

EFFECTS OF SELECTED IONIC LIQUIDS ON THE VAPOR-LIQUID-  
EQUILIBRIA OF WATER-2-PROPANOL SYSTEM

by

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## **Dedication**

*To my Parents*

## Abstract

Separation processes involving vapor and liquid phases represent a typical unit operation in most chemical industries, including distillation and absorption. A large fraction of the capital and operating costs is usually devoted to such operations. Owing to the unlikelihood of the complete separation of azeotropic mixtures by distillation, separation processes involving such mixtures remain one of the most pressing challenges in the chemical industry. Using inorganic salts is a common technique in handling azeotropic systems. However, issues such as corrosion and fouling render this technique ineffective. Recently, ionic liquids were introduced as azeotrope-breakers. In this work, the effect of two ionic liquids, i.e., 1-Butyl-1-methylpyrrolidinium chloride [BMPy][Cl], and 1-Butyl-1-methylpyrrolidinium trifluoromethanesulfonate [BMPy][OTf] on the vapor liquid equilibrium (VLE) of the (azeotropic) water + 2-propanol system is investigated. For this purpose, the corresponding binary VLE for water or 2-propanol with each of the two ionic liquids were experimentally measured and reported at 100, 75, and 50 kPa. Based on the observed boiling point elevation, it has been found that [BMPy][Cl] has a higher interaction with both solvents than [BMPy][OTf]. Furthermore, it has been found that [BMPy][Cl] has a higher interaction with water than with 2-propanol, while [BMPy][OTf] interacts with both solvents in a similar manner. The boiling point elevation was found to be independent of the pressure. Most importantly, [BMPy][Cl], at a mole fraction of 0.31 in the liquid phase, was capable of completely eliminating the azeotrope of water + 2-propanol system. In contrast, [BMPy][OTf] shifted the azeotrope towards the alcohol-rich region, yet it was not able to completely remove the azeotrope of this system at the studied concentrations. Data were modelled with the non-random, two-liquid (NRTL) model, which could describe the experimental data, with a root mean square deviation (RMSD) less than 0.015 for the solvents' activity coefficients in the binary systems. For the ternary systems, the RMSD for temperature was found to be less than 2 °C. Thus, it is concluded that chloride based ionic liquids resemble good entrainers for the extractive distillation of the studied azeotrope.

**Keywords:** *Vapour-liquid equilibrium; 2-Propanol; Pyrrolidinium-based ionic liquids; NRTL model; Azeotropic mixtures.*

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## Nomenclature

### *Abbreviations*

[BMIM]	1-Butyl-3-methylimidazolium
[BMPy]	1-Butyl-1-methylpyrrolidinium
[EMIM]	1-Ethyl-3-methylimidazolium
GRG	Generalized reduced gradient
[HMIM]	1-Hexyl-3-methyl-imidazolium chloride
ICIS	Independent Chemical Information Service
IPA	2-Propanol
KF	Karl Fischer titration
[NTf2]	Bis(trifluoromethylsulfonyl) imide
NRTL	Non-random, two-liquids
[OAc]	Acetate
[OcSO4]	Octyl sulfate
OF	Objective function
[OMIM]	1-Octyl-3-methylimidazolium
[OTf]	Trifluoromethanesulfonate
RMSD	Root mean square deviation
THF	Tetrahydrofuran
VLE	Vapor-liquid equilibrium

### *Symbols*

$x_i$	mole fraction of species $i$ in the liquid phase
$y_i$	mole fraction of species $i$ in the vapor phase
$b_{ij}$	Energy interaction parameter between species $i$ and species $j$
$R$	Universal gas constant
$U$	Uncertainty function
$S$	Entropy
$G$	Gibbs free energy

### *Greek Letters*

$\alpha_{ij}$	Relative volatility of species $i$ to species $j$
$\lambda_i$	Activity coefficient of species $i$
$\mu_i$	Chemical potential

## Chapter 1. Introduction

This chapter presents a summary of the concepts of distillation and azeotropic systems. It also discusses the industrial importance of the alcoholic substance addressed in this work, i.e., 2-propanol, and its production methods. The main objectives of this research, as well as the research contribution, are explained. Finally, the chapter summarizes the overall structure of this thesis.

### 1.1. Overview

**1.1.1. Basic concepts of distillation.** By far, distillation is the most common separation method in the chemical industry. It is estimated that more than a half of the energy cost and a third of the capital cost go to distillation columns and their support facilities in a typical chemical industry [1].

A typical distillation column is an extension of a simple flash vessel (Figure 1-a). When a liquid feed is sent to a flash chamber which is at an elevated temperature, it boils. The lighter part of the feed will be more concentrated in the vapor phase, while the heavier part will be more concentrated in the liquid phase. Usually, such a process results in a limited degree of separation. More separation can be achieved upon cascading more flash vessel. If the liquid stream is sent to another flash vessel at a higher temperature, and if the vapor phase is sent to another chamber at a lower temperature (Figure 1-b), the top stream,  $V_1$ , will be enriched with the lighter fraction, while stream  $L_5$  will be enriched with the heavier fraction. This cascading process can result in pure vapor phase and a pure liquid phase. A typical distillation column (Figure 2) can be thought of as multiple flash vessels, or stages, which are at different equilibrium temperature. Heat is supplied to the column by a reboiler, located at the bottom of the column, causing a part of the bottom product to boil. As the mixture travels toward the top of the column, it gets enriched with the volatile components, until it is condensed to form the distillate, or the top product [2], [3].

At each stage of the distillation column, the vapor and the liquid phases exist at equilibrium. The composition of the vapor in equilibrium with liquid at a given temperature can be determined experimentally using an equilibrium apparatus, such as the Othmer still. The experimental equilibrium data can be easily interpreted into a temperature - composition diagram (T-xy). A T-xy diagram can thus give the boiling point of a mixture and its vapor and liquid phases' compositions [4]. It should be noted

that the vapor and the liquid phase should have different composition at each stage, so that mass transfer of different components can continue. If, at any stage, the vapor and the liquid phases have the same composition, separation can no longer occur by regular distillation.

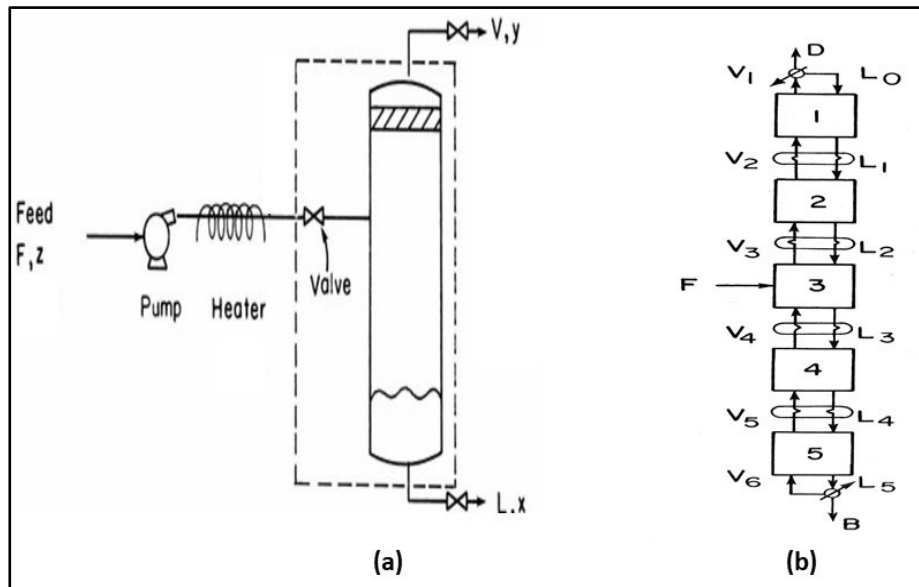


Figure 1: A typical flash chamber (a) and a flash cascade (b) [2].

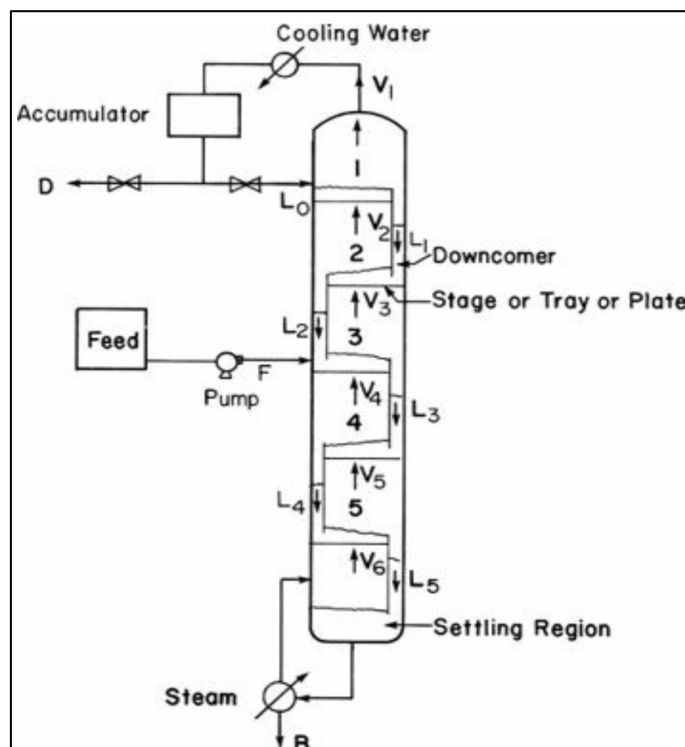


Figure 2: A typical distillation column [2].

**1.1.2. Azeotropic VLE systems.** The word Azeotrope is a Greek word that means ‘no more boiling’. A mixture of two or more components, at a given pressure, forms an azeotrope when the vapor and liquid of that mixture have the same composition. The resulting mixture boils at the azeotropic temperature and no more mass transfer occurs. The azeotrope phenomenon represents one of the oldest problems in the chemical industry. In a number of processes, mixtures of solvents may be produced and accumulated. Separation of such mixtures into pure components is required so that these components can be utilized again. If such mixtures are azeotropic, separating them into their constituents is not possible via regular distillation. Unfortunately, the azeotrope phenomenon is not rare. Researchers surveyed over 18,800 binary systems, and about half of these systems were azeotropic [5], [6].

Azeotrope occurs due to deviations from ideal solution behavior in a mixture, because of different physiochemical force interactions between similar and different molecules [5]. In a positive azeotrope, different components in the mixture ‘dislike’ each other. In other words, in a binary mixture of species A and B, the interaction between A and A and/or B and B is greater than that between A and B. Ethanol/toluene mixture, for example, form a positive azeotrope [7], as shown in Figure 3. In a negative azeotrope, on the other hand, the different molecules like each other, and, hence, the A-B interaction is larger than the A-A and the B-B interactions. An example of this is the Chloroform/tetrahydrofuran system which forms a negative azeotrope [7] as shown in Figure 4.

In certain circumstances, it is possible to anticipate the existence of an azeotrope [5]. For example, the existence of highly interactive atoms such as oxygen, fluorine, chlorine, and nitrogen will probably lead to pronounced nonidealities in the solution, leading to an azeotropic behavior [8]. In general, it has been observed [5] that azeotropes do not usually form when the difference between the boiling points of pure components exceeds 30 °C.

Generally, near ideal behavior is encountered in mixtures of similar species, such as heptane and hexane. In such mixtures, it is unlikely to have an azeotropic point. However, in a mixture such as benzene and cyclohexane, an azeotrope exists. This situation is predicted by Bancroft’s rule, which states that if there is a point in the

composition range at which the two components have an identical vapor pressure, this point might correspond to an azeotropic point [9].

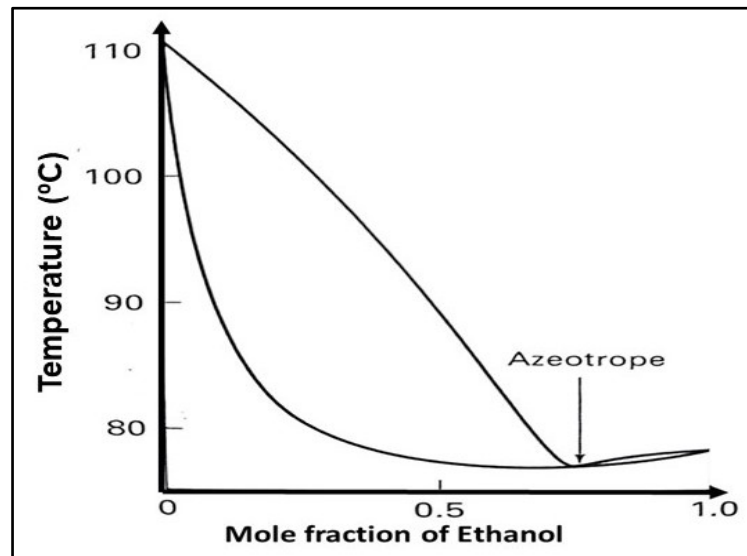


Figure 3: VLE of Ethanol + Toluene at 0.1 MPa as an example of a positive azeotrope [7]

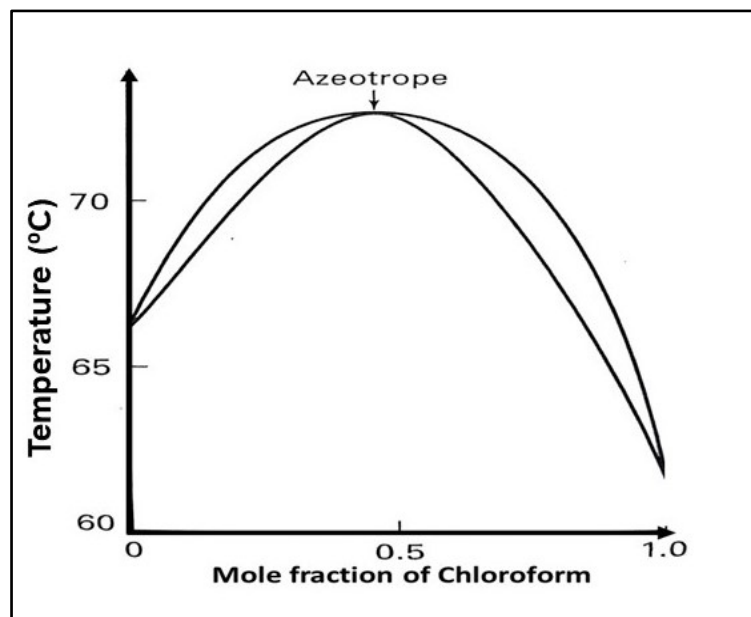


Figure 4: VLE of chloroform + tetrahydrofuran at 0.1 MPa as an example of a negative azeotrope [7]

An important concept in distillation is the relative volatility ( $\alpha_{ij}$ ), which represents the easiness of separation. The relative volatility is defined as:



$$\alpha_{ij} = \frac{\frac{y_i}{x_i}}{\frac{y_j}{x_j}} \quad (1)$$

where  $y_i$  is the mole fraction of species  $i$  in the vapor phase and  $x_i$  is the mole fraction of species  $i$  in the liquid phase. At the azeotropic point, the relative volatility equals 1. Van Winkle [10] stated that if  $0.95 < \alpha < 1.05$ , distillation is not economically viable since a large reflux ratio and a high number of theoretical stages will be required.

**1.1.3. The separation problem in azeotropic mixtures.** There are different methods to separate azeotropic mixtures. A common one is the pressure swing process. Manipulating the pressure can result in changing the azeotrope point. As explained elsewhere [2], if the composition shifts with a minimum mole fraction of 5%, a two-column process using two different pressures can be used.

Water and methyl ethyl ketone mixture can be separated by this method [11]. At 100 kPa, the azeotrope appears at 35 mol% water, while it appears at 50 mol% water if the pressure is 690 kPa. The two-column process is depicted in Figure 5.

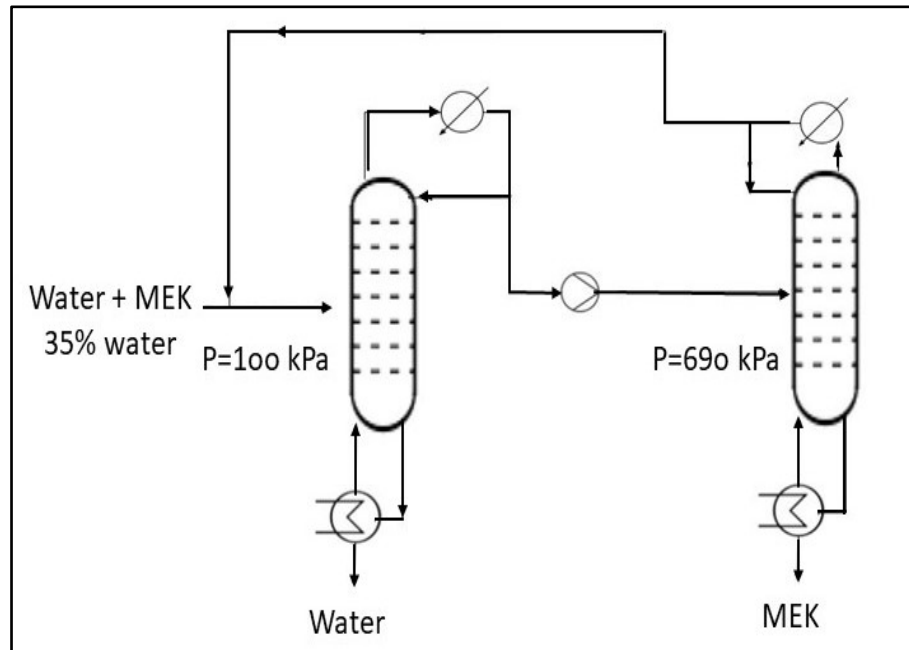


Figure 5: Pressure swing method for separating water + methyl ethyl ketone [2]

The feed usually contains more than 35% water. Thus, the bottom product from the first column is mostly water, while the distillate is at the azeotropic composition. The distillate is then sent to the second column, in which the volatility of methyl ethyl ketone is less. The azeotrope at the high-pressure column is at a water fraction of 0.5.

Thus, the distillate of the second column is 50% water. This means that methyl ethyl ketone is stripped from the feed to the second column and is sent as a bottom product of the second column.

The azeotrope of water + ethanol system can be also completely removed if the pressure is reduced to below 9 kPa. However, this method is not followed to obtain anhydrous ethanol, since it requires a column with a large number of stages and a large diameter [2].

Another process which is used to separate an azeotropic mixture is the addition of a solvent, as depicted in Figure 6. The added solvent should have a higher affinity toward one component. Ethylene glycol can be added to separate a water-ethanol mixture [2].

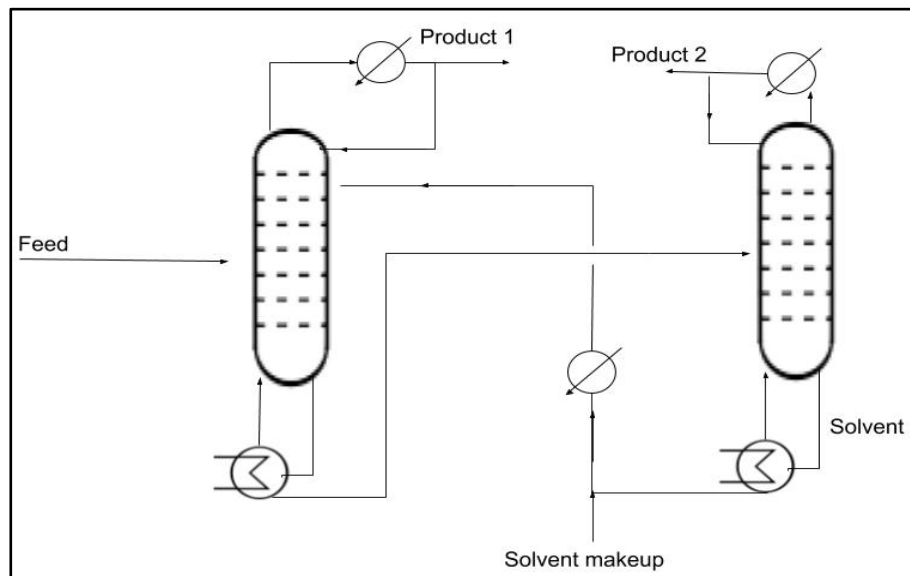


Figure 6: Schematic of an extractive distillation [2]

Ionic liquids represent a new class of solvents that can be used in extractive distillation. During the last decades, there have been increasing attempts to study the effect of ionic liquids on the phase behavior of various azeotropic systems. Ionic liquids, or molten salts, are materials that constitute of ionic bonds with a highly unsymmetrical cation, resulting in having chemicals with ionic bonds whilst still in the liquid state at temperatures below 100 °C [12]. The water + ethanol system is the most widely studied azeotrope, with various ionic liquids, such as 1-ethyl-3

methylimidazolium chloride, 1-butyl-3-methylimidazolium tetrafluoroborate, and 1-ethyl-3-methylimidazolium acetate [12].

## 1.2. Water + 2-Propanol Azeotropic VLE System

2-Propanol, also known as isopropyl alcohol (IPA), is used as a chemical reagent in the production of methyl isobutyl ketone, acetone, and isopropyl acetate. It is also used as a solvent since it has low cost and low toxicity. It is used in preparing, paints, and inks, perfumes, shampoos, lotions, and makeup removal. Further applications include its use as a disinfectant for industry, homes, and hospitals [13].

As explained by the Independent Chemical Information Service ICIS [14], there are two commercial routes for producing 2-propanol. The first method is the indirect hydration of refinery-grade (40-60 wt%) propylene using sulfuric acid. The second, more modern method, is the direct hydration of chemical grade propylene. These processes result in a wet alcohol which must be dried. Water + 2-propanol system has a minimum boiling azeotrope at 87.4 wt % or 67.5 mol % 2-propanol at 80.3 °C [15]. Thus, the binary mixture cannot be separated via distillation. An entrainer [16], such as benzene, diisopropyl ether, or cyclohexane is utilized to obtain anhydrous 2-propanol, since adding such an entrainer results in a new ternary azeotrope at a temperature that is lower than that of the water + 2-propanol azeotropic temperature, water + hydrocarbon azeotropic temperature, or 2-propanol + hydrocarbon azeotropic temperature [17]. This process is illustrated in Figure 7. The first column concentrates the water + 2-propanol mixture such that its top product is at the azeotropic concentration. This azeotropic mixture is sent to the azeotropic distillation unit, where it is mixed with a hydrocarbon to form a ternary heterogeneous azeotrope. Pure 2-propanol leaves as a bottom product, and the top product is condensed to form a biphasic liquid. Its upper phase is hydrocarbon-rich and is recycled back to the column. The lower phase is aqueous and is sent to a separator, where wastewater leaves as a bottom product, while the top product is recycled back to the azeotropic distillation unit.

## 1.3. Problem Statement

Since water/2-propanol mixture is an azeotropic system, the current production of pure 2-propanol requires implementing three distillation columns, necessitating a high amount of energy and a high capital cost. There have been some efforts to reduce

the number of these columns or find an alternative process to produce 2-propanol [18]. One of these methods is using ionic liquids as solvents in the extractive distillation of this system. In this thesis, the effect of two ionic liquids, namely 1-Butyl-1-methylpyrrolidinium chloride [BMPy][Cl] and Butyl-1-methylpyrrolidinium trifluoromethanesulfonate [BMPy][OTf], on the phase behaviour of this system is investigated. Reasons for selecting these particular ionic liquids are given in Chapter 4.

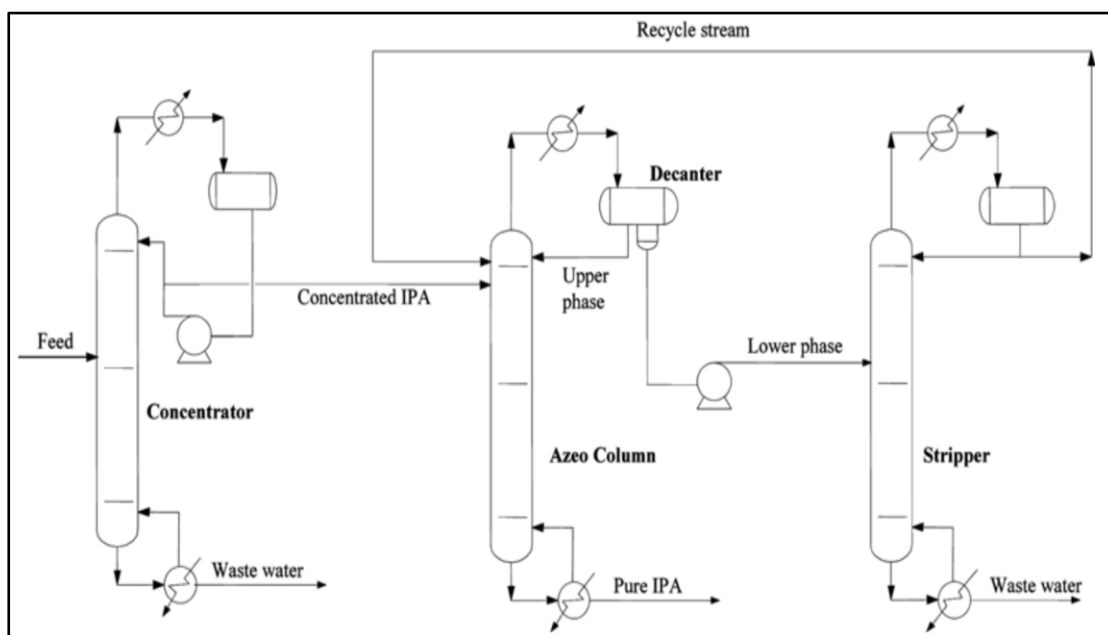


Figure 7: Dehydration of 2-Propanol (IPA) [16]

#### 1.4. Research Contribution

The contribution of this thesis can be summarized as follows:

- Reporting the vapour-liquid equilibria for water and 2-propanol with each of [BMPy][C] and [BMPy][OTf] ionic liquids.
- Getting insight into the molecular interaction between each solvent and each ionic liquid, and verifying whether the resulting binary mixtures form positive or negative azeotropes.
- Studying the effects of these ionic liquids on the VLE of water/2-propanol system.
- Verifying the applicability of the Non-Random, Two-Liquid (NRTL) model for representing the acquired experimental data for the VLE of systems containing water and 2-propanol in the presence of each ionic liquid.

## 1.5. Thesis Organization

This thesis is organized as follows: Chapter 2 describes the nature of ionic liquids, their properties, and their applications in distillation. Chapter 3 describes the methodology that was used to study the VLE of the binary and ternary systems investigated in this work. Also, the NRTL model is described, and its assumptions are outlined. The rationale behind selecting [BMPy][Cl] and [BMPy][OTf] is also presented in Chapter 3. This is followed by describing the experimental procedure and the methods of analysis that were utilized to collect the VLE data in Chapter 4. Chapter 5 presents the experimental and regression results and gives a detailed analysis of the observed phase behaviors. Finally, Chapter 6 summarizes the major findings and suggests recommendations for further future work.

## Chapter 2. Background and Literature Review

This chapter discusses the physical and chemical properties of ionic liquids. A literature review about using ionic liquids in extractive distillation is provided, and the factors that determine an ionic liquid's entrainment ability are summarized.

### 2.1. Properties of Ionic Liquids.

Ionic liquids are a class of chemical compounds composed of ions in the liquid state under 100 °C [19], [20]. The cation is normally a highly asymmetric substituted ion, such as pyridinium, ammonium, imidazolium, pyrrolidinium, or tetraalkylphosphonium (Figure 8). The anion is usually an inorganic ion, such as nitrate, halide, hexafluorophosphate, or tetrafluoroborate. The cations, anions, and the substituents on the cations can be widely varied resulting in a change of the properties of the ionic liquids [21].

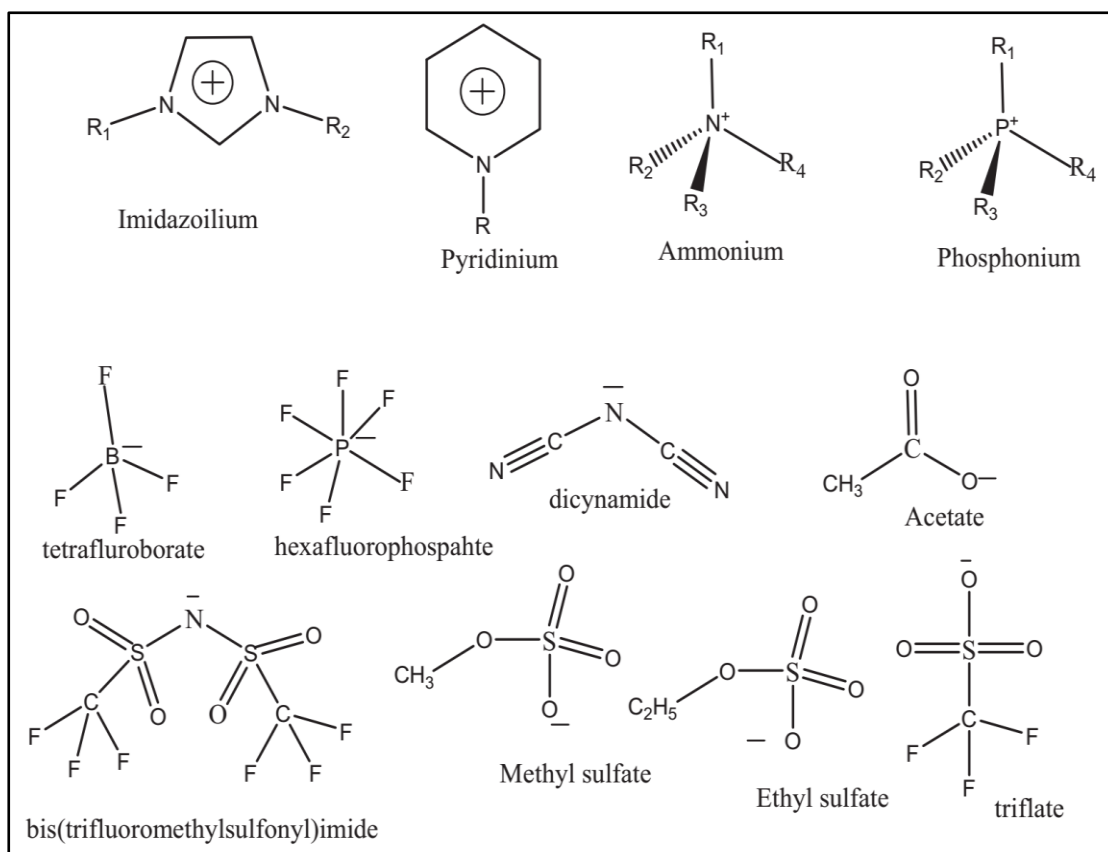


Figure 8: Structures of common cations and anions of ionic liquids [22]

Although research activities on ionic liquids had started long time ago, a surge in such research activities occurred around the turn of the 21<sup>st</sup> century (Figure 9). Ionic

liquids are usually described as ‘designer solvents’. This is due to the fact that a typical ionic liquid consists of two components which can be varied to satisfy a particular need or application, simply changing the structure of the ion [20]. Up to 2004, over 500 ionic liquids were synthesized [23], although the number of theoretically available ionic liquids is by far greater.

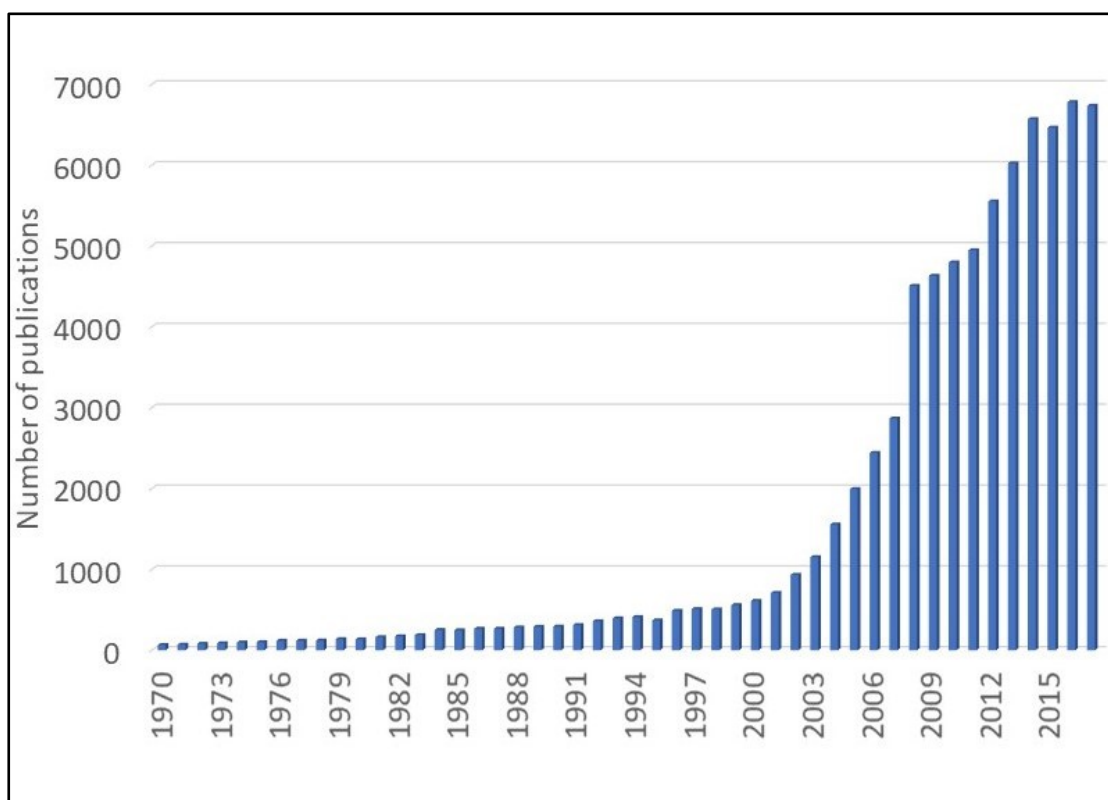


Figure 9: Research activity on ionic liquids (Scopus database).

Ionic liquids have several unique chemical and physical properties that make them superior solvents for many engineering applications. Examples of these properties are negligible vapor pressure, low melting point, wide liquid range, high thermal stability, suitable viscosity, and solubility in both polar and non-polar, organic and non-organic substances[24]. Table 1 summarizes some important properties of ionic liquids. Applications of ionic liquids are numerous; they are used in catalytic reactions, drug delivery, fuel cells, and metal plating [25], [26].

## 2.2. Ionic Liquids in Azeotropic Distillation

The effect of salts on the VLE of various solvents and their mixtures has been well documented in literature [27]. Salts can affect the boiling points of solvents and

affect the VLE of many systems and even eliminate some azeotropes. Salts can affect the equilibrium vapor fractions since they tend to preferentially attract one type of molecule. This results in an enrichment of the liquid phase with the more polar molecule, since the electrostatic field of the ions attracts the latter preferentially. However, they are not used on commercial scales due to issues such as fouling and difficulties in handling the solid salt [28]. Ionic liquids, on the other hand, do not cause such problems when used as solvents in extractive distillation. Due to their properties, ionic liquids have been investigated as solvents in the extractive distillation of many systems, such as water + alcohols [29]–[31], water + tetrahydrofuran [32]–[34], alcohols + esters [19], [35], alcohols + ketones [36], alcohols + halogenated hydrocarbons [37], [38], among others. As Figure 10 shows, most of the ionic liquids (about 75%) studied up to 2012 were imidazolium-based.

Table 1: Properties of ionic liquids [22]

Property	Value
Molecular mass (g/mole)	70-800
Density (g/cm <sup>3</sup> )	0.8-2.10
Viscosity (mPa s)	7-1800
Melting point (°C)	-100 to 113
Water solubility	Variable
Thermal stability (°C)	>500
Physical state	Solid, semisolid, and liquid
Vapor pressure	Negligible
Nature	Acidic, neutral, basic

Important factors that determine the efficiency of a certain ionic liquid as an entrainer are the nature of the cation, the nature of the anion, the concentration of the ionic liquid. The effect of the cation nature has been studied in several papers; For example, water + tetrahydrofuran (THF) system, which has an azeotrope at 64.35 °C at a mole fraction of THF of 0.8. was studied with [EMIM][BF<sub>4</sub>], [BMIM][BF<sub>4</sub>], and [OMIM][BF<sub>4</sub>] [32]. It was concluded that the relative volatility of low boiling compound increases with shortening of the alkyl chain length, from Octyl ([OMIM]) to Butyl ([BMIM]) to Ethyl ([EMIM]), as depicted in Figure 11. Similar results have been obtained for the water + ethanol system. As shown in Figure 12, the separation capacity of [EMIM][Cl], [BMIM][Cl], and [HMIM][Cl] decreases in the order they are presented [12].



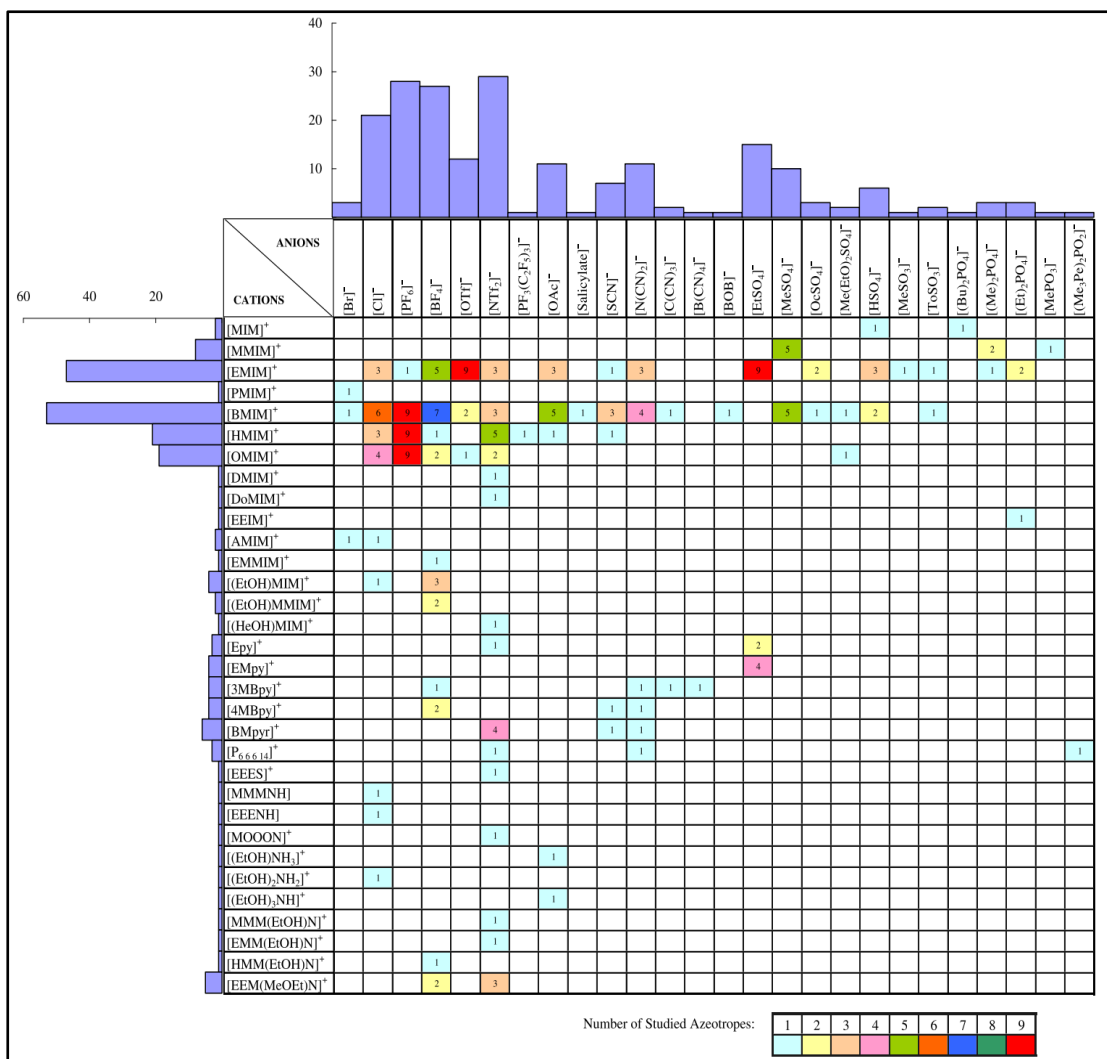


Figure 10: A survey of ionic liquids that have been studied as solvents to remove azeotropes [12]

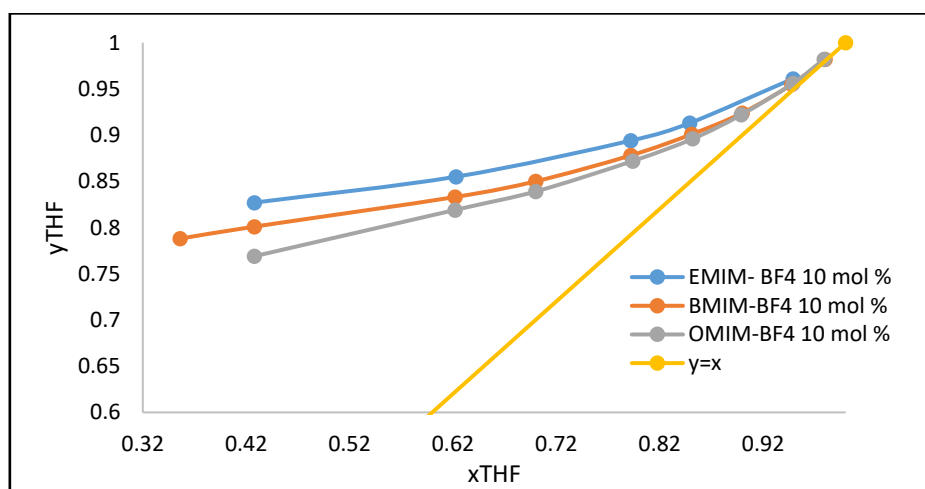


Figure 11: Effect of various ionic liquids on the vapor-liquid equilibrium of water + THF system [32]

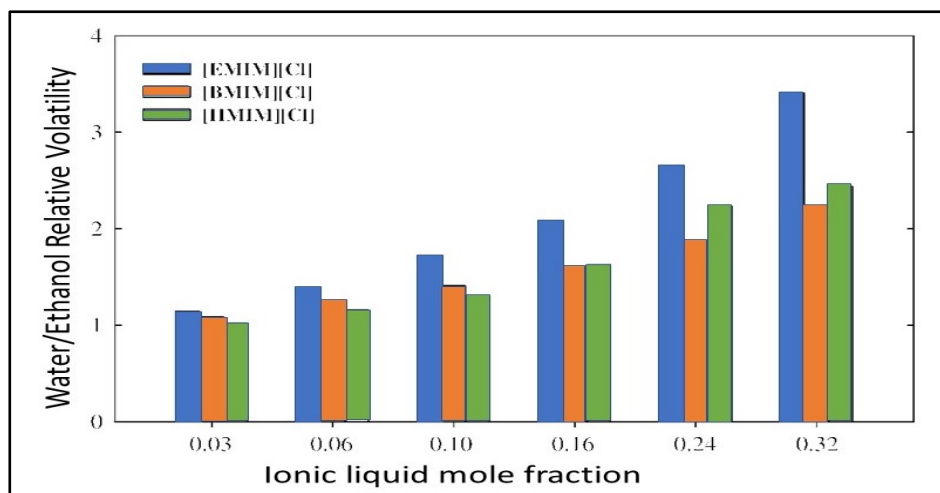


Figure 12: Effect of ionic liquid with different cation length on the VLE of water + ethanol system [12]

Additionally, the effect of the anion has also been investigated. For example, [BMIM][Cl] and [BMIM][Br] have been studied with methyl acetate + methanol azeotrope [39]. It has been shown that both ionic liquids could remove the azeotrope, though [BMIM][Cl] has a higher azeotrope breaking capacity, as depicted in Figure 13.

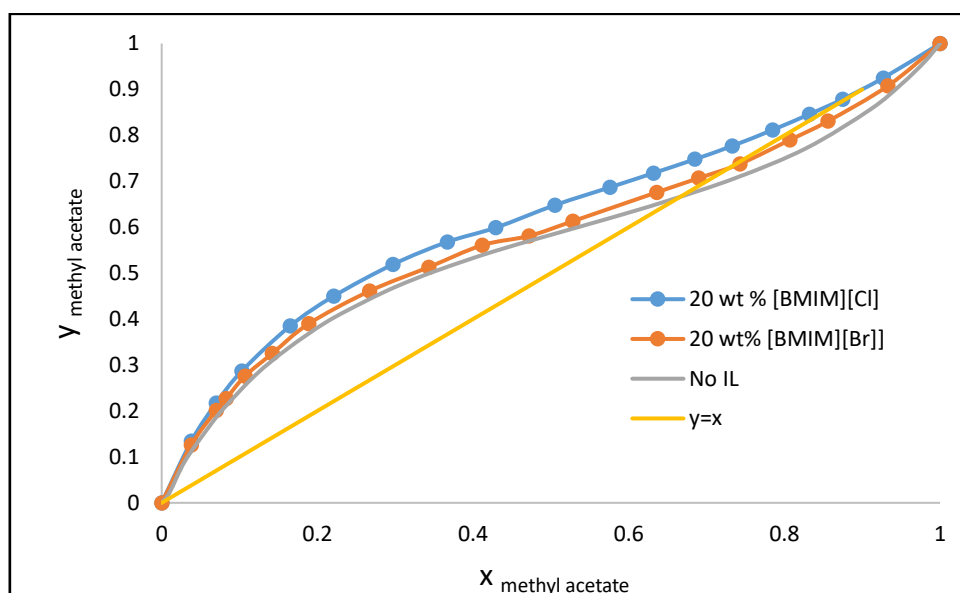


Figure 13: Effect of various ionic liquids on the vapor-liquid equilibrium of methyl acetate + methanol system at 101 kPa [39]

Figure 14 compares the ability of a different ionic liquid to enhance the relative volatility of ethanol to water at ethanol mole fraction (ionic liquid-free basis) of 0.95

and ionic liquid mole fraction of 0.1. It can be observed that ionic liquids with chloride, acetate, or trifluoromethanesulfonate perform generally better than the others

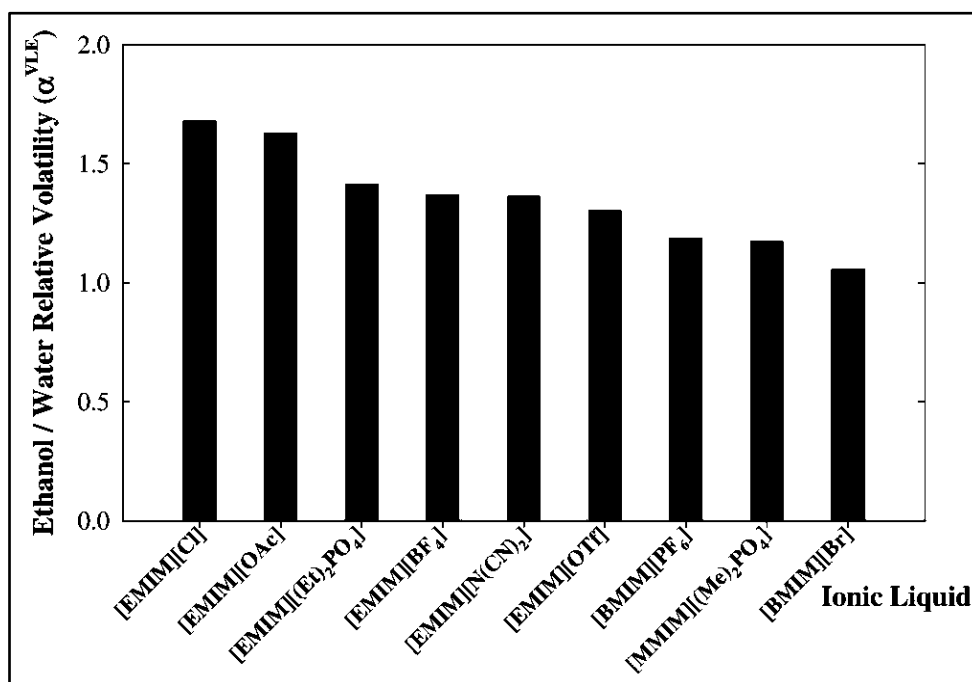


Figure 14: A comparison between ionic liquids ability to enhance the relative volatility of ethanol in ethanol + water mixture [12]

It should be noted that not all ionic liquids have the ability to shift the azeotrope. For example, adding 1-butyl-3-methylimidazolium chloride to water + ethanol mixture eliminates this system's azeotrope, while adding 1-hexyl-3-methylimidazolium chloride to the same system results in shifting the azeotrope toward a higher fraction of water. This occurs despite the structural similarity of two ionic liquids, as shown in Figure 15 [40].

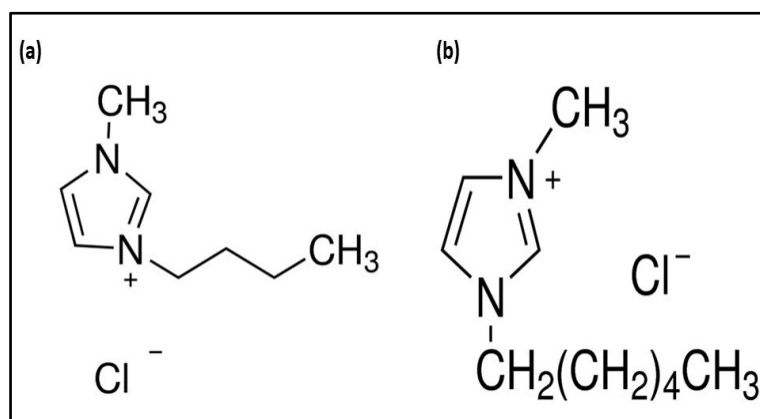


Figure 15: Comparison of BMIM and HMIM ionic liquids [41]

### 2.3. Effect of Ionic Liquids on the VLE of Water + 2-Propanol

The effect of several ionic liquids on the VLE of water + 2-propanol system has been also investigated. In a study that investigated the effect of [BMIM][BF<sub>4</sub>], [EMIM][BF<sub>4</sub>], [BMIM][N(CN)<sub>2</sub>], [EMIM][N(CN)<sub>2</sub>], [BMIM][OAc], [EMIM][OAc], and [BMIM][Cl] on the VLE of this system, it was concluded that the cation does not affect the phase behavior of this system much [42]. The nature of anion, however, has a remarkable effect on the phase behavior. They showed that ionic liquids having chloride or acetate as anions process a higher ability to remove the azeotrope of this system. Similar results were obtained in another study, which demonstrated that [EMIM][OAc] has the highest separation effect, as the mole fraction of [EMIM][OAc], [BMIM][OAc], [EMIM][Br] needed to eliminate the azeotrope are 0.1184, 0.1503, and 0.1989, respectively [43]. Another study showed that 1-ethyl-3-methylimidazolium dicyanamide can remove the azeotrope of this system under atmospheric pressure if its molar concentration is at least 0.085 [44].

## Chapter 3. Methodology

This chapter discusses the computational methodology that was followed to analyse the experimental results generated in this study for the effects of [BMPy][Cl] and [BMPy][OTf] on the VLE of water/2-propanol system. The thermodynamic model that was employed to represent the phase behaviour of the VLE systems under study is explained here. Also, the rationale behind choosing [BMPy][Cl] and [BMPy][OTf] ionic liquids is addressed. The experimental methodology employed for the acquisition of the experimental data will be detailed in a separate chapter, i.e., Chapter 4.

### 3.1 Approach

In order to understand the interaction between a solvent (e.g., water or 2-propanol) and an ionic liquid, binary VLE data of that solvent/ionic liquid system are needed. This is usually done experimentally by having the system studied at equilibrium. At equilibrium, macroscopic properties of VLE systems have no tendency to change macroscopically. Furthermore, these equilibrium states become stable when the conditions of the system at equilibrium do not be change catastrophically when slight disturbances in the external conditions occurs. Classical thermodynamic principles dictate that for an isolated system at equilibrium, the total entropy of the system is maximum, which is equivalent to saying that the total Gibbs free energy of the system is minimum. The Fundamental Property Relation resulting from the combination of the first and second laws of thermodynamics in terms of Gibbs free energy is defined as [27] ;

$$dG = -S dT + V dP + \sum_i \mu_i dn_i \quad (2)$$

where:  $G$ ,  $S$ , and  $V$  represent, respectively, the molar Gibbs energy, molar entropy, and molar volume,  $\mu_i$  and  $n_i$  represent, respectively, the chemical potential and the mole numbers of species ( $i$ ), and  $T$  and  $P$  are the temperature and pressure of the system under study. For a system prevailing in a state of VLE equilibrium at certain  $T$  and  $P$ , the criterion of  $G$  be at a minimum requires that the chemical potential of each species in both phases should be identical, which is equivalent to the equality of the fugacity of each component in both phases [27].

For systems in VLE equilibrium it is usually necessary to determine number of independent variables (properties) which when kept constant (controlled) the system

become fixed and reproducible. The number of such independent variables is called the number of degrees of freedom. The set of variables that can characterize a VLE system can include any thermodynamic properties, like density, internal energy, enthalpy etc... However, the most convenient set of variables include temperature, pressure, and composition of each phase. For systems in a state of equilibrium, the number of degrees of freedom ( $F$ ) can be determined using a simple rule called the phase rule:

$$F = C - P + 2 \quad (3)$$

where  $C$  is the number of components existing at equilibrium in the system and  $P$  is the number of phases. Thus, for binary systems in VLE, two degrees of freedom results indicating that fixing any two independent variables is sufficient for fully defining the system. For the ternary systems, three degrees of freedom exists indicating that fixing any three intensive variables is sufficient for fully defining the system.

### 3.2. Thermodynamic Model

At low to moderate pressure, vapor-liquid equilibrium data usually obey the modified Raoult's law, which is given as [7];

$$y_i P = x_i P_i^{sat} \lambda_i \quad (4)$$

where  $y_i$  is the mole fraction in the vapor phase,  $P$  is the system total pressure,  $x_i$  is the mole fraction in the liquid phase and  $P_i^{sat}$  is the saturation pressure of species  $i$ , and  $\lambda_i$  is the activity coefficient of species  $i$ . This equation is based on the assumption that the vapor phase is an ideal gas mixture. The equilibrium relation above provides a means for the experimental determination of  $\lambda_i$  by measuring  $T$ ,  $P$ , and the composition of both phases coexisting in equilibrium, i.e.,  $x_i$  and  $y_i$ .

Many analytical theorems were used to model activity coefficients. In this work, NRTL model [27] was utilized for data regression. This model is based on the local composition concept, which assumes that the composition around a certain molecule is different from the bulk composition of the solution, due to the difference in interaction between the central molecule with the same kind of molecules and with a different kind of molecules. The local composition assumption is present in other thermodynamic models as well, such as UNIFAQ and Wilson models, which have been successfully used to regress thermodynamic data of systems containing ionic liquid[24], [45]–[50].

When applied to ionic liquids-containing systems, NRTL model treats ionic liquid as non-dissociating species, yet it was able to regress various experimental data, although NMR studies [51] and conductivity tests [52] demonstrate that ionic liquid might exist as non-dissociating ion pairs or dissociated ions. Nevertheless, Lee and Lin [53] examined the dissociation of ionic liquid in various VLE systems by examining the following physical models:

- The free ion model, which assumes complete dissociation of ionic liquids in a solution,
- The dissociation model, which partial dissociation of the ionic liquids in a solution,
- The ion pair model, where ionic liquids exist as non-dissociated ion pairs.

In general, it was concluded that the ion pair model gives the best results in predicting the VLE of systems contains ionic liquids. The effect of dissociation becomes pronounced only at a low concentration of the ionic liquids. In fact, some researchers [54] who utilized the electrolyte NRTL model to study such systems found that the electrolyte model did not provide a significant improvement in prediction. In the view of these findings, The NRTL model is used in this work.

The NRTL model gives a relation between the activity coefficient and the mole fraction. Its mathematical form can be presented as follows [7];

$$\ln(\lambda_1) = x_2^2 \left[ \tau_{21} \left( \frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{G_{12} \tau_{12}}{(x_2 + x_1 G_{12})^2} \right] \quad (5)$$

$$\ln(\lambda_2) = x_1^2 \left[ \tau_{12} \left( \frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{G_{21} \tau_{21}}{(x_1 + x_2 G_{21})^2} \right] \quad (6)$$

$$G_{12} = \exp(-\alpha \tau_{12}) \quad (7)$$

$$G_{21} = \exp(-\alpha \tau_{21}) \quad (8)$$

$$\tau_{12} = \frac{b_{12}}{RT} \quad (9)$$

$$\tau_{21} = \frac{b_{21}}{RT} \quad (10)$$

where  $\lambda_i$  is the activity coefficient of species  $i$ ,  $x$  is the mole fraction,  $b_{12}$  and  $b_{21}$  are the model parameters,  $\alpha$  is the non-randomness parameter, which is usually set equal to 0.3,  $R$  is the universal gas constant and  $T$  is the temperature.

Since in the case solvent/ionic liquid binary systems the vapor phase is almost composed of water only, equation 2 can be rearranged to give the experimental activity coefficient:

$$\lambda_i = \frac{P}{x_i P_i^{sat}} \quad (11)$$

To perform these calculations, vapor pressure correlations for water and 2-Propanol are needed. The vapor pressure of water is [7];

$$\ln P^{sat} = 16.3872 - \frac{3885.7}{T+230.70} \quad (12)$$

where  $P^{sat}$  is the saturation pressure in kPa and  $T$  is the temperature in °C, valid between 0 °C - 200 °C. For 2-propanol, the saturation pressure is given by[55];

$$\ln P^{sat} = C_1 + \frac{C_2}{T} + C_3 \ln T + C_4 T^{C_5} \quad (13)$$

where  $C_1=90.094$ ,  $C_2=-8575.4$ ,  $C_3=-10.292$ ,  $C_4=1.6665 \times 10^{-17}$  and  $C_5=6$ .  $T$  is in K and  $P$  is in Pa. This expression is valid between -88 C to 235 °C.

For the binary mixture, the interaction parameters can be obtained by minimizing the following objective function.

$$OF = \sum_i^n (\ln(\lambda_{exp,s}) - \ln(\lambda_{NRTL,s}))^2 \quad (14)$$

where  $\lambda_{exp,w}$  is the experimental activity coefficient of the solvent, and  $\lambda_{NRTL,s}$  is the activity coefficient obtained from the NRTL model. For the ternary set, the activity coefficients are;

$$\ln(\lambda_i) = \frac{\sum_{j=1}^N x_j G_{ji} \tau_{ji}}{\sum_{j=1}^N x_j G_{ji}} + \sum_{j=1}^N \frac{x_j G_{ji}}{\sum_{k=1}^N x_k G_{kj}} \left( \tau_{ij} - \frac{\sum_{k=1}^N x_k G_{kj} \tau_{kj}}{\sum_{k=1}^N x_k G_{kj}} \right) \quad (15)$$

$$\begin{aligned} \ln(\lambda_1) = & \frac{x_2 G_{21} \tau_{21} + x_3 G_{31} \tau_{31}}{x_1 + x_2 G_{21} + x_3 G_{31}} - \frac{x_1}{x_1 + x_2 G_{21} + x_3 G_{31}} \left( \frac{x_2 G_{21} \tau_{21} + x_3 G_{31} \tau_{31}}{x_1 + x_2 G_{21} + x_3 G_{31}} \right) + \\ & \frac{x_2 G_{12}}{x_1 G_{12} + x_2 + x_3 G_{32}} \left( \tau_{12} - \frac{x_1 G_{12} \tau_{12} + x_3 G_{32} \tau_{32}}{x_1 G_{12} + x_2 + x_3 G_{32}} \right) + \frac{x_3 G_{13}}{x_1 G_{13} + x_2 G_{23} + x_3} \left( \tau_{13} - \frac{x_1 G_{13} \tau_{13} + x_2 G_{23} \tau_{23}}{x_1 G_{13} + x_2 G_{23} + x_3} \right) \end{aligned} \quad (16)$$

$$\begin{aligned} \ln(\lambda_2) = & \frac{x_1 G_{12} \tau_{12} + x_3 G_{32} \tau_{32}}{x_1 G_{12} + x_2 + x_3 G_{32}} + \frac{x_1 G_{21}}{x_1 + x_2 G_{21} + x_3 G_{31}} \left( \tau_{21} - \frac{x_2 G_{21} \tau_{21} + x_3 G_{31} \tau_{31}}{x_1 + x_2 G_{21} + x_3 G_{31}} \right) - \\ & \frac{x_2}{x_1 G_{12} + x_2 + x_3 G_{32}} \left( \frac{x_1 G_{12} \tau_{12} + x_3 G_{32} \tau_{32}}{x_1 G_{12} + x_2 + x_3 G_{32}} \right) + \frac{x_3 G_{23}}{x_1 G_{13} + x_2 G_{23} + x_3} \left( \tau_{23} - \frac{x_1 G_{13} \tau_{13} + x_2 G_{23} \tau_{23}}{x_1 G_{13} + x_2 G_{23} + x_3} \right) \end{aligned} \quad (17)$$



The binary interaction parameters for Water + 2-Propanol system were obtained from literature [56]. There are, thus, 4 interaction parameters that must be regressed. These parameters will be regressed by minimizing the objective function;

$$OF = \sum_i^n (T_{exp} - T_{NRTL})^2 \quad (18)$$

where  $T_{exp}$  is the experiment equilibrium temperature, and  $T_{NRTL}$  is the temperature obtained from the NRTL model. To compare the prediction and the experimental results, the root mean standard error is calculated as follows;

$$RMSE = \sqrt{\frac{(k_{calculated} - k_{predicted})^2}{N}} \quad (19)$$

where  $k$  is the activity coefficient or the temperature, and  $N$  is the number of the data points. Algorithmic flow-charts for the VLE calculations performed, as well as the spreadsheet that was used, are presented in Appendices A, B, and C.

### 3.3. Uncertainty of Measurements

The temperature and pressure experimental uncertainty are governed by the precision of the measuring instruments used, which are 0.01 °C and 0.1 kPa, respectively. The composition analysis is repeated three times to find the standard uncertainty. The (type A) standard uncertainty is defined as:

$$U(x) = \sqrt{\frac{(x_{measurement} - x_{average})^2}{k-1}} \quad (20)$$

where  $k$  is the number of replicas.

### 3.4. Optimization Method

There are different ways of finding a minimum of the objective functions appearing in equations 14 and 18. One possible way is the Generalized, Reduced Gradient (GRG) method, which is incorporated in many commercial software packages. Upon providing an initial guess, the solver finds the gradient by finding the partial derivative with respect to each variable via the forward difference derivation. The presence of the valley can be noted by detecting the change of the signs of the component of the gradient in the objective function [57]. The function reaches a minimum value when the gradient is zero. Figure 16 shows a typical (GRG) search contours. Solid and dashed lines represent different search paths, based on different step sizes.

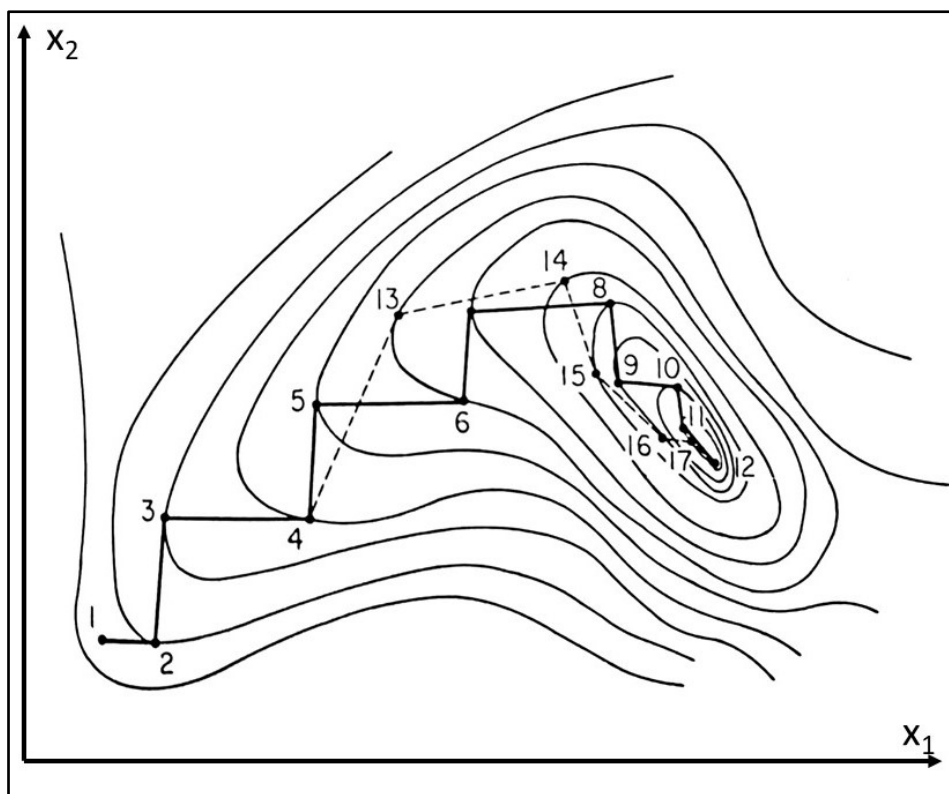


Figure 16: Generalized gradient search [57]

This method is incorporated into Microsoft excel solver routine. It, however, suffers from one drawback which is hitting a local, not global minimum. In the case of ternary component mixtures, there are about 6 adjustable parameters, which may result in multiple solutions. A good initial guess is thus critically in demand. In this work, the binary interaction parameters obtained from regression of binary data were used as an initial guess to obtain the 4 ternary adjustable parameters for each system.

### 3.5. Validation of the Computational Algorithm

As discussed above, finding the interaction parameters and predicting the ternary phase behavior was done using Microsoft Excel. To validate the computational algorithm, published data from the open technical literature on water + ethanol + 1-hexyl-3-methylimidazolium chloride were regressed, using the same spreadsheet that was used in this work. The obtained results are depicted in Figure 17, which are shown to exactly match the results published in that literature source [40].

### 3.6. Ionic Liquids Selection

As it has been addressed in Chapter 2, the effect of an ionic liquid on the phase behavior of a system is mainly determined by the nature of the anion. It is thus

anticipated that acetate, chloride, trifluoromethanesulfonate, and tetrafluoroborate ionic liquids can perform well in removing the azeotrope water + 2-propanol system.

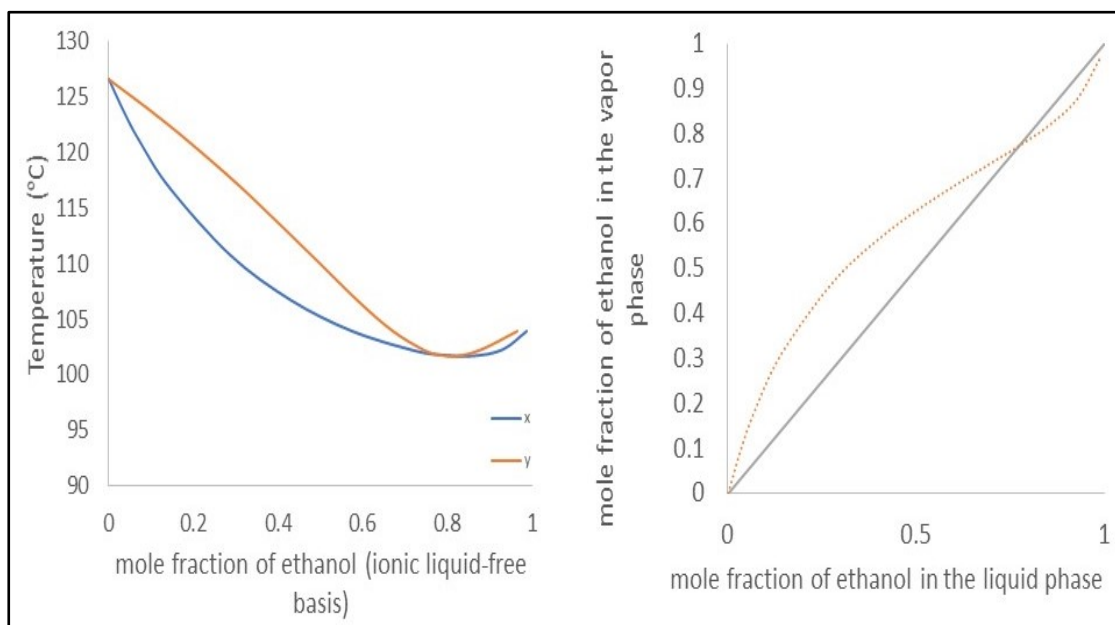


Figure 17. VLE of water + ethanol + ionic liquid at atmospheric pressure [40]

$\text{BF}_4^-$  or  $\text{PF}_6^-$  based ionic liquids were excluded in this study since there is a possibility of hydrolysis of these ionic liquids. It has been demonstrated that  $\text{PF}_6^-$  might remain stable up to a moderate temperature (70 °C) [58]. However, it hydrolyzes beyond this temperature or in basic conditions.  $\text{BF}_4^-$  has a higher tendency for hydrolysis, as it hydrolyzes even at room temperature, yielding hydrofluoric acid. Although such hydrolysis will not invalidate thermodynamic data, it introduces new species into the sample, which complicates thermodynamic treatment.

Although acetate based ionic liquids are promising in breaking azeotropic systems, they were not utilized in this work. This is due to the fact acetate based ionic liquids are known to be less thermally stable when compared other ionic liquids [59]. In fact, thermal decomposition of  $[\text{EMIM}][\text{OAc}]$  starts at around 140 °C [59]. Initially, it was opted to work with this ionic liquid, but we stopped since we observed a change in the color of the solution with time, as shown in Figure 18.

Chloride and trifluoromethanesulfonate-based ionic liquids perform well in the extractive distillation of water + ethanol system. Thus, they present good candidates for this study. As explained before, most studied ionic liquids were imidazolium-based. In our work, pyrrolidinium-based ionic liquids were selected instead. This enables us to

find a general comparison between the separation capacity of imidazolium and pyrrolidinium-based ionic liquids. The chosen ionic liquids are thus;

- 1-Butyl-1-methylpyrrolidinium chloride
- 1-Butyl-1-methylpyrrolidinium trifluoromethanesulfonate

The molecular structures of these ionic liquids are shown in Figure 19.



Figure 18: Color change of [EMIM][OAc]. Image on the left is for new [EMIM][OAc], while the image on the right is for [EMIM][OAc] solution after boiling for long time

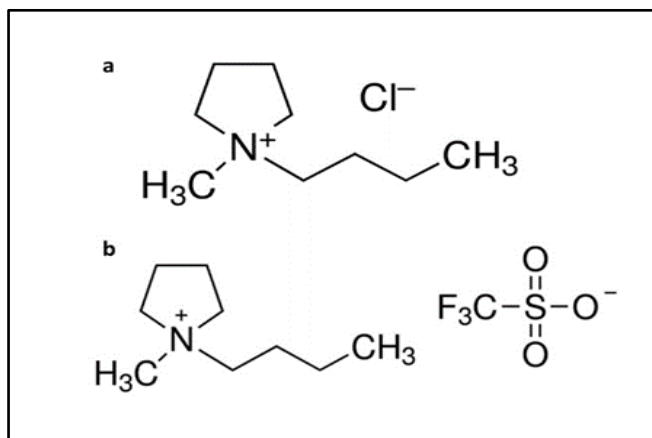


Figure 19: Ionic liquids used in this work. (a) [BMPy][Cl]. (b) [BMPy][OTf] [60]

## Chapter 4. Experimental Setup and Procedure

In this chapter, the experimental procedure used to obtain the VLE data of the binary and ternary systems is described. Analysis techniques and calibration curves are summarized here.

### 4.1. Materials

The materials used in this study, together with their suppliers, purities and the methods of analysis are shown in Table 2. All the materials were used as received without further purification. Water content and purity of the ionic liquids were measured using Karl Fischer (KF) water content apparatus and electrophoresis technique, respectively. These properties were retrieved from the certificate of analysis provided by the supplier.

Table 2: Materials and purities

Chemical	Supplier	Mass fraction	Water content wt%	Analysis Methods
[BMPyr][Cl]	Merck	>0.98	<0.01	Karl Fischer, Electrophoresis
[BMPyr][OTf]	Merck	>0.98	<0.01	Karl Fischer, Electrophoresis
<b>2-Propanol</b>	Panreac	0.99	-	-

### 4.2. Apparatus and Experimental Procedure

The apparatus used in generating the experimental VLE data in this study is a two-phase (liquid/vapor) circulating ebulliometer (model: VLE 100, Pilodist®, Germany). The apparatus, together with its components, are presented in Figure 20.

The liquid mixture is boiled in a boiler using an immersed electrical rod heater. As the liquid mixture is boiled, two-phase vapor-liquid mixture passes through a Cottrell tube where an adequate equilibration between the two phases was achieved. Equilibrium was reached when all instrumental indicators, including temperature indicators, display constant reading. It should be noted that as the concentration of the ionic liquid in the boiler was increased, more time was needed to reach equilibrium. Temperature was measured using the platinum thermocouples supplied with the apparatus (PT 100 KI. A DIN EN 60751). The sub-atmospheric pressure was obtained using a vacuum pump (D.V.P vacuum technologies, Italy). The pressure was measured using the pressure sensor supplied with the apparatus (model: DMU 05 P, Afriso,

Germany). To validate the experimental setup, VLE of water + 2-propanol was obtained and compared with the data reported in the literature [61]. The results were in good agreement, as depicted in Figure 21.

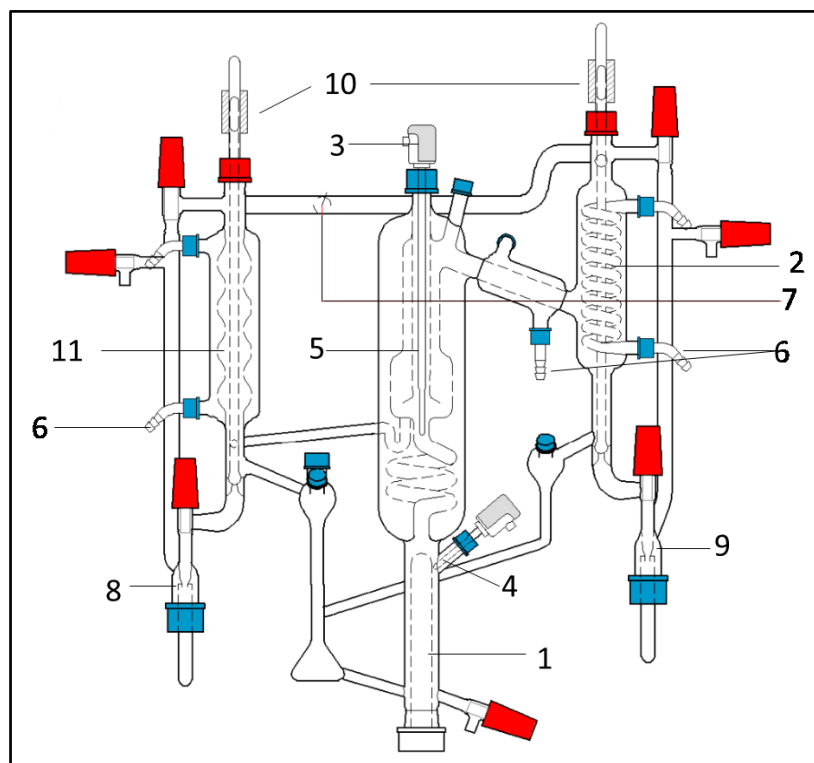


Figure 20: The ebulliometer apparatus used in this study: 1: Boiler with immersed rod heater. 2: Condenser. 3: Vapor temperature sensor. 4: Liquid temperature sensor. 5: Glass body of the phase equilibrium apparatus. 6: hose connection. 7: Pressure equalization line. 8: Liquid sampling port. 9: vapor sampling port. 10: Solenoid valves for sampling. 11: valve plunger liquid phase [62]

If the boiling temperature exceeds 100 °C, it is recommended to use a heating jacket set at 3 °C below the boiling point of the mixture. This is to avoid condensation of the vapor in the internal parts of the apparatus. Heating mantle can be set at the desired temperature and can be controlled with a proportional integral (PI) controller. For optimum controller performance, a proportional gain of 600 and an integral time of 30 seconds is recommended.

#### 4.3 Composition Analysis of Binary Systems

Refractive index (RI) was used to find the composition of the binary mixtures. A refractometer (model: HI 96800, Hanna, Romania) with a precision of  $\pm 0.0001$  was used for this purpose. Sodium spectrum was utilized to find the refractive index at 20 °C. An analytical balance (model: AS 220/C/2, Radwag, Germany) with a precision of

$\pm 0.1$  mg was used in the gravimetric synthesis of the liquid mixtures such as those needed in the preparation of the calibration curves. The calibration curve for water + 2-propanol system is depicted in Figure 22. It must be noted that the determination of composition for a sample with refractive index exceeding 1.365 becomes tedious owing to the non-linear behavior of the calibration curve shown in Figure 22. As a consequence of this non-linear behavior, any refractive index value exceeding 1.365 can correspond to more than one composition value. To resolve this issue, sample dilution is required where a sample of a known mass is mixed with a known amount of pure water. Diluting the sample with water reduces the refractive index to fall within the linear region of the calibration curve. Thus, the composition of the diluted sample can easily be determined after applying simple mass balance principle.

In order to determine the composition of binary systems consisting of a solvent (water or 2-propanol) and an ionic liquid, the calibration curves displayed in Figure 23 were used. All the calibration curves were prepared three times in order to ensure reproducibility.

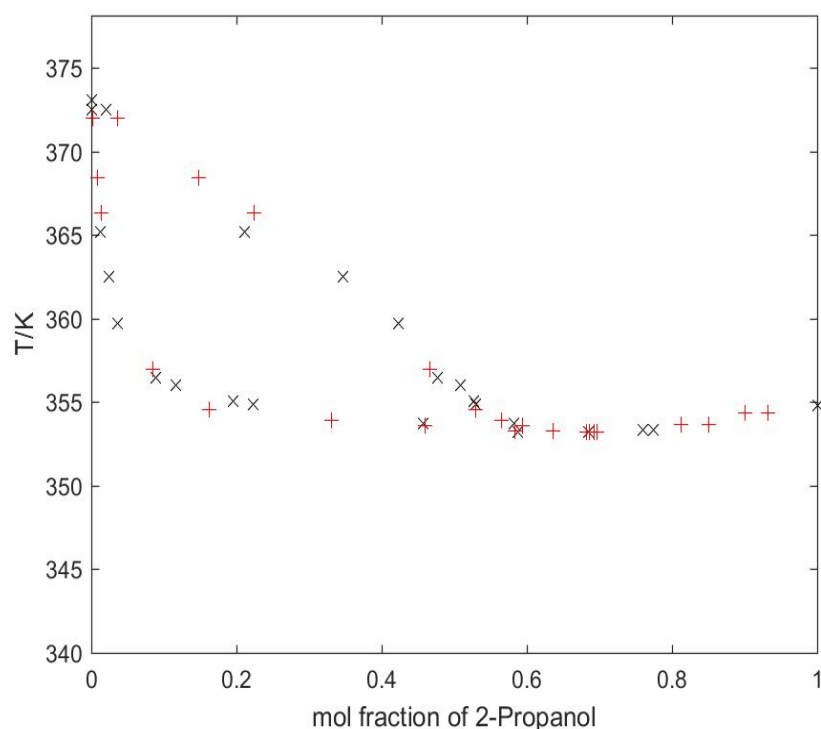


Figure 21: VLE of water + 2-propanol system at 101 kPa (x: This work, + : data from Ref. [61]).

#### 4.4. Composition Analysis of Ternary Systems

In case of VLE of ternary systems, the vapor phase consisted of only two components (water and 2-propanol) owing to the negligible vapor pressure of the ionic liquids.

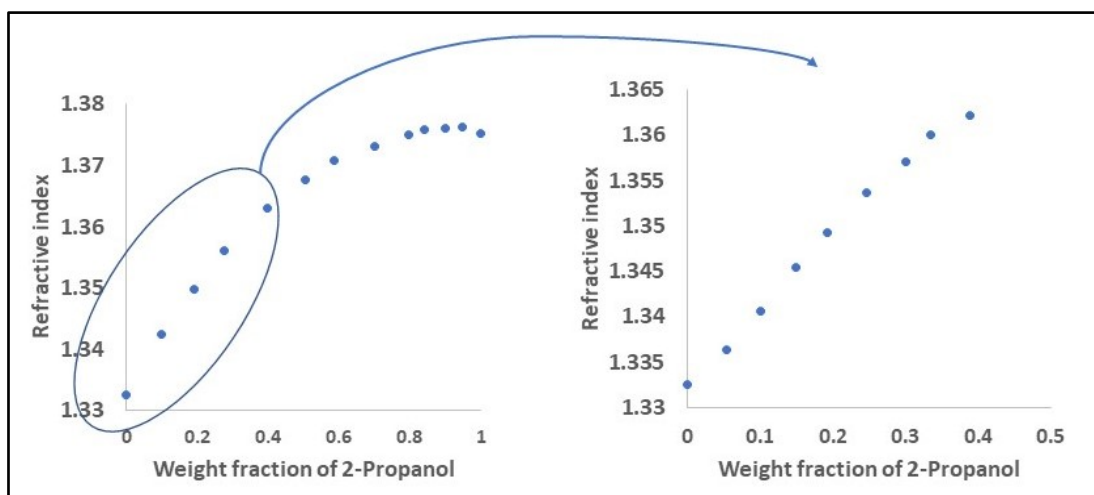


Figure 22: Refractive index of water + 2-propanol system

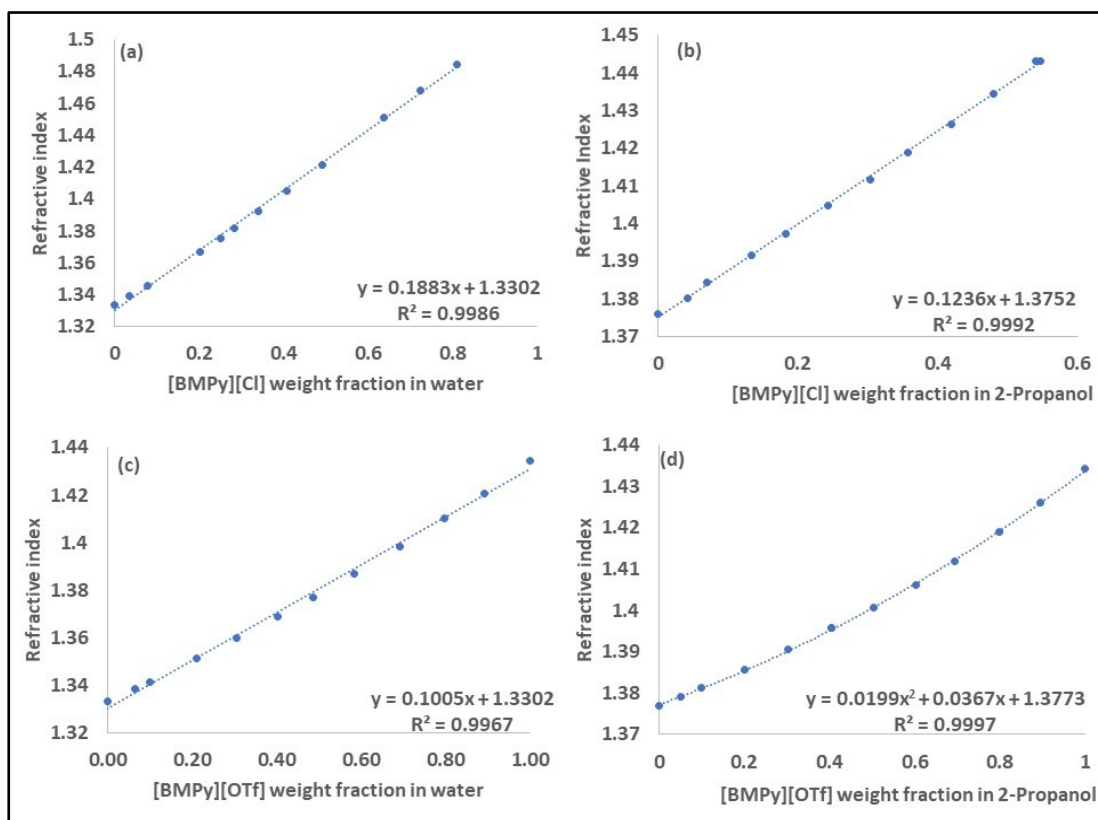


Figure 23: Refractive index at 20 °C as a function of ionic liquid composition (a) water + [BMPy][Cl], (b) 2-propanol + [BMPy][Cl], (c) water + [BMPy][OTf], (d) 2-propanol + [BMPy][OTf]



As a result, refractive index was again utilized to determine the composition of the vapor samples (binary mixtures). The liquid phase, on the other hand, was a ternary mixture and was analyzed for its composition using the gravimetric method. This was done by heating a small sample of known mass to an elevated temperature ( $\sim 180$  °C) and under reduced pressure in a long neck round bottom distillation flask for about 90 minutes. The vapors, consisting of water and 2-propanol, from the distillation flask were condensed and collected for composition analysis. Upon reaching the boiling end point, the residue mass (consisting of only ionic liquid) was determined in order to calculate the mass fraction of the ionic liquid in the original ternary sample. The compositions of the condensate samples (binary mixtures of water and 2-propanol) were determined by refractive index measurements.

While performing the gravimetric method, the thermal decomposition of ionic liquids must be taken into consideration. In fact, ionic liquids decompose in a complex mechanism that depends on the heating rate, heating period, and the flow of atmosphere during the heating process. Some studies demonstrated that the thermal decomposition of ionic liquids can occur at temperatures below the onset decomposition temperature [63]. Many ionic liquids have decomposition temperatures above 200 °C, and will not decompose below this temperature unless the heating period is long. For example, N-butyl-pyridinium trifluoroethane sulfonate has an onset temperature of 362 °C. However, it loses 1% of its mass when heated to 226 °C for 10 hours [63]. In order to prevent any thermal decomposition in the performed experiments, the temperature was kept below 200 °C, and the heating duration was always less than 90 minutes.

#### **4.5. Uncertainty Analysis**

For each binary mixture, the calibration curve was repeated three times. The standard deviation between the three calibration curves for each binary system was 0.0015.

To ensure reproducibility of the VLE data in the binary systems, three samples were collected at each equilibrium point. Each sample was taken five minutes after the sample that preceded it. The standard uncertainty in composition was about 0.001. For the case of ternary mixtures, the uncertainty in the vapor and liquid phase compositions was estimated to be 0.002 and 0.03, respectively.

## Chapter 5. Results and Analysis

This chapter presents the experimental and modelling results of this work. In Section 5.1, the effect of each ionic liquid on the boiling point of each solvent is presented. This is followed by demonstrating the effect of each ionic liquid on the phase behavior of water/2-propanol system, presented in a pseudo-binary basis. The results are then analyzed based on the electrostatic interaction theory.

### 5.1. Binary Systems

In this section, the effect of each ionic liquid on the boiling point of water or 2-propanol is demonstrated. The results are fitted using the NRTL model, and the interaction parameters are presented.

**5.1.1. Solvents + [BMPy][Cl].** Water (1) + [BMPy][Cl] (2) phase behavior was studied at three different isobars: 50 kPa, 75 kPa, and 100 kPa. The results are depicted in Table 3 and Figure 24.

Table 3: Phase behavior of water (1) + [BMPy][Cl] (2) system

P=50 kPa		P=75 kPa		P=100 kPa	
x <sub>2</sub>	T (°C)	x <sub>2</sub>	T (°C)	x <sub>2</sub>	T (°C)
0	81.06	0	91.62	0	99.62
0.022	82.23	0.022	92.61	0.022	100.3
0.041	83.10	0.042	93.74	0.041	101.62
0.059	84.09	0.060	94.15	0.059	102.65
0.065	84.86	0.065	95.42	0.066	103.51
0.079	85.70	0.079	96.52	0.080	104.43
0.095	87.42	0.096	98.15	0.098	105.89
0.106	88.16	0.105	98.68	0.105	107.15
0.127	89.67	0.128	100.06	0.138	109.5
0.140	91.55	0.138	102.31	0.161	111.14
0.158	93.55	0.158	104.48	-	-

Results for 2-propanol (1) + [BMPy][Cl] (2) are reported in Table 4 and are depicted in Figure 25. As stated previously, these data have been modeled using the NRTL model. As shown in Figures 24 and 25, the model can very well describe the phase behavior of the data. The model parameters, as well as the RMSD, are summarized in Table 5.

**5.1.2. Solvents + [BMPy][OTf].** Water (1) + [BMPy][OTf] (2) phase behavior was studied at three different isobars: 50 kPa, 75 kPa, and 100 kPa. The results are depicted in Table 6 and in Figure 26.

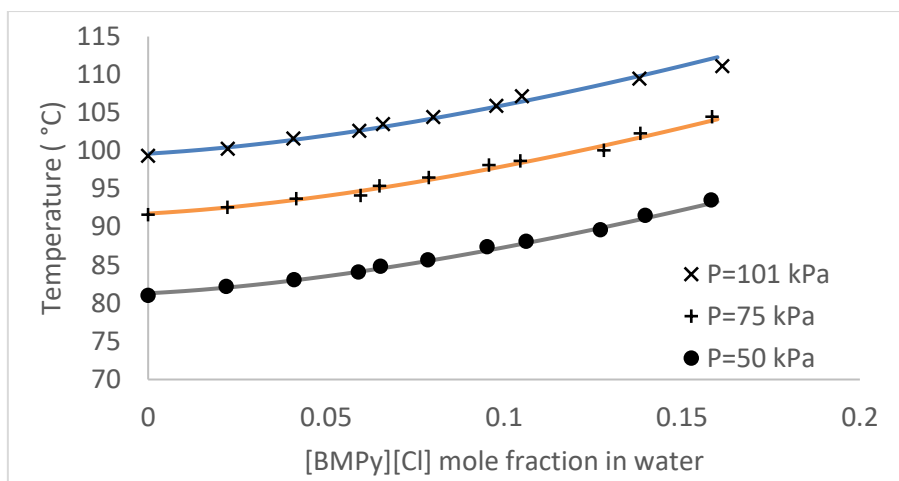


Figure 24: VLE of water (1) + [BMPy][Cl] (2) system. x: 100 kPa, +: 75 kPa, •: 50 kPa. Solid lines represent NRTL predictions

Table 4: VLE of 2-propanol (1) + [BMPy][Cl] (2) system

P=50 kPa		P=75 kPa		P=100 kPa	
x <sub>2</sub>	T (°C)	x <sub>2</sub>	T (°C)	x <sub>2</sub>	T (°C)
0	65.25	0	74.50	0	81.62
0.011	65.50	0.012	74.74	0.012	81.93
0.033	65.82	0.032	74.63	0.034	82.00
0.048	66.12	0.048	75.52	0.044	82.50
0.073	66.74	0.073	75.83	0.052	82.59
0.095	67.50	0.097	76.93	0.073	83.24
0.125	68.69	0.127	77.50	0.099	84.14
0.147	69.35	0.150	79.02	0.131	85.58
0.163	70.39	0.162	79.94	0.148	86.56
0.177	70.70	0.177	80.02	0.163	87.27

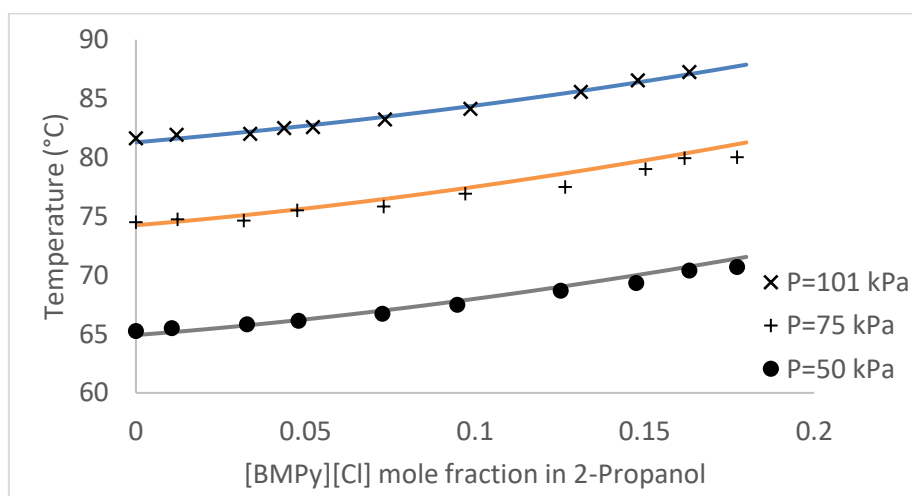


Figure 25: VLE of 2-propanol (1) + [BMPy][Cl] (2) system. x: 100 kPa, +: 75 kPa, •: 50 kPa. Solid lines represent NRTL predictions

Table 5: NRTL parameters for the solvent (1) and [BMPy][Cl] (2)

Solvent	$b_{12}$ (J/mol)	$b_{21}$ (J/mol)	$\alpha$	RMSD
Water	-4517.78	-8510.5	0.3	0.015
2-Propanol	-4534	-1585	0.3	0.011

For 2-propanol (1) + [BMPy][OTf] (2) systems, results are presented in Table 7 and in Figure 27. The NRTL parameters are displayed in Table 8.

Table 6: Phase behavior of water (1) + [BMPy][OTf] (2) system

50 kPa		750 kPa		101 kPa	
$x_2$	T (°C)	$x_2$	T (°C)	$x_2$	T (°C)
0.000	81.06	0.000	91.62	0.000	99.9
0.005	81.25	0.005	91.62	0.005	100.03
0.014	81.5	0.014	91.75	0.015	100.11
0.021	81.6	0.020	91.95	0.021	100.32
0.046	81.67	0.041	92.27	0.046	100.62
0.063	82.01	0.066	92.55	0.066	100.88
0.098	82.4	0.097	92.99	0.097	101.33
0.121	82.61	0.124	93.31	0.124	101.77
0.172	83.75	0.172	94.58	0.172	103.06
0.214	84.64	0.212	95.43	0.214	104.16
0.245	85.45	0.252	96.59	0.248	105.11
0.282	86.19	0.280	97.18	0.285	106.19

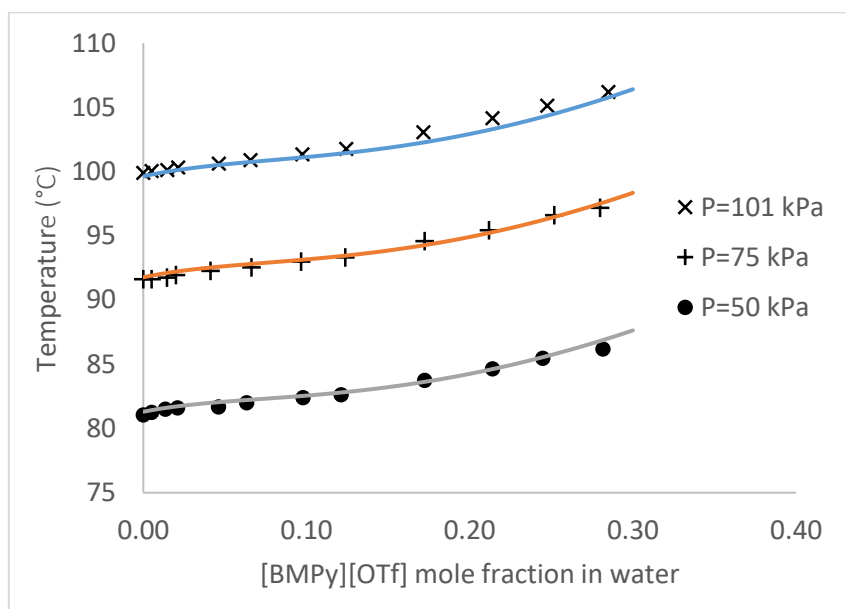


Figure 26: VLE of water (1) + [BMPy][OTf] (2) system. x: 100 kPa, +: 75 kPa, ●: 50 kPa. Solid lines represent NRTL prediction

## 5.2. Ternary Systems

In this section, ternary data of the systems water (1) + 2-propanol (2) + [BMPy][Cl] (3) and water (1) + 2-propanol (2) + [BMPy][OTf] (3) are presented. These data are regressed using the NRTL model. The model parameters are then used to predict the VLE of the ternary systems at a fixed ionic liquid concentration.

Table 7: VLE of 2-propanol (1) + [BMPy][OTf] (2) system

50 kPa		750 kPa		101 kPa	
x <sub>2</sub>	T (°C)	x <sub>2</sub>	T (°C)	x <sub>2</sub>	T (°C)
0	65.25	0	74.5	0	81.62
0.011	65.51	0.010	74.81	0.010	81.85
0.029	65.78	0.031	74.95	0.033	81.99
0.050	66	0.052	74.08	0.051	81.96
0.082	66.24	0.082	75.26	0.082	82.34
0.110	66.4	0.108	75.11	0.111	82.6
0.146	67	0.146	76.27	0.154	82.91
0.164	67.13	0.165	76.49	0.202	84.46
0.202	68.08	0.202	77.29	0.227	84.88
0.224	68.23	0.220	77.98	0.269	86.66
0.265	69.18	0.259	78.75	0.290	87.3
0.297	69.6	0.303	80.12	-	-

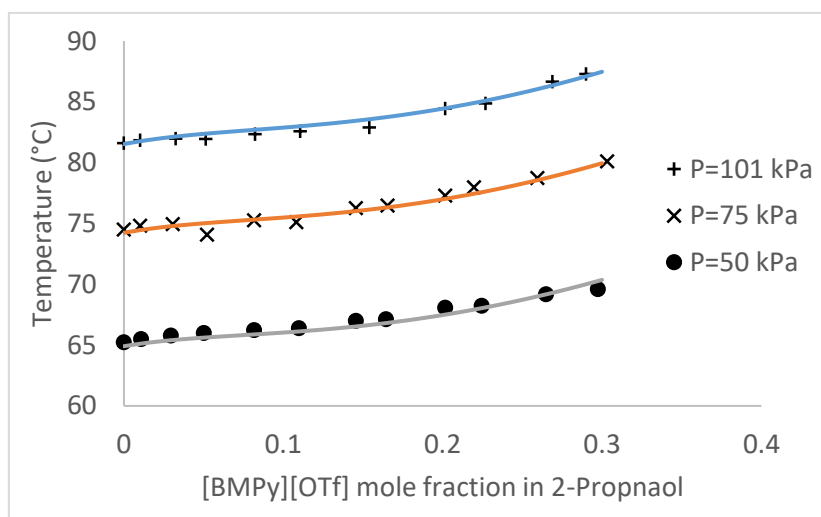


Figure 27: VLE of 2-propanol (1) + [BMPy][OTf] (2) system. x: 100 kPa, +: 75 kPa, •: 50 kPa. Solid lines represent NRTL prediction

Table 8: NRTL parameter for the solvent (1) and [BMPy][OTf] (2)

Solvent	b <sub>12</sub> (J/mol)	b <sub>21</sub> (J/mol)	α	RMSD
Water	13401	-5593	0.3	0.0095
2-Propanol	12573	-5207	0.3	0.015

**5.2.1. Water (1) + 2-Propanol (2) + [BMPy][Cl] (3) system.** Ternary VLE data of this system is presented in Table 9, while the T-x-y diagram and the equilibrium curves are presented in Figures 28 and 29, respectively.

Table 9: VLE data of water (1) + 2-propanol (2) +[BMPy][Cl] (3) at 100 kPa

T c	x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>	y <sub>1</sub>	y <sub>2</sub>
83.54	0.66	0.25	0.09	0.396	0.604
84.83	0.79	0.14	0.08	0.394	0.606
86.52	0.76	0.16	0.08	0.486	0.514
88.7	0.78	0.11	0.11	0.370	0.630
89.22	0.85	0.08	0.06	0.495	0.505
90.09	0.81	0.09	0.10	0.507	0.493
91.76	0.87	0.06	0.07	0.547	0.453
93.23	0.85	0.05	0.10	0.556	0.444
94.98	0.90	0.04	0.07	0.653	0.347
97.32	0.92	0.02	0.06	0.762	0.238
97.83	0.79	0.07	0.15	0.560	0.440
99.83	0.83	0.04	0.13	0.720	0.280
99.96	0.92	0.02	0.07	0.861	0.139
102.29	0.90	0.01	0.09	0.892	0.108
104.14	0.91	0.01	0.08	0.970	0.030
105.52	0.89	0.01	0.10	0.902	0.098
107.06	0.88	0.01	0.12	0.984	0.016
109.67	0.80	0.02	0.17	0.770	0.230

The NRTL parameters for this system are displayed in Table 10, while the phase behavior of this system is depicted in Figure 27. It can be observed, [BMPy][Cl] can shift and eliminate the azeotrope at a mole fraction of 0.3.

Table 10: NRTL parameters for the ternary system water (1) + 2-propanol (2) + [BMPy][Cl] (3)

Parameter	b <sub>12</sub>	b <sub>21</sub>	b <sub>13</sub>	b <sub>31</sub>	b <sub>23</sub>	b <sub>32</sub>	RMSD (°C)
Value (J/mol)	6901	77	-2188	-9410	-4396	-3172	1.9

**5.2.2. Water (1) + 2-Propanol (2) + [BMPy][OTf] (3) system.** Ternary VLE data of this system is presented in Table 11, while NRTL parameters are shown in Table 12. T-x-y and equilibrium curves are displayed in Figure 30 and 31, respectively.

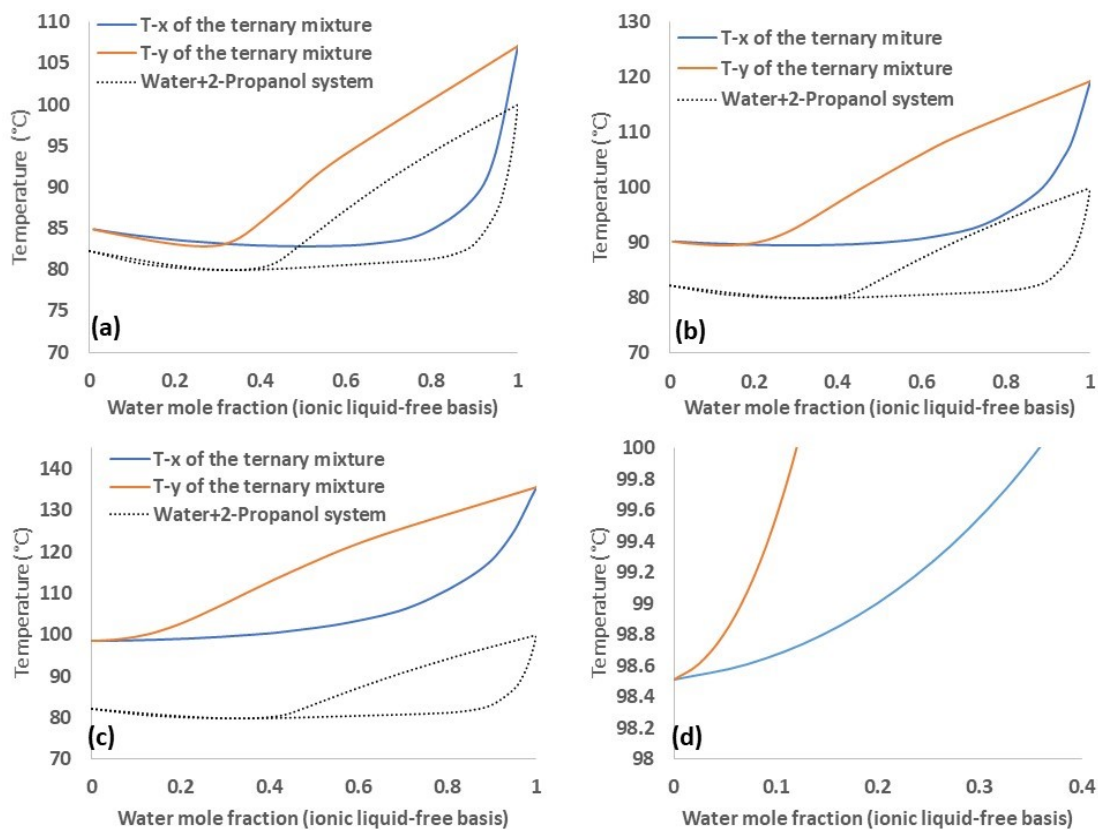


Figure 28: T-x-y of water (1) + 2-propanol (2) + [BMPy][Cl] (3) at 100 kPa at ionic liquid concentration of (a) 10 mol% (b) 20 mol% (c) 31 mol% (d) zoomed in depiction of (c)

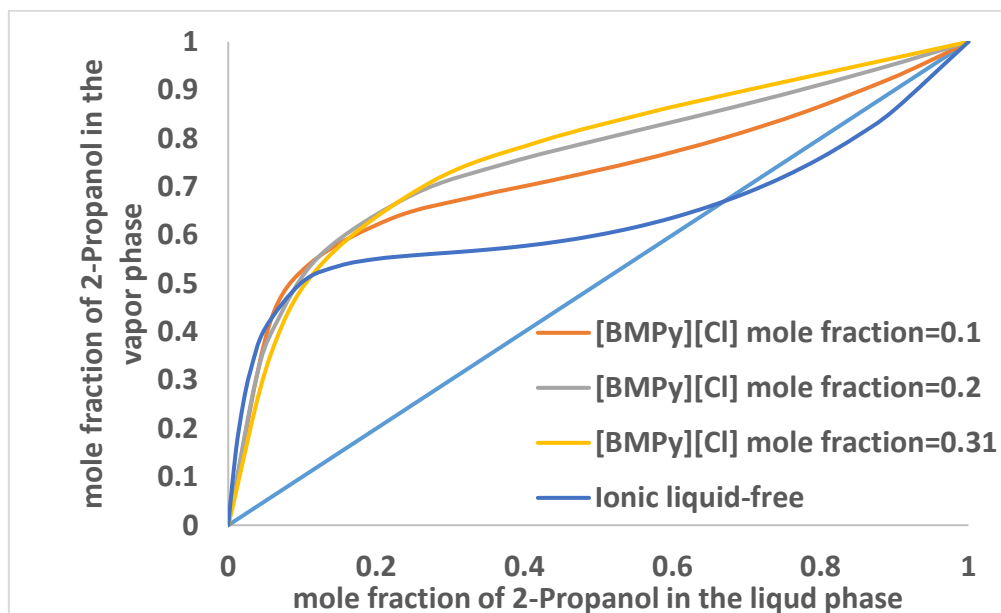


Figure 29: Equilibrium curve of water (1) + 2-propanol (2) system at different concentrations of [BMPy][Cl] (3) at 100 kPa

Table 11: VLE data of water (1) + 2-propanol (2) +[BMPy][OTf] (3) at 100 kPa

T (°C)	x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>	y <sub>1</sub>	y <sub>2</sub>
82.35	0.45	0.46	0.09	0.367	0.633
83.1	0.82	0.11	0.06	0.468	0.532
84.03	0.53	0.36	0.11	0.468	0.532
85.11	0.62	0.27	0.10	0.862	0.138
86.22	0.63	0.24	0.12	0.517	0.483
87.2	0.76	0.16	0.08	0.527	0.473
88.52	0.77	0.14	0.09	0.514	0.486
89.5	0.77	0.13	0.10	0.567	0.433
90.6	0.77	0.12	0.11	0.580	0.420
92.33	0.78	0.10	0.12	0.638	0.362
93.65	0.86	0.06	0.08	0.694	0.306
94.4	0.88	0.04	0.07	0.734	0.266
95.26	0.89	0.04	0.07	0.764	0.236
97.38	0.89	0.03	0.09	0.846	0.154
97.66	0.82	0.04	0.14	0.816	0.184
98.17	0.87	0.02	0.10	0.870	0.130
98.72	0.89	0.02	0.09	0.877	0.123
99.31	0.87	0.02	0.11	0.902	0.098
99.81	0.88	0.01	0.11	0.897	0.103
100.61	0.87	0.01	0.12	0.926	0.074
101.75	0.82	0.01	0.17	0.957	0.043
102.59	0.80	0.01	0.20	0.988	0.012

Table 12: NRTL parameters for the ternary system water (1) + 2-propanol (2) + [BMPy][OTf] (3)

Parameter	b <sub>12</sub>	b <sub>21</sub>	b <sub>13</sub>	b <sub>31</sub>	b <sub>23</sub>	b <sub>32</sub>	RMSD (°C)
Value (J/mol)	6901	77	4423	-1805	12570	-5000	1.24

### 5.3. Analysis of Results

**5.3.1. Binary VLE results.** The two ionic liquids have a common cation, i.e., [BMPy]. Thus, the differences in the phase behavior of the studied binary systems may be attributed to the nature of the anion and the solvent present. It can be observed that the boiling point elevation, upon adding [BMPy][Cl] to water, is higher than that caused by adding the same ionic liquid to 2-propanol. To illustrate, when the mole fraction of [BMPy][Cl] was about 15%, the boiling point elevation for water was about 11 °C. This result is similar to the one obtained when other chloride ionic liquids are added to water, as was show in earlier work [64].



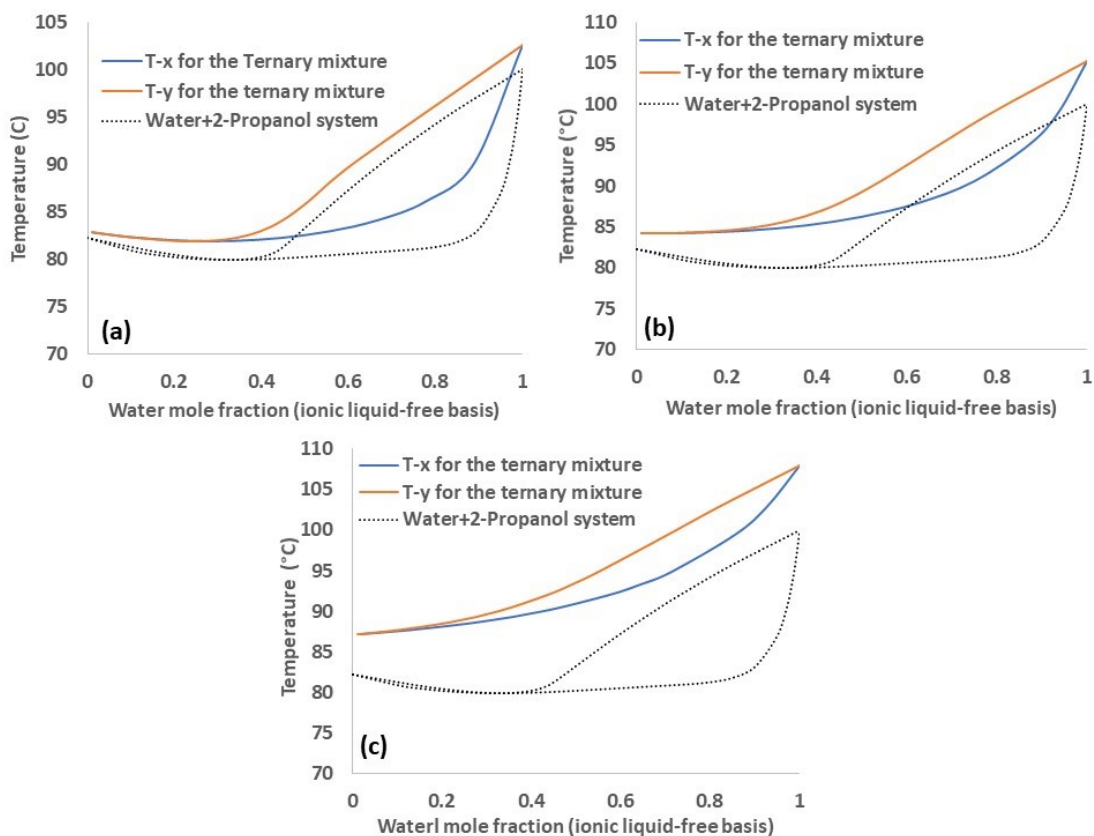


Figure 30: T-x-y of water (1) + 2-propanol (2) + [BMPy][Cl] (3) at 100 kPa at ionic liquid concentration of (a) 10 mol% (b) 20 mol% (c) 30 mol %

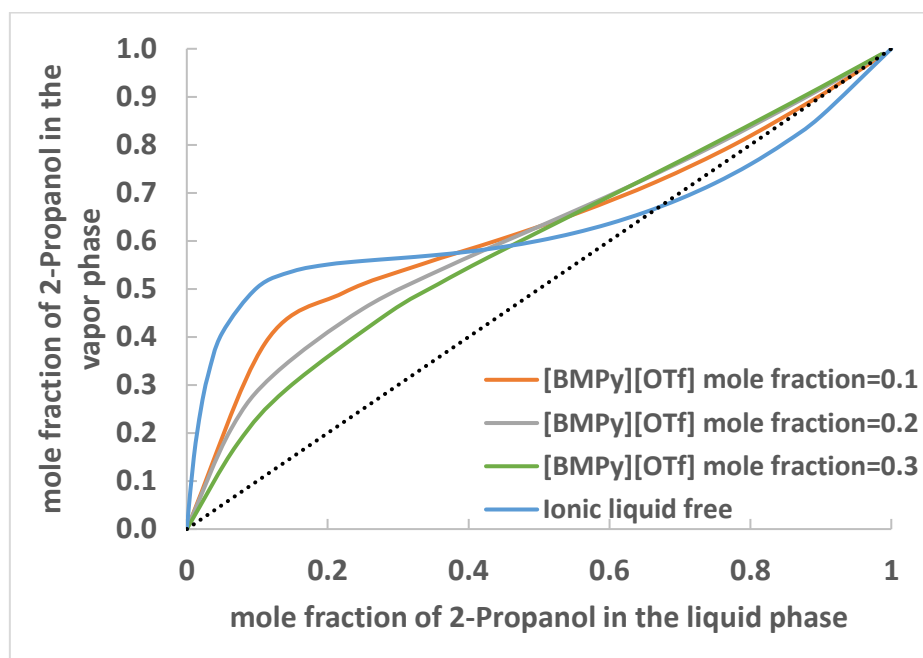


Figure 31: Equilibrium curve of water (1) + 2-propanol (2) system at different concentrations of [BMPy][OTf] (3) at 100 kPa

For 2-propanol, the boiling point elevation was observed to be around 5°C at the same mole fraction. Referring to Figure 30-a, it is observed that the activity coefficient of water in water (1) + [BMPy][Cl] (2) system is less than unity over the whole range of the studied composition. This indicates that the liquid mixture of water (1) + [BMPy][Cl] (2) is deviating negatively from the ideal solution model. Moreover, as evident from the decline in water activity coefficient with the increasing ionic liquid concentration (Figure 32-a), water (1) + [BMPy][Cl] (2) system exhibits higher deviation from the ideality as the concentration of the ionic liquid increases. However, the same figure shows that 2-propanol forms nearly an ideal solution with [BMPy][Cl] as indicated by nearly unit activity coefficient for 2-propanol over the entire composition range (Figure 32-a). This suggests that [BMPy][Cl] could be a better candidate entrainer to break the azeotrope in the water (1) + 2-propanol (2) system. This is, however, not the case observed for the two binary systems involving [BMPy][OTf]. As depicted in Figure 32-b, the activity coefficient values for both (water and 2-propanol) solvents are higher than unity over the entire composition range. Moreover, as seen in Figure 32-b, [BMPy][OTf] equally affects the activities of both solvents in the liquid phase. In other words, the activity coefficients of both water and 2-propanol have the same functional dependence on the ionic liquid concentration in the liquid phase. Similar behavior has been noticed with imidazolium-based ionic liquids in other studies in the literature [64]. Such behavior can be typically attributed to the ionic liquid's ability to form hydrogen bonds with solvents [65]. Ionic liquids with higher hydrogen bond-forming capability tend to strongly interact with water [64], [66], [67], whereas fluorinated anions can only form weak hydrogen bonds with water [68].

The phenomenon of weak hydrogen bonding formed by covalently bonded fluoride ion in ionic liquids has also been addressed in previous works of other investigators [69], [70] where it was shown that the attachment of fluorine atoms to a carbon atom tends to decrease the proton accepting capability during the formation of hydrogen bonds. Indeed, it was concluded that a (C-F) group has a weaker tendency than (C-OH) or (C=) to form a hydrogen bond with (C-H), (O-H), or (N-H) groups despite the fact that fluorine has the highest electronegativity. This is because a covalently bounded fluorine atom is an extremely weak base and cannot act as a proton acceptor [69].

The strength of the interaction between water and ionic liquids has also been attributed to the hydrophobicity of ionic liquids[64]. Although both [BMPy][Cl] and [BMPy][OTf] ionic liquids used in this work are hydrophilic, the former has a more pronounced hydrophilic character. It has been demonstrated that highly hydrophilic ionic liquids tend to strongly interact with water [64].

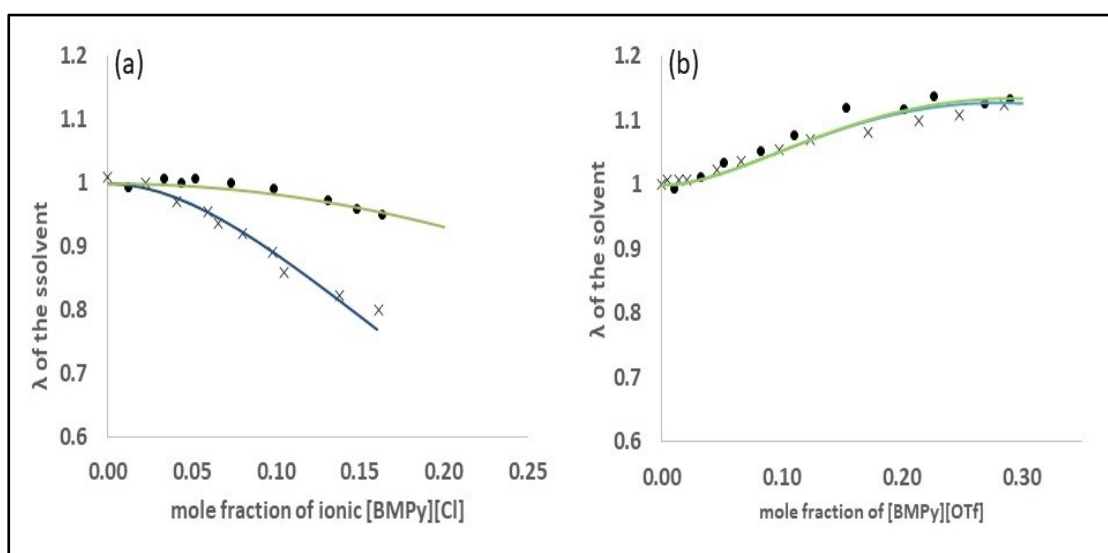


Figure 32: Activity coefficients of water (x) and 2-propanol (●) in the presence of (a) [BMPy][Cl] and (b) [BMPy][OTf] at 100 kPa

In Figures 23 through 26, it can be observed that the isobars are almost parallel, indicating that the boiling point elevation is not a strong function of the pressure. Also, it can be seen that in the case of [BMPy][OTf], the elevation is almost linear, while a stronger, nonlinear elevation is observed in the case of [BMPy][Cl]. Also, the activity coefficients of both solvents were found to be independent of pressure in the studied composition range (Figure 33). Similar results were obtained in previous research [64].

**5.3.2. Ternary VLE results.** For the ternary systems studied in this work, it was found that the addition of [BMPy][Cl] increases the concentration of 2-propanol in the vapor phase. The concentration of 2-propanol in the vapor phase increases as the ionic liquid concentration increases. This allows complete elimination of the azeotrope at [BMPy][Cl] mole fraction of about 0.31 (Figure 28). In contrast, the addition of [BMPy][OTf] does not have a significant effect on the azeotrope (Figure 30). Also, as observed in Figure 31, a complicated salt effect was observed for the VLE of water (1)

+ 2-propanol (2) system. In particular, a salting-in effect of 2-propanol in the water rich region, and a slight salting-out effect in vicinity of the azeotrope point is observed.

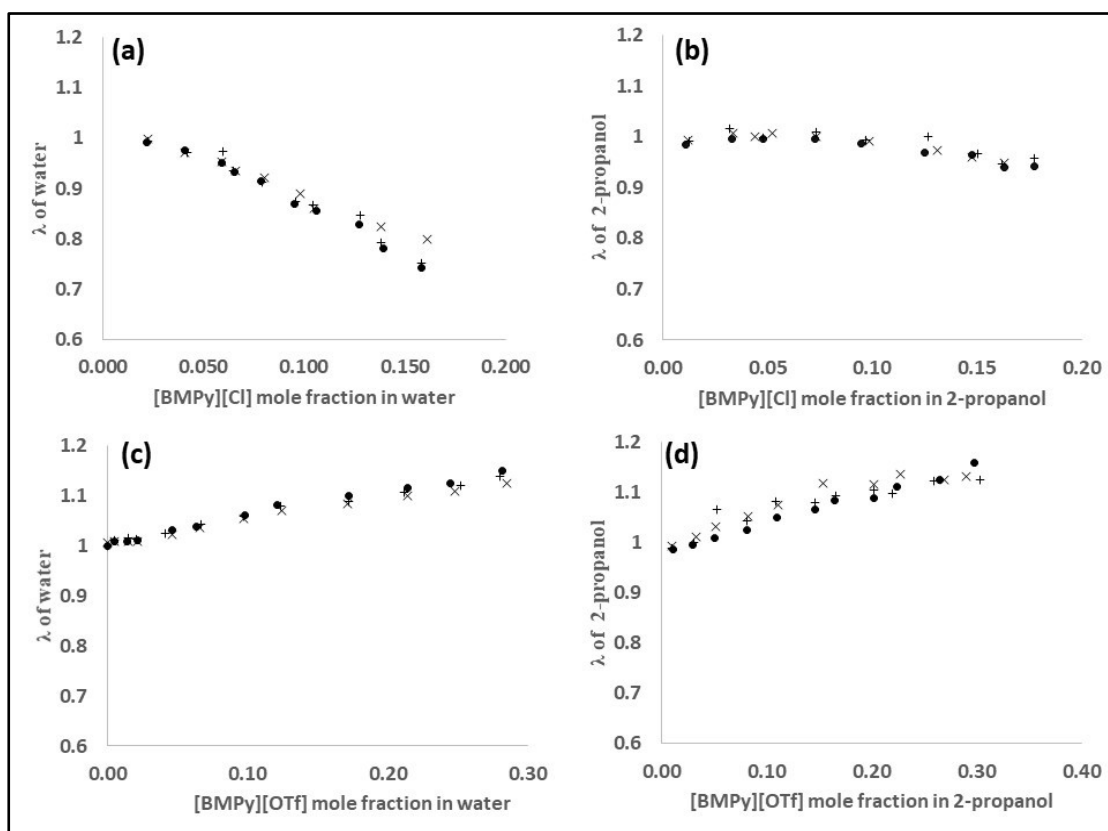


Figure 33: Activity coefficients of solvents in presence of ionic liquids at different pressures: (a) water in water (1) + [BMPy][Cl] (2) system, (b) 2-propanol in 2-propanol (1) + [BMPy][Cl] (2) system, (c) water in water (1) + [BMPy][OTf] (2) system, and (d) 2-propanol (1) + [BMPy][OTf] (2) system. x: 100 kPa, +: 75 kPa, ●: 50 kPa.

The influence of ionic liquids on the phase behavior of the water (1) + 2-propanol (2) system can be explained by electrostatic interaction theory [71]. Since water and 2-propanol have different polarities, water molecules tend to surround the [BMPy][Cl] molecules. However, 2-propanol does not interact in the same manner due to its lower dipole moment. On the other hand, [BMPy][OTf] does not interact in the same manner due to the presence of fluorinated ion which weakly interacts with water [69].

The phase behavior of the water (1) + 2-propanol (2) system can be better understood by examining the activity coefficients of water and 2-propanol in the presence of different ionic liquids, as depicted in Figure 34, which was generated at an ionic liquid mole fraction of 0.2. In case of [BMPy][Cl], it is observed in Figure 34-a

that the activity of water is strongly depressed in the 2-propanol-rich region, while the activity coefficient of 2-propanol is not changed much. This means that more water is preserved in the liquid phase and a higher proportion of 2-propanol is rejected to the vapor phase. When [BMPy][OTf] is added (Figure 33-b), there is no significant change in the activity coefficient of water, but there is a slight increase in the activity coefficient of 2-propanol. This indicates that a higher proportion of 2-propanol is rejected to the vapor phase. The azeotrope is, thus, slightly pushed towards the 2-propanol-rich region.

The system of water (1) + 1-propanol (2) has been thoroughly investigated in the literature [72], [73]. Orchillés and coworkers [30] investigated the effect of several trifluoromethanesulfonate based ionic liquids on the phase behavior of this system and observed that [BMPy][OTf] could not eliminate the azeotrope of this system at the studied concentrations, although it could shift the azeotrope towards the alcohol-rich region.

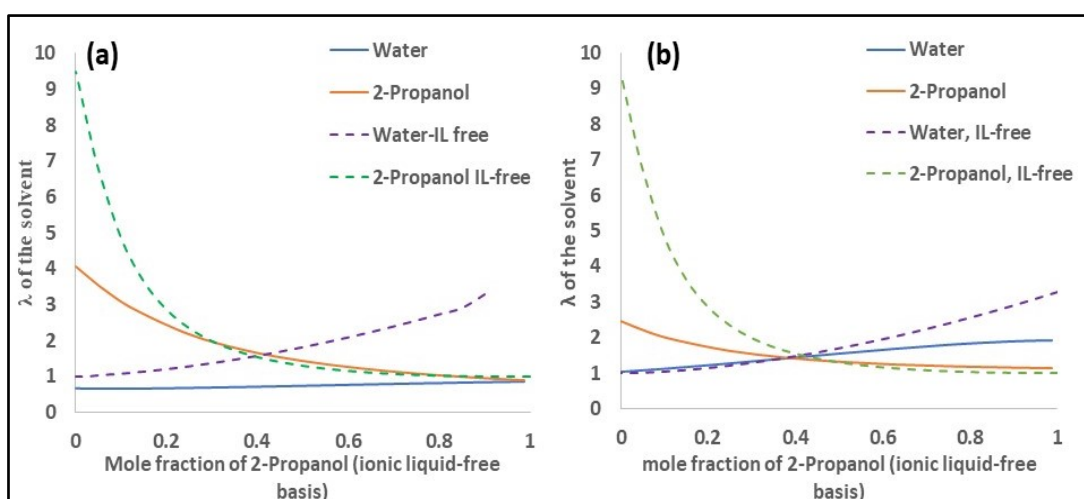


Figure 34: Activity coefficients of the solvents in the presence of (a) [BMPy][Cl] and (b) [BMPy][OTf]

**5.3.3 Modelling results.** As shown in Table 5 and 8, the RMSD of the activity coefficients of the solvents in the binary systems were always less than 0.015, and the RMSD of the equilibrium temperature in the ternary systems was less than 2.0 °C as shown in Tables 10 and 12. This indicates that the model can very well describe the experimental data. Figure 35 depicts the residuals between the experimental activity coefficients of the solvents and the predicted values. The calculated residuals are small, indicating that the NRTL model can accurately correlate the phase behavior of the studied systems.

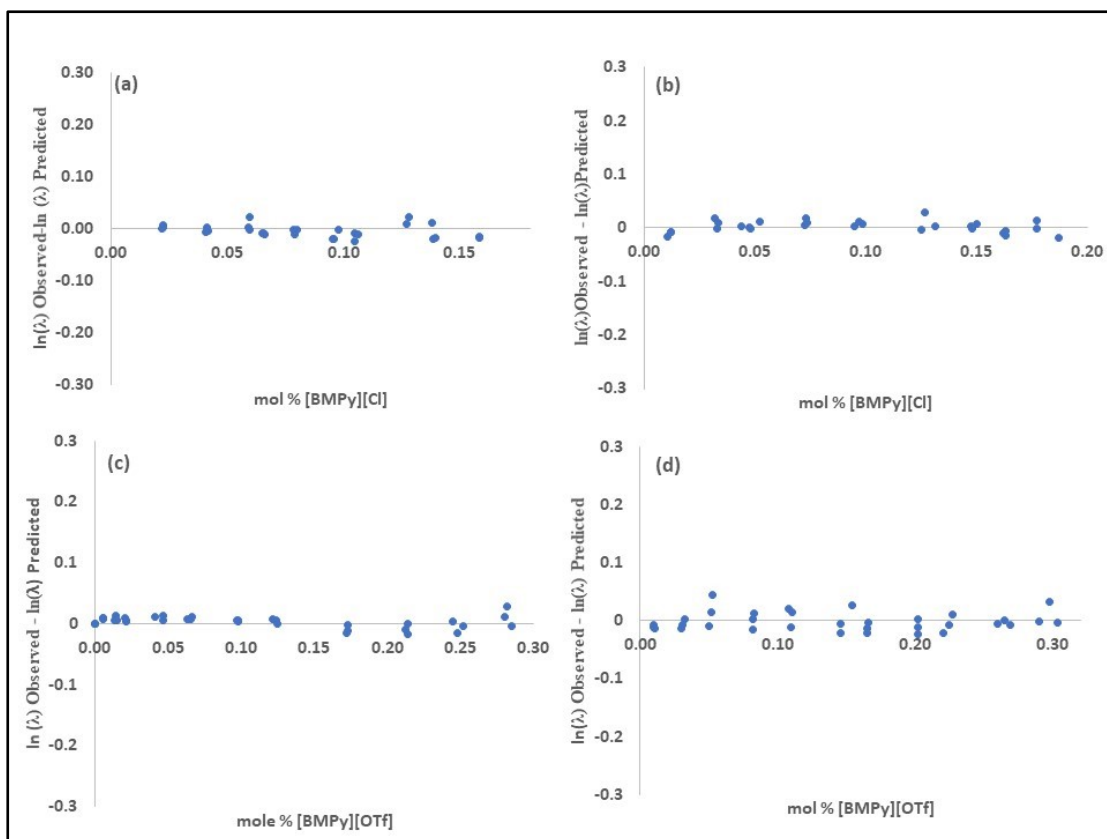


Figure 35: Residual activity coefficients for (a) water (1) + [BMPy][Cl] (2), (b) 2-propanol (1) + [BMPy][Cl] (2), (c) water (1) + [BMPy][OTf] (2), and (d) 2-propanol (1) + [BMPy][OTf] (2)

The binary NRTL interaction parameters should be, in principle, close to the parameters obtained by regressing the ternary experimental data. For instance, the binary interaction parameters for 2-propanol and ionic liquid obtained by regressing the binary VLE data should be close to the ones obtained by regressing the ternary data. A comparison between these parameters is presented in Figure 36. Although these parameters share the same sign and order of magnitude, they are not identical, particularly in the case of [BMPy][OTf]. Thus, binary interactions parameters obtained from regressing binary systems data cannot give an accurate description of the VLE of the ternary systems.

Figure 37 shows the minimum mole fraction [42], [43] of each ionic liquid that is required to break the azeotrope of the water (1) + 2-propanol (2) system. It can be observed that [BMPy][Cl] is not as effective as other ionic liquids in breaking the azeotrope of this system. It can also be inferred that the nature of the cation has a significant effect on the ionic liquid's ability to break the azeotrope.

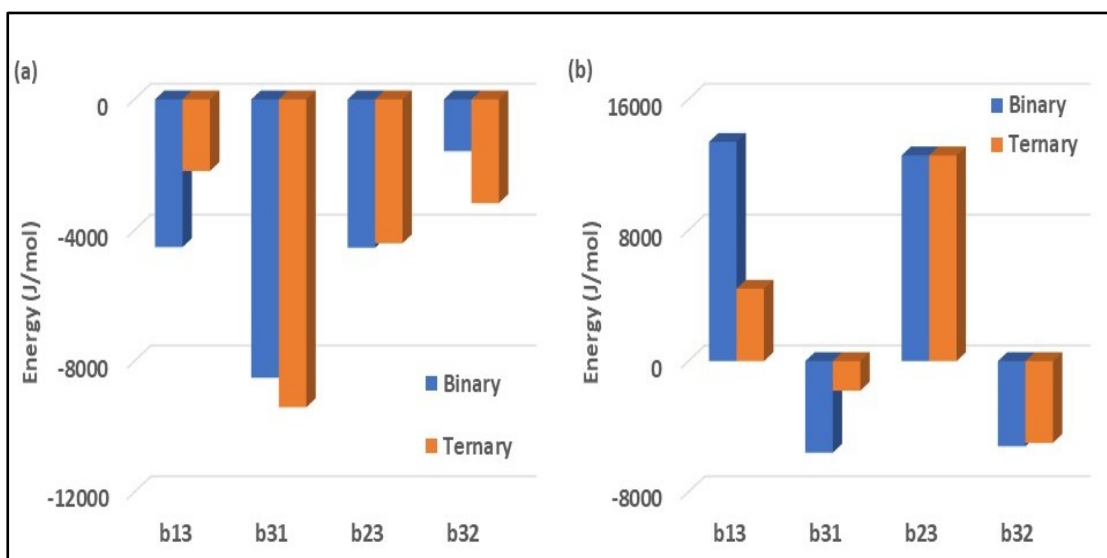


Figure 36: NRTL parameter of water (1), 2-propanol (2), and (a) [BMPy][Cl] (3) and (b) [BMPy][OTf] (3).

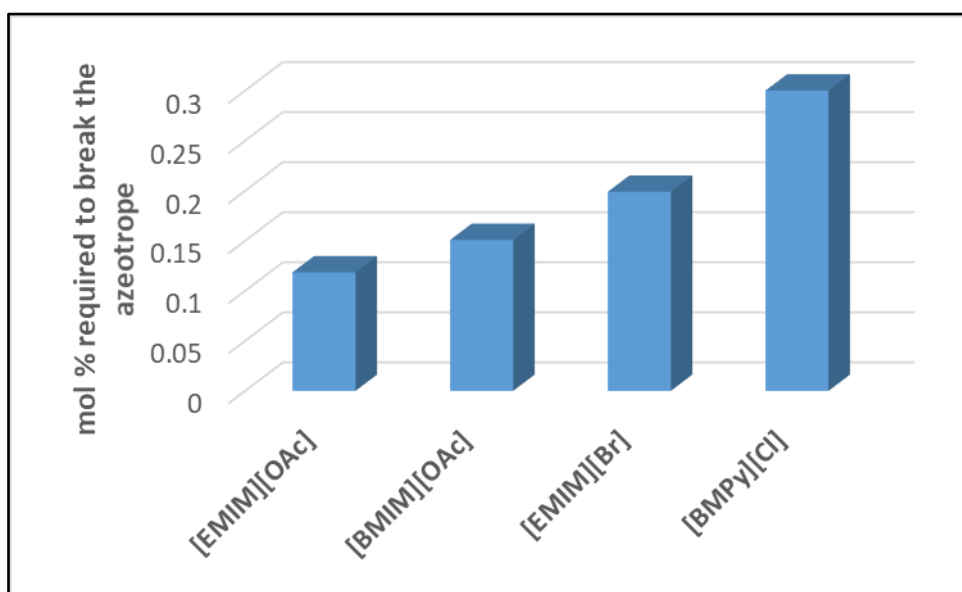


Figure 37: A comparison between ionic liquids' ability to remove the azeotrope

## Chapter 6. Conclusion

This chapter summarizes the major findings of this thesis. Possible improvements to the experimental techniques, future work to be undertaken, and the applications of this study are also outlined.

### 6.1. Major Findings

Binary vapor-liquid equilibrium of four systems: water (1) + [BMPy][Cl] (2), water (1) + [BMPy][OTf] (2), 2-propanol (1) + [BMPy][Cl] (2), and 2-propanol (1) + [BMPy][OTf] (2) were experimentally measured and reported at 100, 75, and 50 kPa. It was observed that [BMPy][Cl] had a higher interaction with both solvents. However, this interaction was more pronounced with water. Upon adding [BMPy][Cl] to each solvent, the activity coefficient of that solvent decreased, indicating a negative deviation from the ideal solution model. On the contrary, it was observed that [BMPy][OTf] had a lower interaction with both solvents, as the activity of each solvent slightly increased above unity upon addition of this ionic liquid. This can be attributed to the fluorinated anion in this ionic liquid, which does not interact with the hydrogen bonds in both solvents.

The phase behavior of water (1) + 2-propanol (2) system in the presence of the two ionic liquids was also investigated. It was observed that [BMPy][Cl] eliminated the azeotrope for this system, while [BMPy][OTf] shifted the azeotrope towards the alcohol-rich region but was incapable of completely removing it from the system.

### 6.2. Recommendations for Future Work

This research can be utilized in future work in various aspects. For example, binary VLE data of water and ionic liquids can be used to predict the applicability of such binary systems in absorption refrigeration processes. Water and ionic liquids can be used as a working fluid pair in absorption refrigeration. Such working fluids do not present operational issues such as corrosion, crystallization, and toxicity hazards, which are common problems that arise from the common working fluid pairs.

A proper working fluid should exhibit a negative deviation from the Raoult's law in order to have a strong absorption performance. This means that the activity coefficient should be less than one and a depression in the vapor pressure or an elevation in the boiling point must occur. Due to the inherent characteristics such as negligible



vapor pressure and high thermal stability, ionic liquids are potential candidates as working fluids. By finding the interaction parameters of an ionic liquid with water, the coefficient of performance can be estimated, which can allow for performance comparison studies between water and ionic liquid pairs and the conventional water and LiBr pair.

The feasibility of employing ionic liquids in commercial scale extractive distillation units is another important consideration. Although many ionic liquids have been utilized as entrainers in azeotropic systems, most studies are only based on a laboratory scale. Therefore, the economic feasibility of large scale ionic liquid-based distillation requires extensive investigation. Ionic liquids are currently produced in small quantities with high production costs. The prices of ionic liquids may exceed 2000 Euro per  $\text{dm}^3$ . However, it is expected that this price will be heavily reduced if ionic liquids are produced on a large scale. Other issues such as the long-term thermal stability and the entrainer recovery require further research investigations.

The suitability of different thermodynamic models in predicting the phase behavior of systems containing ionic liquids should be addressed. Most of the models currently applied, such as the NRTL and the UNIFAC model, are quite successful in describing the phase behavior of many ionic liquid-containing systems. However, such models do not take into account the concentration-dependent degree of dissociation of the ionic liquids.

## References

- [1] V. Julka, M. Chiplunkar, and L. O'Young, "Selecting entrainers for azeotropic distillation," *Chem. Eng. Prog.*, vol. 105, no. 3, pp. 47–53, Mar. 2009.
- [2] P. C. Wankat, *Separation Process Engineering: Includes Mass Transfer Analysis*. Ann Arbor, MI, USA: Prentice Hall, 2011, pp. 13-83.
- [3] R. Turton, R. Bailie, W. Whiting, J. Shaeiwitz, and D. Bhattacharyya, *Analysis, Synthesis and Design of Chemical Processes*, 4th ed. Pearson Higher Ed, 2012, pp. 350-400
- [4] J. Richardson, J. Harker, J. R. Backhurst, and J. Coulson, *Coulson and Richardson's Chemical Engineering. Vol. 2, Particle Technology and Separation Processes*. Oxford, UK: Butterworth-Heinemann, 2002, pp. 543-555.
- [5] E. Hilmen, "Separation of Azeotropic Mixtures: Tools for Analysis and Studies on Batch Distillation Operation," M.S. thesis. Dept. Che. Eng., Norwegian University of Science and Technology, 2000.
- [6] U. Onken, "Azeotropic Data Part I," *Chemie Ing. Tech.*, vol. 67, no. 5, pp. 623–623, May. 1995.
- [7] J. M. Smith, H. C. Van Ness, and M. Abbott, *Introduction to Chemical Engineering Thermodynamics*. New York : McGraw-Hill, 2005, pp. 337-378.
- [8] L. Horsley, "Azeotropic Data-III," in *Advances in Chemistry Series*, vol. 116, R. Gould, Ed. Washington, DC, USA: American Chemistry Society, 1973, pp. 615-632.
- [9] W. Malesinkski, *Azeotropy and other Theoretical Problems of Vapour-Liquid Equilibrium*. New York, USA: Interscience, 1965, pp. 10-17.
- [10] M. Van Winkle, *Distillation*. New York, USA: McGraw-Hill, 1967, pp. 46-55
- [11] P. A. Schweitzer, *Handbook of Separation Techniques for Chemical Engineers*. New York, USA: McGraw-Hill, 1997.
- [12] A. B. Pereiro, J. M. M. Araújo, J. M. S. S. Esperança, I. M. Marrucho, and L. P. N. Rebelo, "Ionic liquids in separations of azeotropic systems - a review," *J. Chem. Thermodyn.*, vol. 46, pp. 2–28, Mar. 2012.
- [13] J. I. Kroschwitz and M. Howe-Grant, *Kirk-Othmer Encyclopedia of Chemical Technology.*, 4th ed. New York, USA: Wiley-Interscience, 1996, pp. 216-236.
- [14] ICIS, "Isopropanol (IPA) Production and Manufacturing Process," 2007. [Online]. Available: <https://www.icis.com/>. [Accessed: 30-Apr-2017].
- [15] M. Mujiburohman, W. B. Sediawan, and H. Sulisty, "A preliminary study: distillation of isopropanol – water mixture using fixed adsorptive distillation method," *Sep. Purif. Technol.*, vol. 48, no. 1, pp. 85–92, Feb. 2006.
- [16] J. Cho and J. Jeon, "Optimization study on the azeotropic distillation process for isopropyl alcohol dehydration," *Korean J. Chem. Eng.*, vol. 23, no. 1, pp. 1–7, Jan. 2006.
- [17] M. Pokhrel, D. O. Asante, and J. H. Cho, "Three column configuration for the separation of IPA-water using by heteroazeotropic distillation," *Int. J. Appl. Eng.*

*Res. ISSN*, vol. 11, no. 12, pp. 973–4562, 2016.

- [18] K. Morizane, T. Shirahata, K. Higashi, S. Senoo, and K. Doi, “Process for producing 2-propanol,” European Patent EP 2243762B11, Feb. 7, 2009.
- [19] A. V. Orchillés, P. J. Miguel, E. Vercher, and A. Martínez-Andreu, “Isobaric vapor–liquid equilibria for ethyl acetate + ethanol + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate at 100 kPa,” *J. Chem. Eng. Data*, vol. 52, no. 6, pp. 2325–2330, Nov. 2007.
- [20] M. J. Earle and K. R. Seddon, “Ionic liquids. Green solvents for the future,” *Pure Appl. Chem.*, vol. 72, no. 7, pp. 1391–1398, Nov. 2000.
- [21] J. F. Brennecke and E. J. Maginn, “Ionic liquids: innovative fluids for chemical processing,” *AIChE J.*, vol. 47, no. 11, pp. 2384–2389, Nov. 2001.
- [22] B. Ghosh and N. Sulemana. “Application of ionic liquids in the upstream oil industry- a review,” *J. Pet. Res.*, vol. 1, no. 1, pp. 50-60, May. 2017.
- [23] K. N. Marsh, J. A. Boxall, and R. Lichtenthaler, “Room temperature ionic liquids and their mixtures - A review,” *Fluid Phase Equilib.*, vol. 219, no. 1, pp. 93–98, May. 2004.
- [24] M. Docker, “Measurement and prediction of vapor – liquid equilibria of ternary systems containing ionic liquids,” *Fluid Phase Equilib.*, vol. 227, no. 2, pp. 255–266, Jan. 2005.
- [25] N. V. Plechkova and K. Seddon, “Applications of ionic liquids in the chemical industry,” *Chem. Soc. Rev.*, vol. 37, no. 1, pp. 123–150, Nov. 2007.
- [26] A. Eguizábal, J. Lemus, and M. P. Pina, “On the incorporation of protic ionic liquids imbibed in large pore zeolites to polybenzimidazole membranes for high temperature proton exchange membrane fuel cells,” *J. Power Sources*, vol. 222, no. 1, pp. 483–492, Jan. 2013.
- [27] J. M. Prausnitz, R. N. Lichtenthaler, and E. G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed. New Jersey: Prentice Hall, 1999, pp. 13-50.
- [28] L. Cao, P. Liu, B. Wang, and Q. Li, “Vapor – liquid equilibria for tetrahydrofuran + ethanol system containing three different ionic liquids at 101 . 3 kPa,” *Fluid Phase Equilib.*, vol. 372, pp. 49–55, Apr. 2014.
- [29] L. Zhang, B. Qiao, Y. Ge, D. Deng, and J. Ji, “Effect of ionic liquids on (vapor + liquid) equilibrium behavior of (water + 2-methyl-2-propanol),” *J. Chem. Thermodyn.*, vol. 41, no. 1, pp. 138–143, Jan. 2009.
- [30] A. V. Orchillés, P. J. Miguel, V. González-Alfaro, E. Vercher, and A. Martínez-Andreu, “Isobaric vapor-liquid equilibria of 1-propanol + water + trifluoromethanesulfonate-based ionic liquid ternary systems at 100 kPa,” *J. Chem. Eng. Data*, vol. 56, no. 12, pp. 4454–4460, Aug. 2011.
- [31] L. Zhang, J. Han, R. Wang, X. Qiu, and J. Ji, “Isobaric vapor–liquid equilibria for three ternary systems: water + 2-propanol + 1-ethyl-3-methylimidazolium tetrafluoroborate, Water + 1-Propanol + 1-ethyl-3-methylimidazolium tetrafluoroborate, and Water + 1-Propanol + 1-butyl-3-methylimidazolium tetrafluoroborate,” *J. Chem. Eng. Data*, vol. 52, no. 4, pp. 1401–1407, Jun. 2007.

- [32] J. Carsten, M. Seiler, Y. Beste, and W. Arlt, "Influence of ionic liquids on the phase behavior of aqueous azeotropic systems," *J. Chem. Eng. Data*, vol. 49, no. 1, pp. 852–857, Jun. 2004.
- [33] C. Jork *et al.*, "Tailor-made ionic liquids," *J. Chem. Thermodyn.*, vol. 37, no. 6, pp. 537–558, Jun. 2005.
- [34] X. Hu, J. Yu, and H. Liu, "Separation of THF and water by room temperature ionic liquids," *Water Sci. Technol.*, vol. 53, no. 11, pp. 245–249, Jun. 2006.
- [35] Y. Ge, L. Zhang, X. Yuan, W. Geng, and J. Ji, "Selection of ionic liquids as entrainers for separation of (water + ethanol)," *J. Chem. Thermodyn.*, vol. 40, no. 8, pp. 1248–1252, Aug. 2008.
- [36] A. Orchillés, P. Miguel, E. Vercher, and A. Andreu, "Ionic Liquids as entrainers in extractive distillation: isobaric vapor - liquid equilibria for acetone + methanol + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate," *J. Chem. Eng. Data*, vol. 52, no. 1, pp. 141–147, Nov. 2007.
- [37] A. V. Orchillés, P. J. Miguel, E. Vercher, and A. Martínez-Andreu, "Isobaric vapor–liquid and liquid–liquid equilibria for chloroform + methanol + 1-ethyl-3-methylimidazolium trifluoromethanesulfonate at 100 kPa," *J. Chem. Eng. Data*, vol. 55, no. 3, pp. 1209–1214, Mar. 2010.
- [38] A. V. Orchillés, P. J. Miguel, E. Vercher, and A. Martínez-Andreu, "Isobaric vapor–liquid and liquid–liquid equilibria for chloroform + ethanol + 1-ethyl-3-methylimidazolium Trifluoromethanesulfonate at 100 kPa," *J. Chem. Eng. Data*, vol. 53, no. 11, pp. 2642–2648, Nov. 2008.
- [39] Z. Zhang, A. Hu, T. Zhang, Q. Zhang, Z. Yang, and W. Li, "Isobaric vapor–liquid equilibrium for methyl acetate + methanol system containing different ionic liquids at 101.3kPa," *Fluid Phase Equilib.*, vol. 408, pp. 20–26, Jan. 2016.
- [40] N. Calvar, G. Elena, and A. Dom, "Study of the behaviour of the azeotropic mixture ethanol – water with imidazolium-based ionic liquids," *Fluid Phase Equilib.*, vol. 259, pp. 51–56, Oct. 2007.
- [41] Sigma-Aldrich, "1-Butyl-3-methylimidazolium chloride  $\geq 98.0\%$  (HPLC) | Sigma-Aldrich." [Online]. Available: <https://www.sigmaaldrich.com/>. [Accessed: 29-Apr-2018].
- [42] L. Zhang, J. Han, D. Deng, and J. Ji, "Selection of ionic liquids as entrainers for separation of water and 2-propanol," *Fluid Phase Equilib.*, vol. 255, no. 2, pp. 179–185, Jul. 2007.
- [43] Z. Zhang *et al.*, "Separation of 2-propanol and water azeotropic system using ionic liquids as entrainers," *Fluid Phase Equilib.*, vol. 412, pp. 94–100, Mar. 2016.
- [44] A. V. Orchillés, P. J. Miguel, V. González-Alfaro, F. J. Llopis, E. Vercher, and A. Martínez-Andreu, "Isobaric vapor-liquid equilibria for the extractive distillation of 2-propanol+water mixtures using 1-ethyl-3-methylimidazolium dicyanamide ionic liquid," *J. Chem. Thermodyn.*, vol. 110, pp. 16–24, Jul. 2017.
- [45] Y. Xiao, P. Bai, and Z. Jiang, "Vapour-liquid equilibrium for systems containing ionic liquids," *Asian J. Chem.*, vol. 24, no. 9, pp. 3775–3780, Apr. 2012.

- [46] N. Calvar, B. González, E. Gómez, and A. Domínguez, “Vapor–liquid equilibria for the ternary system ethanol + water + 1-butyl-3-methylimidazolium methylsulfate and the corresponding binary systems at 101.3 kPa,” *J. Chem. Eng. Data*, vol. 54, no. 3, pp. 1004–1008, Mar. 2009.
- [47] A. Arce, A. Arce, J. M. Martínez-Ageitos, and A. Soto, “Isobaric vapor–liquid equilibria of 1,1-dimethylethoxy-butane + methanol or ethanol + water at 101.32kPa,” *Fluid Phase Equilib.*, vol. 259, no. 1, pp. 57–65, 2007.
- [48] U. Domańska and K. Walczak, “Ternary liquid-liquid equilibria for mixtures of {ionic liquid + thiophene or benzothiophene + heptane} at T = 308.15 K,” *J. Solution Chem.*, vol. 44, no. 3, pp. 382–394, Dec. 2014.
- [49] M. B. Oliveira, E. A. Crespo, F. Llovel, L. F. Vega, and J. A. P. Coutinho, “Modeling the vaporeliquid equilibria and water activity coefficients of alternative refrigerant-absorbent ionic liquidwater pairs for absorption systems,” *Fluid Phase Equilib.*, vol. 426, no. 25, Oct. 2016.
- [50] C. Tsanas, A. Tzani, A. Papadopoulos, A. Detsi, and E. Voutsas, “Ionic liquids as entrainers for the separation of the ethanol/water system,” *Fluid Phase Equilib.*, vol. 379, pp. 148–156, Oct. 2014.
- [51] T. Hiroyuki, T. Seiji, S. Md. Abu Bin Hasan, K. Hayamizu, and W. Masayoshi, “How ionic are room-temperature ionic liquids? an indicator of the physicochemical properties,” *J. Phys. Chem. B.*, vol. 110, no. 39, pp. 19593-19600, Sep. 2006.
- [52] S. Katsuta, R. Ogawa, N. Yamaguchi, T. Ishitani, and T. Yasuyuki, “Ion pair formation of 1-Alkyl-3-methylimidazolium salts in water,” *J. Chem. Eng. Data.*, vol. 52, no. 1, pp. 248-251, Dec. 2007.
- [53] B. S. Lee and S. T. Lin, “A priori prediction of dissociation phenomena and phase behaviors of ionic liquids,” *Ind. Eng. Chem. Res.*, vol. 54, no. 36, pp. 9005–9012, Aug. 2015.
- [54] N. Calvar, B. González, E. Gómez, and Á. Domínguez, “Vapor–liquid equilibria for the ternary system ethanol + water + 1-Ethyl-3-methylimidazolium ethylsulfate and the corresponding binary systems containing the ionic liquid at 101.3 kPa,” *J. Chem. Eng. Data*, vol. 53, no. 3, pp. 820–825, Mar. 2008.
- [55] R. H. Perry and D. W. Green, *Perry’s Chemical Engineers’ Handbook*, 8th ed. McGraw-Hill, 2008, pp 48-56.
- [56] P. Marzal, J. Montón, and M. Rodrigo, “Isobaric vapor–liquid equilibria of the water + 2-propanol system at 30, 60, and 100 kPa,” *J. Chem. Eng. Data*, vol. 41, no. 3, pp. 608-611, May. 1996.
- [57] D. M. Himmelblau, *Applied Nonlinear Programming*. New York, USA: McGraw-Hill, 1972, pp. 252-258.
- [58] M. Freire, C. Neves, I. Marrucho, and A. Coutinho, “Hydrolysis of tetrafluoroborate and hexafluorophosphate counter ions in imidazolium-based ionic liquids,” *J. Phys. Chem. A*, vol. 114, no. 11, pp. 3744–3749, Jul. 2010.
- [59] V. Losetty, M. Sivapragasam, and C. D. A. Wilfred, “Recent advances and thermophysical properties of acetate-based protic ionic liquids,” *Chem. Sci. J.*,

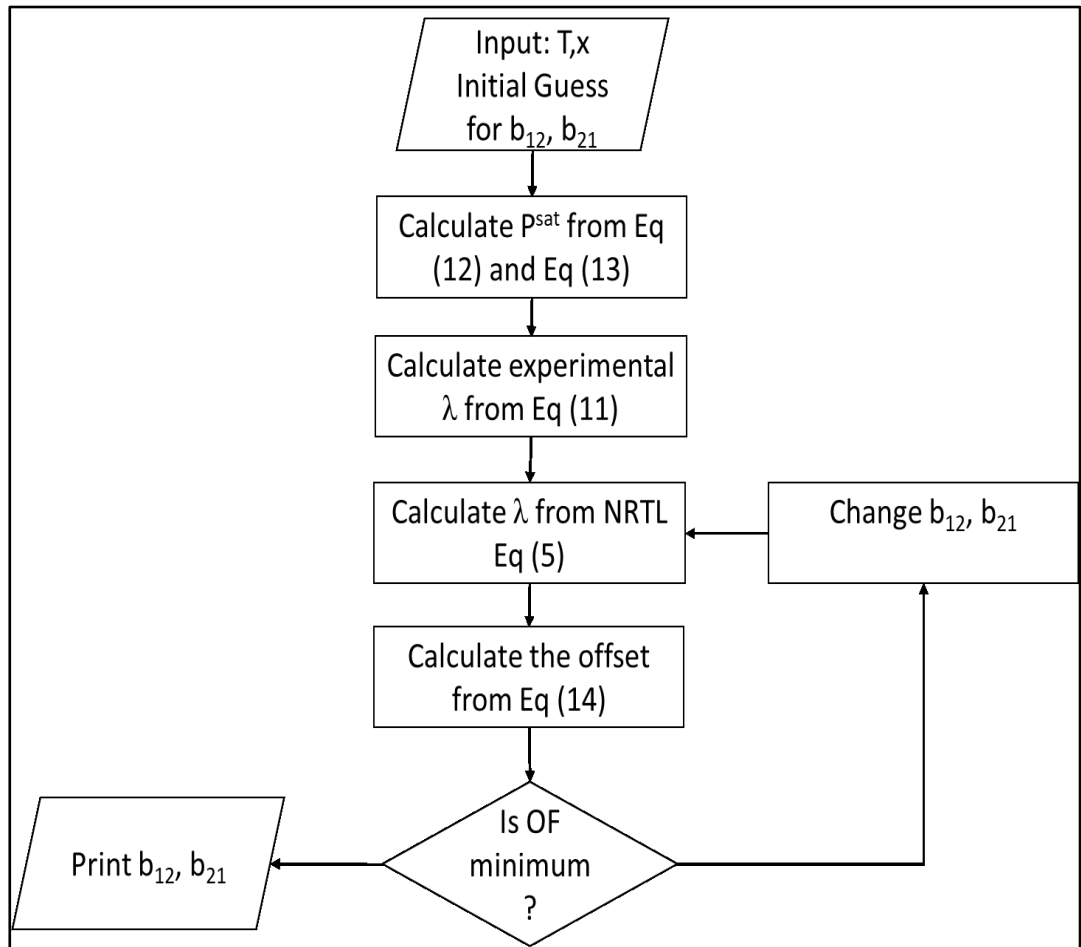
vol. 7, no. 2, May. 2016.

- [60] Sigma-Aldrich, "1-Butyl-1-methylpyrrolidinium chloride." [Online]. Available: <https://www.sigmaaldrich.com>. [Accessed: 29-Apr-2018].
- [61] A. S. Brunjes and M. J. P. Bogart, "Vapor-liquid equilibria for commercially important systems of organic solvents," *Ind. Eng. Chem.*, vol. 35, no. 2, pp. 255–260, Feb. 1943.
- [62] Pilodist. Meckenheim, Germany, "Manual for Vapor/Liquid-Phase Equilibrium Apparatus," Available: <http://www.pilodist.de/>. Accessed: Dec. 2, 2016.
- [63] Y. Cao and T. Mu, "Comprehensive investigation on the thermal stability of 66 ionic liquids by thermogravimetric analysis," *Ind. Eng. Chem. Res.*, vol. 53, no. 20, pp. 8651–8664, Apr. 2014.
- [64] H. Passos *et al.*, "Vapor-liquid equilibria of water + alkylimidazolium-based ionic liquids: Measurements and perturbed-chain statistical associating fluid theory modeling," *Ind. Eng. Chem. Res.*, vol. 53, no. 9, pp. 3737–3748, Feb. 2014.
- [65] C. Held, "Measuring and Modeling Thermodynamic Properties of Biological Solutions," Ph.D. dissertation, Institute of Thermodyn., Technische Universität Dortmund, 2011.
- [66] J. Zhao, X.-C. Jiang, C.-X. Li, and Z.-H. Wang, "Vapor pressure measurement for binary and ternary systems containing a phosphoric ionic liquid," *Fluid Phase Equilib.*, vol. 247, no. 1–2, pp. 190–198, Sep. 2006.
- [67] F. Heym, J. Haber, W. Korth, B. J. M. Etzold, and A. Jess, "Vapor pressure of water in mixtures with hydrophilic ionic liquids - a contribution to the design of processes for drying of gases by absorption in ionic liquids," *Chem. Eng. Technol.*, vol. 33, no. 10, pp. 1625–1634, Sep. 2010.
- [68] H. Passos, A. R. Ferreira, A. F. M. Cláudio, J. A. P. Coutinho, and M. G. Freire, "Characterization of aqueous biphasic systems composed of ionic liquids and a citrate-based biodegradable salt," *Biochem. Eng. J.*, vol. 67, pp. 68–76, Aug. 2012.
- [69] J. D. Dunitz and R. Taylor, "Organic fluorine hardly ever accepts hydrogen bonds," *Chemistry-A Euro. J.*, vol. 3, no.1, pp. 89–98, Jan. 1997
- [70] L. Shimoni and J. P. Glusker, "The geometry of intermolecular interactions in some crystalline fluorine-containing organic compounds," *Struct. Chem.*, vol. 5, no. 6, pp. 383–397, Dec. 1994.
- [71] J. Fang, R. Zhao, H. Wang, C. Li, and J. Liu, "Salting-out effect of ionic liquids on isobaric vapor-liquid equilibrium of acetonitrile-water system," *Chinese J. Chem. Eng.*, vol. 23, no. 8, pp. 1369–1373, Aug. 2015.
- [72] Q. Li, F. Xing, Z. Lei, B. Wang, and Q. Chang, "Isobaric vapor-liquid equilibrium for isopropanol + water + 1-ethyl-3-methylimidazolium Tetrafluoroborate," *J. Chem. Eng. Data*, vol. 53, no. 1, pp. 275–279, Jan. 2008.
- [73] H. Kim, I. Hwang, and S. Park, "Isothermal vapor-liquid equilibrium data at  $T = 333.15$  K and excess molar volumes and refractive indices at  $T = 298.15$  K for

the dimethyl carbonate + methanol and isopropanol + water with ionic liquids,”  
*J. Chem. Eng. Data*, vol. 55, no. 7, pp. 2474–2481, Jul. 2010.

## Appendix A

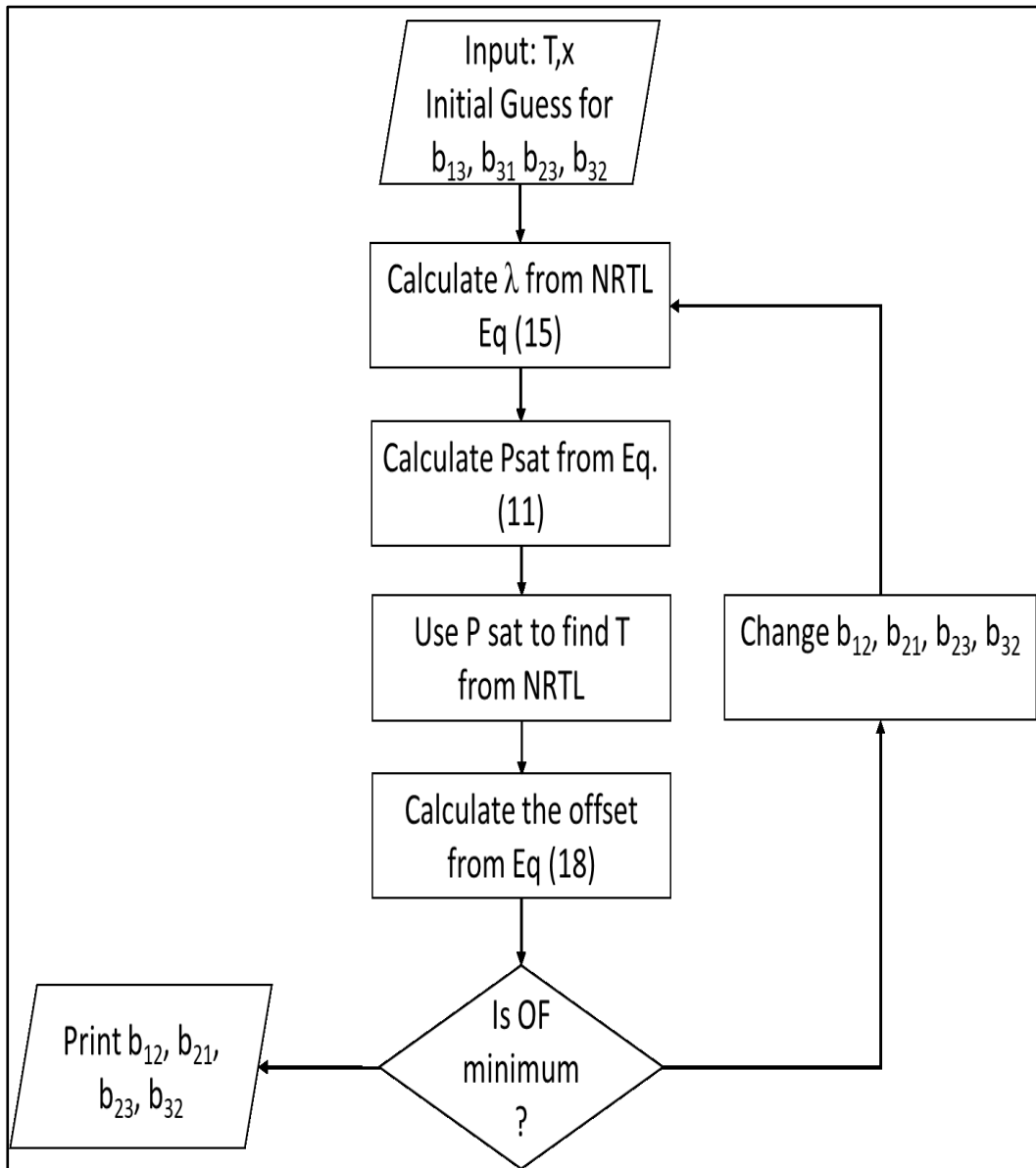
Flow-Chart for the computational algorithm used in optimization of binary VLE data





## Appendix B

Flow-Chart for the computational algorithm used in optimization of ternary VLE data





## Vita

Faisal Al-Samaraie was born in Baghdad, Iraq in 1993. He graduated from Al-Shola High School in Sharjah, in 2011 with a high distinction. Then he joined the American University of Sharjah in 2012 as a chemical engineering student. He graduated magna cum laude in 2016 with a B.Sc. degree in Chemical Engineering.

Faisal joined the MS program at the American university of Sharjah in 2016. He received a graduate teaching assistantship from the chemical engineering department. During his studies, Faisal co-authored a paper entitled “*Forward osmosis desalination using ferric sulfate draw solute,*” which was published in *Desalination* in 2017, and he co-authored another paper, entitled “*Generalized binary interaction parameters for hydrogen-heavy-n-alkane systems using Peng–Robinson equation of state*”, which was published in *Chemical Engineering Communications* in 2017. He also participated in the United Arab Emirates Graduate Research Conference that was held in 2018, where he presented a paper entitled “*Effect of 1-Butyl-1-methylpyrrolidinium chloride on the phase behaviour of water+2-Propanol system at 101 kPa*”.