooling circulator (LAUDA Microcool MC250, Germany) and returned to the liquid chamber as reflux, thereby enhancing the internal circulation and

thermal homogeneity. These measurements collectively guaranteed the temperature stability and uniformity throughout the experiments.

At equilibrium, approximately 1.5 mL of both the liquid and condensed vapor was sampled. Liquid-phase samples were withdrawn via a sampling valve, and vapor-phase samples were collected as condensed droplets by using a syringe. The composition of each sample was subsequently determined by GC analysis via an autosampler.

2.3. Analysis

The compositions of the vapor and liquid phases were determined using an Agilent 8890 GC equipped with FID, and chromatographic data were processed using OpenLab CDS software. Ultrahigh-purity hydrogen (mass fraction >0.99999) was used as the carrier gas at a constant flow rate of 40 mL·min⁻¹. For the analysis of the {NMP + GBL} system, the column temperature was maintained at 353.15 K, while the injector and detector temperatures were set at 523.15 K. Each sample was analyzed in triplicate to ensure quantitative accuracy, and the average value was used for subsequent calculations. The standard uncertainties for pressure, temperature, and phase compositions were quantified following the guidelines of Taylor and Kuyatt,⁶⁶ with calculation equations provided in the Supporting Information (eqs S1–S4). Quantitative analysis was performed using the area normalization method, which eliminates the need for additional calibration as the relative component concentrations are determined directly from the integrated peak areas.

2.4. Water Content Determination

Water content is routinely measured for hygroscopic materials to ensure the reliability of experimental measurements. The water contents of NMP and GBL were measured by coulometric KF titration using a METTLER TOLEDO C30S (Switzerland) Compact Coulometer equipped with a generator electrode without diaphragm. HYDRANAL-Coulomat AG (Honeywell, Germany) was used as the anolyte. Prior to measurements, the system was conditioned to a stable drift below 10 μ g·min⁻¹. Approximately 2 mL of sample was injected through a septum into the titration cell using a gastight syringe. The exact sample mass was determined by weighing the syringe before and after injection, using the Sartorius BP210S electronic balance. Each sample was analyzed in triplicate, and the water mass content is reported in Table 1.

3. RESULTS AND DISCUSSION

3.1. Validation of the Apparatus

To verify the reliability of the Fischer Labodest VLE 602 ebulliometer and our experimental methodology, the isobaric VLE data for the {acetone (1) + isopropanol (2)} binary system at atmospheric pressure were measured and compared with literature data.^{67,68} Both sets of literature data have successfully passed thermodynamic consistency tests, ensuring their reliability for the purpose of validation purposes. The results, presented in Table 2 and Figure 1, show excellent agreement between the experimental and literature values, confirming the accuracy of the experimental apparatus. The extended Antoine equation parameters with the corresponding applicable temperature ranges for the pure components of the binary system are summarized in Table S1.

3.2. Experimental Data

According to the extended Antoine equation (eq 1), the saturated vapor pressure equations of pure reagents NMP and GBL are obtained. The corresponding parameters (C_1 to C_9) for the applicable temperature ranges are retrieved from the Aspen Plus property database and are listed in Table 3.

Table 2. Experimental VLE Data and Activity Coefficients for the Binary System of {Acetone (1) + Isopropanol (2)} at 101.3 kPa^a

No.	<i>T</i> /K	<i>x</i> ₁	<i>y</i> ₁	<i>γ</i> ₁	<i>γ</i> ₂
1	354.95	0.000	0.000		1.000
2	349.71	0.095	0.267	1.404	1.014
3	347.22	0.143	0.365	1.482	1.017
4	343.02	0.237	0.509	1.355	1.071
5	339.80	0.353	0.630	1.271	1.091
6	338.14	0.412	0.677	1.235	1.120
7	335.65	0.551	0.770	1.130	1.183
8	334.36	0.626	0.813	1.083	1.262
9	332.15	0.759	0.870	1.038	1.477
10	329.97	0.934	0.964	1.008	1.729
11	329.31	1.000	1.000	1.000	

^aStandard uncertainties: $u(T) = 0.09$ K, $u(p) = 0.05$ kPa, and $u(x_1) = u(y_1) = 0.003$. A comparison of the pure-compound vapor pressures of acetone and isopropanol with literature data leads to the recommendation of an additional temperature uncertainty of $\Delta(T) = 0.2$ K.

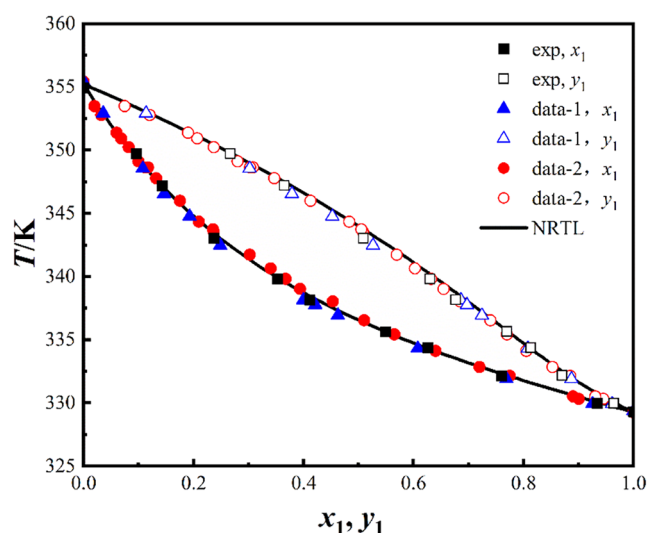


Figure 1. *T*–*x*–*y* diagram for {acetone (1) + isopropanol (2)} binary system at 101.3 kPa; (■) experimental liquid and (□) vapor phases in this work; (red solid circle) experimental liquid and (red open circle) vapor phases from the literature data-1;⁶⁷ (blue triangle solid) experimental liquid and (blue triangle open) vapor phase from the literature data-2;⁶⁸ (solid line) regressed with the NRTL model.

$$\ln(p_i^s) = C_{1i} + \frac{C_{2i}}{T/K + C_{3i}} + C_{4i}(T) + C_{5i} \ln(T) + C_{6i}(T)^{C_{7i}} \quad \text{for } C_{8i} \leq T \leq C_{9i} \quad (1)$$

where p_i^s (kPa) is the vapor pressure of pure component *i* at system temperature *T* (K).

The reference vapor pressures for NMP and GBL were obtained from the NIST ThermoData Engine (TDE) database

accessed via Aspen Plus V14, which implements the critically evaluated Wagner-type equation (Wagner25) for pure-component vapor pressure calculations. As shown in Figure S1, the GBL data between experimental and calculated vapor pressures show small random deviations within $\pm 1.5\%$, which can be attributed to trace moisture, minor nonvolatile impurities, or slight offsets in temperature calibration. For NMP, a minor systematic positive offset is observed, likely due to the formation of oxidative products of NMP upon heating with trace oxygen.

We present the isobaric VLE data for the binary system {NMP + GBL} at 10.0, 20.0, and 101.3 kPa in Table 4. The relative volatilities α_{12} (eq 2) listed in Table 4 are all close to unity, indicating that the separation of NMP and GBL by conventional distillation is a particular challenge. The activity coefficient for each component is calculated from the experimental data using eq 3.

$$\alpha_{12} = \frac{y_1/(1 - y_1)}{x_1/(1 - x_1)} \quad (2)$$

$$y_i \phi_i^s p = x_i \gamma_i \phi_i^s p_i^s \exp \left[\frac{V_i^l(p - p_i^s)}{RT} \right] \quad (3)$$

The y_i and x_i are the mole fractions of component *i* in the vapor and liquid phases, respectively; *p* is system pressure, and p_i^s is the vapor pressure of pure component *i* at system temperature *T*. γ_i is the activity coefficient of component *i*. The terms ϕ_i and ϕ_i^s represent the fugacity coefficients of pure component *i* in the vapor phase. ϕ_i is evaluated at the system temperature *T* and total pressure *p*, while ϕ_i^s is estimated at the system temperature *T* and vapor pressure (p_i^s). V_i^l is the molar volume of pure liquid component *i*, and *R* is the universal gas constant.

The vapor phase can be considered ideal at the low pressures of 10.0, 20.0, and 101.3 kPa employed in this study, in which the exponential terms $\exp \left[\frac{V_i^l(p - p_i^s)}{RT} \right]$, as well as ϕ_i and ϕ_i^s , are all equal to 1. Consequently, eq 3 can be simplified to eq 4.

$$y_i p = x_i \gamma_i p_i^s \quad (4)$$

3.3. Consistency Test

To validate the thermodynamic consistency of the measured VLE data, we performed the Herington area test and the Van Ness point test. The Herington test criteria, which are derived from the Gibbs–Duhem⁶⁹ equation, are given in eqs 5 and 6.

$$D = 100 \times \left| \frac{S_+ - S_-}{S_+ + S_-} \right| \quad (5)$$

where S_+ and S_- are obtained from $\ln(\gamma_1/\gamma_2) - x_1$ plot. S_+ is the area above the *x* axis of the plot, and S_- is the area below the *x* axis.

Table 3. Parameters of the Extended Antoine Equation^a

component	<i>C</i> ₁	<i>C</i> ₂	<i>C</i> ₃	<i>C</i> ₄	<i>C</i> ₅	<i>C</i> ₆	<i>C</i> ₇	<i>C</i> ₈ (K)	<i>C</i> ₉ (K)
NMP	61.3564	−8349.8	0	0	−6.3622	3.2235×10^{-18}	6	249	722
GBL	35.5502	−6906.6	0	0	−2.6687	2.5849×10^{-19}	6	230	731

^aFrom Aspen Plus, version 14.

Table 4. Experimental Isobaric VLE Data of Liquid and Vapor Mole Fractions (x_1 , y_1), Activity Coefficients (γ_1 , γ_2), and Absolute Deviations between Experimental and Calculated Values for Temperature (ΔT) and Vapor-Phase Mole Fraction (Δy) for the {NMP (1) + GBL (2)} System at 10.0, 20.0, and 101.3 kPa^a

T/K	x_1	y_1	γ_1	γ_2	α_{12}	NRTL		Wilson		UNIQUAC	
						Δy_1	ΔT	Δy_1	ΔT	Δy_1	ΔT
$p = 10.0 \text{ kPa}$											
398.00	1.000	1.000	1.000			0.000	0.00	0.000	0.00	0.000	0.00
398.46	0.905	0.919	1.002	0.909	1.191	0.002	0.07	0.002	0.09	0.002	0.08
398.70	0.886	0.899	0.995	0.972	1.145	0.001	0.24	0.001	0.26	0.001	0.24
398.90	0.797	0.812	0.994	0.977	1.100	0.005	0.11	0.005	0.14	0.005	0.13
399.08	0.712	0.729	0.989	0.989	1.088	0.005	0.01	0.006	0.04	0.006	0.04
399.46	0.561	0.585	0.985	0.996	1.103	0.004	0.01	0.003	0.00	0.003	0.00
399.64	0.492	0.506	0.984	0.996	1.058	0.003	0.02	0.004	0.02	0.004	0.02
399.67	0.442	0.453	0.978	1.002	1.045	0.004	0.04	0.005	0.05	0.005	0.04
399.90	0.321	0.331	0.972	1.003	1.047	0.001	0.01	0.000	0.01	0.000	0.00
399.99	0.221	0.228	0.982	1.000	1.041	0.001	0.00	0.001	0.02	0.001	0.02
400.02	0.193	0.202	0.975	1.002	1.058	0.004	0.00	0.004	0.02	0.004	0.01
400.11	0.074	0.075	1.006	0.999	1.015	0.001	0.01	0.001	0.02	0.001	0.01
400.16	0.000	0.000		1.000		0.000	0.04	0.000	0.04	0.000	0.03
$p = 20.0 \text{ kPa}$											
417.90	1.000	1.000	1.000			0.000	0.00	0.000	0.00	0.000	0.00
418.15	0.924	0.935	1.006	0.895	1.183	0.002	0.06	0.003	0.03	0.003	0.03
418.51	0.824	0.839	0.994	0.986	1.113	0.001	0.07	0.001	0.02	0.001	0.03
418.82	0.746	0.761	0.987	0.994	1.084	0.003	0.01	0.004	0.03	0.004	0.03
419.05	0.658	0.671	0.981	1.003	1.060	0.006	0.03	0.007	0.01	0.006	0.00
419.23	0.557	0.567	0.973	1.013	1.041	0.007	0.09	0.008	0.06	0.008	0.07
419.44	0.463	0.472	0.969	1.010	1.037	0.005	0.06	0.006	0.06	0.006	0.06
419.76	0.343	0.354	0.971	0.999	1.050	0.000	0.07	0.000	0.04	0.000	0.05
419.92	0.253	0.262	0.969	0.998	1.048	0.001	0.10	0.001	0.07	0.001	0.07
420.03	0.161	0.171	0.991	0.995	1.075	0.003	0.08	0.004	0.06	0.004	0.06
420.07	0.117	0.126	1.003	0.995	1.088	0.003	0.05	0.004	0.04	0.004	0.04
420.10	0.074	0.076	0.956	1.003	1.029	0.002	0.01	0.002	0.01	0.002	0.01
420.20	0.000	0.000		1.000		0.000	0.04	0.000	0.04	0.000	0.04
$p = 101.3 \text{ kPa}$											
475.65	1.000	1.000	1.000			0.000	0.01	0.000	0.01	0.000	0.01
475.98	0.923	0.932	1.002	0.909	1.143	0.003	0.02	0.003	0.05	0.003	0.04
476.19	0.862	0.869	0.995	0.972	1.062	0.002	0.01	0.002	0.06	0.002	0.04
476.38	0.781	0.79	0.994	0.977	1.055	0.001	0.04	0.002	0.01	0.002	0.00
476.49	0.737	0.744	0.989	0.989	1.037	0.003	0.03	0.004	0.01	0.004	0.00
476.7	0.598	0.604	0.985	0.996	1.025	0.001	0.06	0.002	0.05	0.002	0.04
476.76	0.541	0.547	0.984	0.996	1.024	0.001	0.05	0.000	0.06	0.000	0.05
476.82	0.468	0.471	0.978	1.002	1.012	0.000	0.04	0.001	0.06	0.000	0.05
476.96	0.282	0.283	0.972	1.003	1.005	0.001	0.07	0.001	0.04	0.001	0.04
476.98	0.218	0.221	0.982	1.000	1.018	0.002	0.08	0.003	0.07	0.003	0.06
477.01	0.132	0.133	0.975	1.002	1.009	0.001	0.07	0.000	0.08	0.000	0.08
477.05	0.074	0.077	1.006	0.999	1.044	0.001	0.05	0.001	0.07	0.001	0.07
477.15	0.000	0.000		1.000		0.000	0.02	0.000	0.02	0.000	0.01

^aStandard uncertainties u are $u(T) = 0.09$ K, $u(p) = 0.05$ kPa, and $u(x_1) = u(y_1) = 0.003$. On the basis of comparison of pure-compound vapor pressures with literature data, an additional temperature uncertainty estimate of $u(T) = 1$ K is recommended.

$$J = 150 \times \frac{T_{\max} - T_{\min}}{T_{\min}} \quad (6)$$

where $T_{\max}$ and $T_{\min}$ represent the maximum and minimum temperatures of the system, respectively.

According to the Herington area test, isobaric VLE data are considered thermodynamically consistent when the $|D - J|$ value does not exceed 10.⁵⁶ Our calculations yield $|D - J|$ values of 5.93, 9.39, and 3.88 for the {NMP + GBL} binary system at 10.0, 20.0, and 101.3 kPa, respectively, confirming the thermodynamic consistency of the experimental data.

To evaluate the agreement between the experimental and calculated values, Table 4 lists the absolute deviations for both vapor-phase mole fraction and equilibrium temperature. The absolute deviations of the vapor-phase mole fraction (Δy_i) and the equilibrium temperature (ΔT) are calculated using the following eqs 7 and 8.

$$\Delta y_i = |y_i^{\text{exp}} - y_i^{\text{cal}}| \quad (7)$$

$$\Delta T = |T^{\text{exp}} - T^{\text{cal}}| \quad (8)$$

In these equations, the symbols y_i^{exp} and y_i^{cal} refer to the experimental and calculated vapor-phase mole fractions of

component i , and T^{exp} and T^{cal} are the corresponding experimental and calculated equilibrium temperatures, respectively. The calculated values (y_i^{cal} , T^{cal}) are obtained from the NRTL, Wilson, and UNIQUAC models.

We further validate the VLE data using the Van Ness point test, for which the average deviation of the vapor-phase mole fraction (Δy) is defined by eq 9.

$$\Delta y = \frac{1}{N} \sum_{i=1}^N |y_i^{\text{exp}} - y_i^{\text{cal}}| \quad (9)$$

where N is the total number of experimental points.

For the Van Ness point method, Gmehling and Onken⁷⁰ have suggested that isobaric VLE data are thermodynamically consistent if Δy does not exceed 0.01. The results presented in Table 5 indicate that all Δy_i values are less than 0.01, satisfying

Table 5. Deviations Δy from Correlation Models and Van Ness Test Results

p/kPa	model	Δy	result
10.0	NRTL	0.003	passed
	Wilson	0.003	passed
	UNIQUAC	0.003	passed
20.0	NRTL	0.003	passed
	Wilson	0.004	passed
	UNIQUAC	0.003	passed
101.3	NRTL	0.002	passed
	Wilson	0.002	passed
	UNIQUAC	0.001	passed

the criterion of the Van Ness test for thermodynamic consistency. In addition, according to the Van Ness test, the VLE data are regarded as thermodynamically consistent if the residual distribution of $\ln(\gamma_1/\gamma_2)$ exhibits random behavior without any systematic trend. As shown in Figure S4, the residuals display satisfactory randomness, which affirms the thermodynamic consistency of the experimental VLE data.

3.4. Data Correlation

The NRTL, Wilson, and UNIQUAC models are commonly applied to nonideal systems under low-pressure conditions. We correlate all the experimental VLE data using the NRTL, Wilson, and UNIQUAC activity coefficient models with the maximum likelihood method. The equations for these models are provided in Table 6, and the objective function (OF) is shown in eq 10.⁷¹

$$\text{OF} = \sum_{i=1}^N \left[\left(\frac{T_i^{\text{exp}} - T_i^{\text{cal}}}{\sigma_T} \right)^2 + \left(\frac{p_i^{\text{exp}} - p_i^{\text{cal}}}{\sigma_p} \right)^2 + \left(\frac{x_i^{\text{exp}} - x_i^{\text{cal}}}{\sigma_x} \right)^2 + \left(\frac{y_i^{\text{exp}} - y_i^{\text{cal}}}{\sigma_y} \right)^2 \right] \quad (10)$$

where N is the number of experimental points and σ is the standard deviation. The symbols T , p , x , and y denote the equilibrium temperature (K), pressure (kPa), liquid mole fraction, and vapor mole fraction, respectively. The superscripts “exp” and “cal” abbreviate “experimental” and “calculated”, respectively.

In the NRTL model, $g_{ij} - g_{ji}$ represents the binary interaction energy parameter. The nonrandomness parameter α in the

Table 6. Mathematical Forms of the Activity Coefficient Equations Used in This Work

NRTL
$\ln \gamma_i = x_j^2 \left[\frac{G_{ji}^2 \tau_{ji}}{(x_i + x_j G_{ji})^2} + \frac{G_{ij}^2 \tau_{ij}}{(x_j + x_i G_{ij})^2} \right]$ $\tau_{ij} = \frac{g_{ij} - g_{ji}}{RT}, G_{ij} = \exp(-a_{ij} \tau_{ij}), a_{ij} = a_{ji}$
Wilson
$\ln \gamma_i = -\ln(x_i + \Lambda_{ij} x_j) + x_j \left(\frac{\Lambda_{ij}}{x_i + \Lambda_{ij} x_j} - \frac{\Lambda_{ji}}{x_j + \Lambda_{ji} x_i} \right)$ $\Lambda_{ij} = \frac{V_j}{V_i} \exp \left(-\frac{\lambda_{ji} - \lambda_{ii}}{RT} \right)$ $V_i = \frac{RT_{c,i}}{P_{c,i}} Z_{c,i}, \tau_i = 1 + (1 - T/T_{c,i})^{2/7}, T/T_{c,i} \leq 0.75$
UNIQUAC
$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} - q_i \ln t'_i - q'_i \sum_j \frac{\theta'_j \tau_{ij}}{t'_j} + l_i + q'_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j$ $\Phi_i = \frac{r_i x_i}{\sum_k r_k x_k}, \theta_i = \frac{q_i x_i}{\sum_k q_k x_k}, \theta'_i = \frac{q'_i x_i}{\sum_k q'_k x_k}, t'_i = \sum_j \theta'_j \tau_{ji}$ $l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1), \tau_{ij} = \exp \left(-\frac{u_{ij} - u_{ji}}{RT} \right)$

NRTL model is fixed at 0.3, as originally recommended. The value of α generally varies between 0.20 and 0.47 depending on the system.⁵⁸ For polar–polar mixtures such as {NMP + GBL}, $\alpha = 0.3$ is the most commonly adopted value and has been extensively used for VLE correlation of similar systems.⁷² The good agreement between the experimental data and the NRTL model supports the appropriateness of this selection. For the Wilson model, the parameter $\lambda_{ji} - \lambda_{ii}$ is the binary interaction energy parameter.⁷³ The critical properties temperature ($T_{c,i}$, K), pressure ($P_{c,i}$, kPa), and compressibility factor ($Z_{c,i}$) required for the calculations are obtained from the Aspen Plus database and summarized in Table 7. For the UNIQUAC

Table 7. Critical Constants (T_c , P_c , Z_c)^a

compound	T_c/K	P_c/kPa	Z_c
NMP	721.6	4520	0.234
GBL	731.0	5130	0.230

^aFrom Aspen Plus V14.

model, the corresponding binary interaction energy parameter is $u_{ij} - u_{ji}$. In this model, Φ_i represents the segment fraction, while θ and θ' denote the area fractions. The coordination number, specified as z , is assigned a value of 10. The structural parameters q_i , q'_i , and r_i are dependent on the molecular architecture. Specifically, the UNIQUAC model parameters for NMP and GBL, as retrieved from Aspen Plus V14, yield $q_i = q'_i = 3.2$ and 3.5, respectively, with corresponding r_i values of 3.981 (NMP) and 3.025 (GBL).

To further evaluate the overall agreement between the models and the entire data set, we calculated the root-mean-square deviation (RMSD), which is defined by the following eq 11.

$$\text{RMSD} = \sqrt{\frac{1}{N} \sum_{i=1}^N (U_i^{\text{exp}} - U_i^{\text{cal}})^2} \quad (11)$$

In the equation, U_i^{exp} and U_i^{cal} represent the experimental and calculated values, respectively, and N is the number of data points. The binary interaction parameters (BIPs) and the RMSD for the vapor-phase mole fraction and equilibrium temperature at the three different pressures are summarized in Table 8.

Table 8. Binary Interaction Parameters, RMSD(y_1) and RMSD(T) for the NRTL, Wilson, and UNIQUAC Models in the Correlation of the {NMP (1) + GBL (2)} System at 10.0, 20.0, and 101.3 kPa

	10.0 kPa	20.0 kPa	101.3 kPa
NRTL			
$g_{12} - g_{22}$ (J·mol ⁻¹)	-3018.7	-3127.7	-3759.6
$g_{21} - g_{11}$ (J·mol ⁻¹)	3814.9	4066.0	5065.6
RMSD(y_1)	0.003	0.004	0.002
RMSD(T) (K)	0.08	0.06	0.05
Wilson			
$\lambda_{21} - \lambda_{11}$ (J·mol ⁻¹)	3317.3	3250.9	3814.9
$\lambda_{12} - \lambda_{22}$ (J·mol ⁻¹)	-2388.5	-2255.8	-2454.8
RMSD(y_1)	0.004	0.004	0.002
RMSD(T) (K)	0.09	0.04	0.05
UNIQUAC			
$u_{12} - u_{22}$ (J·mol ⁻¹)	-1592.3	-1559.1	-1725.0
$u_{21} - u_{11}$ (J·mol ⁻¹)	2056.7	1990.4	2355.3
RMSD(y_1)	0.003	0.004	0.002
RMSD(T) (K)	0.08	0.04	0.05

The regression meets satisfactory criteria, where RMSD(T) values are less than 0.08 K and RMSD(y_i) values are less than 0.004. Meanwhile, from Table 4, the maximum absolute deviations in vapor mole fraction for the NRTL model at 10.0, 20.0, and 101.3 kPa are 0.005, 0.007, and 0.003, those for the Wilson model are 0.006, 0.008, and 0.004, and those for the UNIQUAC model are 0.006, 0.008, and 0.004, respectively. Regarding the equilibrium temperature, the maximum absolute deviations for the NRTL model are 0.24, 0.10, and 0.08 K at the respective pressures, for the Wilson model, they are 0.26, 0.07, and 0.08 K, and for the UNIQUAC model, they are 0.24, 0.07, and 0.08 K, respectively. These low deviation values confirm satisfactory agreement between the experimental data and the correlated results from all three models.

The VLE behavior of the {NMP + GBL} system is depicted in the T - x - y diagrams at 101.3, 20.0, and 10.0 kPa (Figures 2–4). The NRTL, Wilson, and UNIQUAC models all show excellent agreement with the experimental data across the entire composition range. The T - x - y curves at the three investigated pressures exhibit distinct characteristics that reflect the underlying thermodynamic behavior of the system. As shown in Figure 2, the curve shows a combination of concave ($x_1 = 0$ –0.3) and convex ($x_1 = 0.3$ –1) behavior at 101.3 kPa. This curvature variation arises from the composition-dependent nonideality of the mixture, as reflected in the excess Gibbs free energy (GE). Due to the close boiling points of NMP and GBL and correspondingly low relative volatility, the T - x - y curve sensitively captures subtle changes in molecular interactions across the composition range. The concave region in the GBL-rich zone corresponds to local positive deviations,

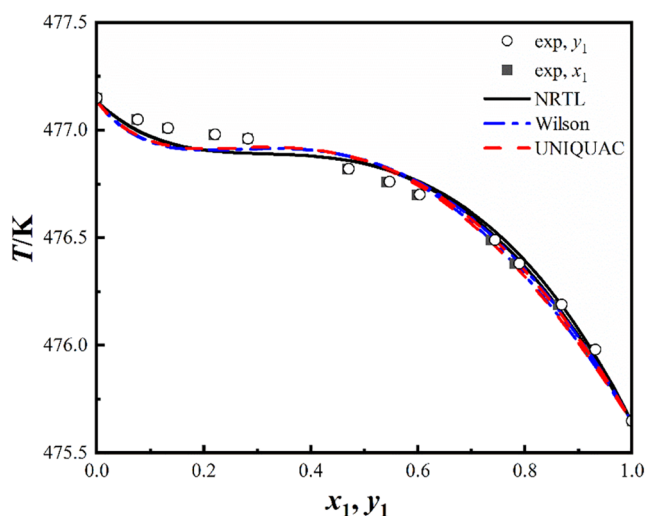


Figure 2. VLE data of {NMP (1) + GBL (2)} system at 101.3 kPa. (■) Experimental liquid and (□) vapor phases in this work; (solid line) regressed with the NRTL model; (dashed-dotted line) regressed with the Wilson model; (dashed line) regressed with the UNIQUAC model.

while the convex region reflects the overall negative deviations that dominate as NMP content increases. Figures 3 and 4 show

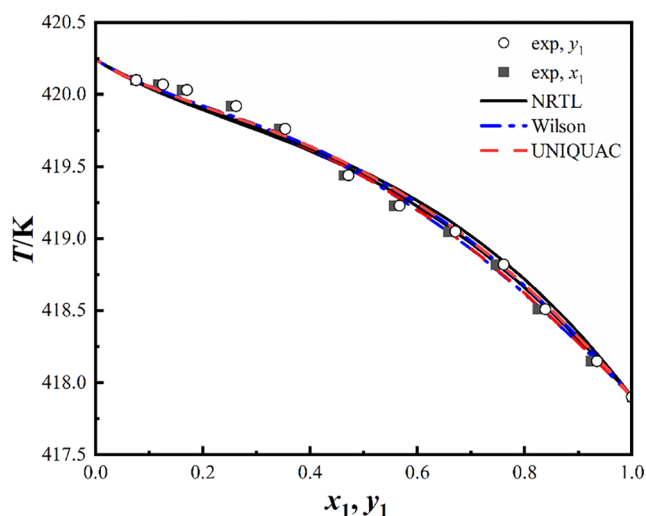


Figure 3. VLE data of {NMP (1) + GBL (2)} system at 20.0 kPa. (■) Experimental liquid and (□) vapor phases in this work; (solid line) regressed with the NRTL model; (dashed-dotted line) regressed with the Wilson model; (dashed line) regressed with the UNIQUAC model.

that at reduced pressures (10.0 and 20.0 kPa), the T - x - y curves are consistently convex across the entire composition range, in contrast to the mixed curvature observed at 101.3 kPa. This uniformity indicates that vacuum conditions lead to a more regular composition dependence of the GE, resulting in smoother temperature profiles.

The GE as a function of composition at different pressures for the {NMP + GBL} system is calculated by eq 12, and the results are presented in Figure 5, along with the correlations obtained from the NRTL model.⁷⁴ Wilson and UNIQUAC models provide nearly equivalent descriptions of the GE data, as illustrated in Figures S2 and S3. At 10.0 and 20.0 kPa, GE is

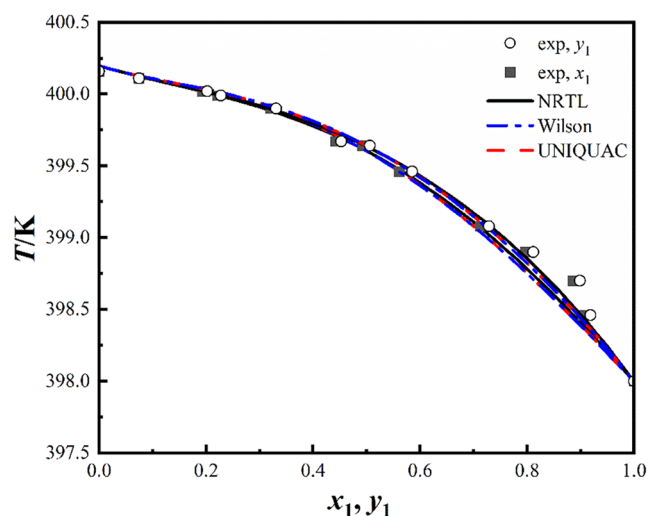


Figure 4. VLE data of {NMP (1) + GBL (2)} system at 10.0 kPa. (■) Experimental liquid and (□) vapor phases in this work; (solid line) regressed with the NRTL model; (dashed-dotted line) regressed with the Wilson model; (dashed line) regressed with the UNIQUAC model.

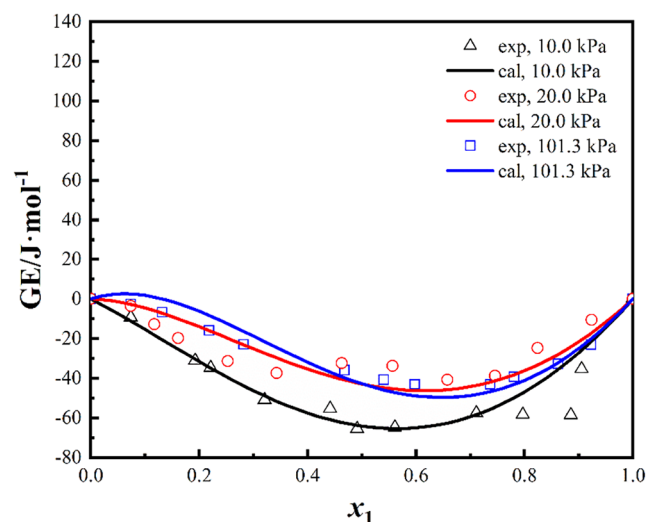


Figure 5. Relationship between the GE of NMP and the liquid mole fraction of NMP in the binary mixture of {NMP (1) + GBL (2)}. The exp point is calculated from the experimental data, and the cal line represents the NRTL model fitting.

negative across the entire composition range, indicating negative deviations from Raoult's law. At 101.3 kPa, GE is slightly positive when x_1 is less than 0.1 and becomes negative when x_1 is greater than 0.1. This transition from positive to negative GE aligns with the change in curvature observed in Figure 2, where the curve shifts from concave to convex at approximately the same composition. It should be noted, however, that although the system exhibits negative deviations from Raoult's law, no maximum-boiling azeotrope is formed at 101.3 kPa. The boiling points of NMP and GBL differ by only approximately 1.5 K, and α_{12} remains near unity but never reaches exactly 1 throughout the entire composition range as shown in Figure 7, which confirms that no azeotrope is formed.

$$GE = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad (12)$$

The analyses of α_{12} are important for the separation of the close-boiling {NMP + GBL} mixture because the T - x - y diagrams cannot quantify the prediction uncertainty of three activity coefficient models, especially at infinite dilution.⁴⁶ The separation characteristics of the {NMP + GBL} system under reduced pressure are further illustrated in Figures 6 and 7. The

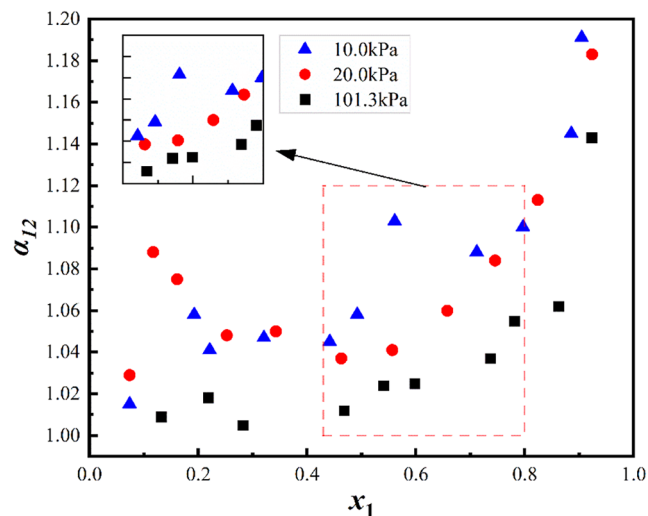


Figure 6. α_{12} - x_1 for the {NMP (1) + GBL (2)} system at 10.0, 20.0, and 101.3 kPa.

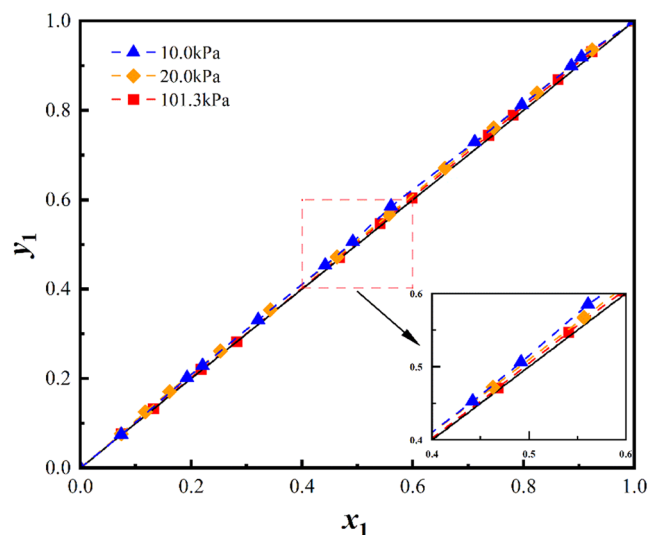


Figure 7. y - x diagram of {NMP (1) + GBL (2)} at 10.0, 20.0, and 101.3 kPa.

relative volatility profiles in Figure 6 reveal that the values remain close to 1 across the entire composition range at all investigated pressures, indicating the high separation difficulty of the system via conventional distillation. The local magnification inset further highlights that although reduced pressure can slightly enhance α_{12} , with values at 10.0 kPa marginally higher than those at 20.0 and 101.3 kPa, the improvement remains extremely limited. This suggests that vacuum distillation alone cannot effectively overcome the inherent separation challenges of the system.

Figure 7 further confirms the high separation difficulty of the system. All data points lie very close to the diagonal line $y_1 = x_1$, reflecting a very small driving force for vapor-liquid

separation. The magnified inset reveals that the vertical distance between the equilibrium curve and the diagonal, which serves as a direct indicator of separation driving force, increases only modestly with decreased pressure. The results further verify that vacuum operation yields merely a marginal enhancement in separation performance. Accordingly, conventional vacuum distillation alone is not sufficiently efficient for the separation of this system. Instead, the thermodynamic data and fitted parameters obtained in this study can be readily applied to the design of more efficient and economically feasible separation strategies.

3.5. Comparison between Predictive and Experimental Results

To further verify the reliability of the experimental VLE data and evaluate the predictive performance of group contribution methods for the {NMP + GBL} system, the comparisons between experimental data and predictions from the UNIFAC model were carried out, with detailed results presented in Table S2. In addition, the NRTL correlation curve was incorporated into the T - x - y diagram for a direct comparison with the predicted curve.

The measured boiling points of pure NMP and GBL are in good agreement with those calculated from the extended Antoine equation with a maximum absolute deviation of 0.04 K, indicating that the experimental data possess satisfactory thermodynamic consistency. Meanwhile, the boiling points predicted by the UNIFAC model are in excellent agreement with the experimental values with a maximum absolute deviation of 0.06 K, confirming that the UNIFAC model can accurately represent the pure-component vapor pressures of the investigated system.

For the binary mixture, a detailed comparison is provided in Table S2 and Figure 8, while the corresponding results at 10.0 and 20.0 kPa are depicted in Figures S5 and S6. The UNIFAC model yields RMSD values for vapor mole fraction within 0.005, indicating acceptable predictive capability for vapor composition. However, the RMSD for temperature reaches up to 0.38 K, representing a significant fraction of the overall temperature variation in the mixture. This discrepancy is

clearly illustrated in Figure 8, as the UNIFAC-predicted T - x - y curves exhibit an approximately linear temperature–composition relationship that deviates from the experimental trend. The same discrepancy is also observed in Figures S5 and S6. These results indicate that while UNIFAC provides reasonable estimates for vapor composition, it still cannot adequately describe the specific molecular interactions that dominate the phase behavior of the {NMP + GBL} mixture. In summary, the experimental VLE data reported in this work serve as an essential benchmark for validating predictive models, highlighting the necessity of experimentally determined measurements for accurate process design when dealing with systems exhibiting complex nonideal behavior.

4. CONCLUSIONS

This study reports a comprehensive set of isobaric VLE data for the {NMP + GBL} binary system at 10.0, 20.0, and 101.3 kPa. The system is identified as a close-boiling nonazeotropic mixture over the investigated pressure ranges. Although the reduction in the system pressure can lead to a slight increase in relative volatility, the improvement remains marginal. This result highlights the challenge and limited efficacy of employing conventional distillation to separate NMP and GBL to the stringent purity levels required for electronic-grade applications. On the basis of the reliable VLE data and thermodynamic model parameters established, further exploration of feasible separation processes for {NMP + GBL} is recommended. The thermodynamic consistency of the measured VLE data is verified, with all data passing the Herington area test and the Van Ness point test. Furthermore, the NRTL, Wilson, and UNIQUAC activity coefficient models successfully correlate the experimental data with excellent agreement. The experimental results were also used to evaluate the predictive performance of the UNIFAC model. The reliable VLE data and the regressed binary interaction parameters provide a critical foundation for the simulation, design, and optimization of advanced separation processes aimed at producing high-purity NMPs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jced.6c00186>.

Uncertainty analysis for the experimental measurements; comparison of experimental pure-component vapor pressures of NMP and GBL with literature data (NIST Wagner25 equation) in a deviation plot; relationship between excess Gibbs free energy and liquid mole fraction; residual distribution of $\ln(\gamma_1/\gamma_2)$; T - x - y diagrams comparing experimental data with NRTL regression and UNIFAC predictions; comparison of measured, correlated, and UNIFAC-predicted pure-component boiling points; comparison of experimental VLE data with UNIFAC predictions (PDF)

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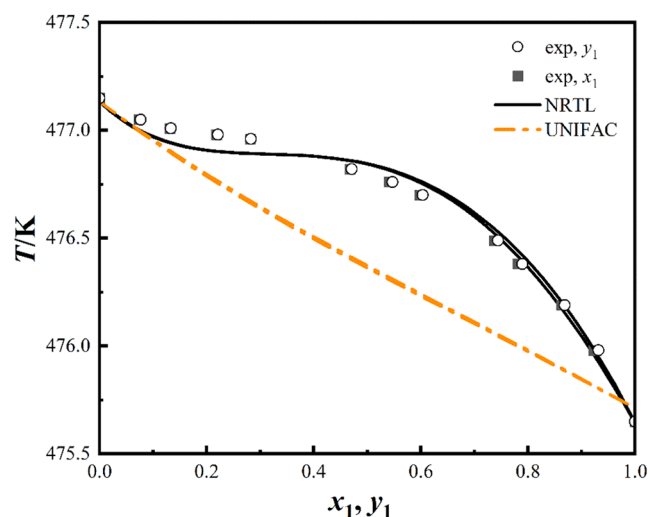


Figure 8. T - x - y diagram for the binary system {NMP (1) + GBL (2)} at 101.3 kPa: (■) experimental liquid and (□) vapor phase from this work; (solid line) NRTL model regression; (dashed-dotted line) UNIFAC prediction.

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L.H.: Writing—original draft, Investigation, Formal analysis, and Data curation. L.Q.: Resources, Project administration, and Conceptualization. Liang Chen: Resources, Validation, and Writing—review and editing. Lifang Chen: Writing—review and editing, Supervision, and Methodology. Z.Q.: Supervision, Project administration, and Writing—review and editing.

Notes

The authors declare no competing financial interest.

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