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Design of distillation systems assisted with ionic liquids

Diploma Thesis that to complete the requirements of the Honors Program
presents the student

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Design of distillation systems assisted with ionic liquids

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Abstract

In recent years, research has been focused on the design and application of greener and more efficient solvents to use as entrainers in extractive distillation. Ionic liquids (ILs) have been recognized as an interesting option due to their nonvolatility, high selectivity, heat capacity, and easy operation and regeneration. 1-ethyl-3-methylimidazolium acetate ([emim][OAc]), 1-methylimidazolium chloride ([mim][Cl]), and 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) are promising ionic liquids for industrial applications in the separation of azeotropic mixtures, such as water-ethanol. This paper proposes a simplified methodology for the design of extractive distillation columns for the separation of ethanol and water assisted by the ionic liquids. The vapor-liquid equilibrium was predicted with the thermodynamic model NRTL and then fitted to the empirical relative volatility model for non-ideal solutions. The McCabe-Thiele method was employed for the estimation of the minimum reflux ratio and with the relative volatility model the stage-by-stage calculations were performed. The addition of the solvent eliminates the azeotropic behavior and increases relative volatility of the system. Thus, proving that [emim][OAc], [mim][Cl] and [bmim][Cl] are suitable entrainers in the dehydration of ethanol. The results show that an increment in IL concentration decreases the number of stages required for the separation and that the number of stages estimated with the simplified method is similar to the results in the literature. Therefore, it was demonstrated that the relative volatility model can be used to perform the stage-by-stage calculations.

Keywords: extractive distillation, ionic liquids, ethanol-water, separation process, relative volatility model

1 Introduction

Mixtures of chemical components that have different molecules and structures present an azeotropic behavior. Azeotropes are difficult or impossible to separate by conventional distillation since liquid and vapor phases in equilibrium with each other have the same compositions (Luyben & Chien, 2011). Extractive distillation is an extensively used method to separate minimum-boiling binary azeotropes. It consists in the addition of a third heavy chemical compound as separating agent, called solvent or entrainer, which increases the relative volatility and makes it easier to separate in high-purity components (Pereiro, Araújo, Esperança, Marrucho, & Rebelo, 2012).

This process is widely popular in petrochemical and chemical industries, with applications for the separation of azeotropic mixtures including alcohol-water, acetic acid-water, acetone-methanol, and ethanol-ethyl acetate (Lei, Li, & Chen, 2003). Nonetheless, the conventional organic solvents have gained disapproval as result of the incorporation of the Green Chemistry Principles and the search for sustainable materials and processes (S. L. Tang, Smith, & Poliakoff, 2005). As stated by Chávez-Islas, Vásquez-Medrano, and Flores-Tlacuahuac (2011) “solvents comprise two-thirds of all industrial emissions and one-third of all volatile organic content (VOC) emissions nationwide”. Additionally, the majority of the solvents are toxic materials. For instance, ethylene glycol and benzene are the most common entrainers for the dehydration of ethanol (Górak & Olujić, 2014). Moreover, conventional designs have incredibly high operation and energy costs, and require high reflux ratios to obtain the product specifications (Pereiro et al., 2012; Quijada-Maldonado, Aelmans, Meindersma, & de Haan, 2013).

For this reason, current research is focused on the design and application of greener and more efficient solvents. Up until recently, using salt as the separating agent had been ignored because of the complexity of determining and modeling phase equilibrium and thermodynamic properties for solvent/electrolyte systems (Llano-Restrepo & Aguilar-Arias, 2003). However, it was found that relatively small amounts of salt can increase considerably the relative volatility of the mixtures, eliminating the azeotrope completely (Fu, 1996). Thus, salt-containing extractive distillation represented a great interest for researchers as a method for separating azeotropic mixtures. However, introducing salt as a solid in the column had its

drawbacks such as problems of transport, corrosion, dissolution and obstruction (Gil, Uyazán, Aguilar, Rodríguez, & Caicedo, 2008). Therefore, investigations shifted their attention to a compound with the same “salt effect”: ionic liquids.

Ionic liquids (ILs) are organic salts conformed of a cation and an anion and are liquid at room conditions. They are considered “green solvents”, representing an attractive opportunity in a range of applications due to their properties like negligible vapor pressure, miscibility with polar and nonpolar compounds, high thermal stability, large liquid phase range of temperatures, electrolytic attributes, among others. Some industrial applications involve them as heat-transfer fluids, electrolytes, liquid crystals, supported IL membranes, and plasticizers (Brennecke & Gurkan, 2010; Chávez-Islas, Vasquez-Medrano, & Flores-Tlacuahuac, 2011; Haghtalab & Paraj, 2012; Shen, Li, Lu, & Li, 2011).

As separating agents in extractive distillation, ILs have demonstrated great potential because they are nonvolatile at the temperature range of this process and can produce high-purity products. They combine the main advantages of liquid solvents and solid salts: easy operation and high separation ability, respectively (Lei et al., 2003). ILs have a strong selective interaction with water in the liquid phase. This forces the low-boiling component into vapor phase, increasing its relative volatility and breaking the azeotrope (Jork, Seiler, Beste, & Arlt, 2004). Since they are nonvolatile, they are not present in the distillate and can be regenerated without the need of a secondary distillation column by simpler separation processes, such as stripping, evaporation, drying, or crystallization (Calvar, González, Gómez, & Domínguez, 2006; Seiler, Jork, Kavarnou, Arlt, & Hirsch, 2004).

Several publications have developed extractive distillation systems using ionic liquids as entrainers. Ma, Shang, Zhu, Li, and Sun (2019) investigated [emim][N(CN)₂] for the separation of isopropanol from water. Using two evaporators for solvent recovery, improved the efficiency indicator of extractive section and the thermodynamic efficiency by 25.96% and 26.09%, respectively, and the total annual cost decreased by 4.26%. Similarly, Aniya, De, and Satyavathi (2016) compared the dehydration of *tert*-butyl alcohol through extractive distillation with [emim][Cl] against triethylene glycol, obtaining a reduction of 13.9% in the total annual cost. Seiler et al. (2004) carried out the process simulation of a distillation column followed by a flash drum and an atmospheric stripping column for solvent

regeneration. They demonstrated that the heat duty of the system can be decreased by 24% applying [emim][BF₄] as entrainer.

The dehydration of ethanol has also become very important due to ethanol's application as a biofuel, as well as a raw material of many chemical products and as an organic solvent and chemical reagent (Lee, Tang, Bi, & Row, 2014; Lei, Dai, Zhu, & Chen, 2014). Therefore, recent research on extractive distillation using ionic liquids is on ethanol purification, proposing design methodologies for the distillation columns where products with high purities are achieved (Chen, Chen, Chen, & Chien, 2017; Ramírez-Corona, Ek, & Jiménez-Gutiérrez, 2015; Zhu et al., 2016). Experimental procedures in pilot plants have also showed promising results (Meindersma, Quijada-Maldonado, Aelmans, Hernandez, & de Haan, 2012; Quijada-Maldonado et al., 2013). Graczová and Steltenpohl (2015) carried out simulation calculations for extractive distillation and solvent regeneration with [bmim][MSO₄] and [emim][ESO₄]. The first solvent achieved the distillate composition of 99.5 mol% in 10 theoretical stages, while the latter in 15.

The aim of this study is to propose a simplified design methodology for the distillation system of the binary mixture ethanol-water assisted by three ionic liquids: 1-ethyl-3-methylimidazolium acetate ([emim][OAc]), 1-methylimidazolium chloride ([mim][Cl]), and 1-butyl-3-methylimidazolium chloride ([bmim][Cl]).

2 Literature Review

ILThermo is the IUPAC Ionic Liquid database, which contains information based on scientific publications of approximately 2200 ionic liquids and more than 700000 data points. The system most reported is the binary mixture ethanol-water due to its industrial relevance (Orchillés, Miguel, Vercher, & Martínez-Andreu, 2010). Therefore, this mixture was selected, since it was certain that information could be found with several ILs.

For the design of the distillation process, it is necessary to know the effect of the IL in the vapor-liquid equilibrium data as well as the values of the density, viscosity, and heat capacity, as function of temperature or composition. The physicochemical properties of ILs can be easily modified and tailored depending on the conditions of the system they are used

on, hence they are called “designer solvents” (Ferro, Ruiz, de Riva, & Palomar, 2012). This is done by the selection of determined cations and anions out of a large collection. However, only a few of them present the chemical characteristics, such as chemical stability, water stability, viscosity, and melting temperature, that are required for the distillation of ethanol-water mixtures (Chávez-Islas, Vasquez-Medrano, et al., 2011).

The most important effect ILs have on the ethanol-water mixture is the increase the relative volatility of the system, which causes the ethanol to be more volatile, eliminating the azeotropic system behavior (Tsanas, Tzani, Papadopoulos, Detsi, & Voutsas, 2014). The cation most reviewed in the literature is the imidazolium class because it is stable in water, remains liquid at a wide range of temperatures, and has advantageous thermophysical properties (Chávez-Islas, Vasquez-Medrano, et al., 2011; Ramdin, de Loos, & Vlugt, 2012).

When analyzing the effect on the activity coefficients and the relative volatility of the mixtures, authors have found that the effect of the cation is less significant, and in the order of $[\text{emim}]^+ > [\text{bmim}]^+$ (Zhang, Han, Deng, & Ji, 2007). On the other hand, the anion has much more influence. Ge, Zhang, Yuan, Geng, and Ji (2008) determined the order of interaction of the anions with ethanol to be $[\text{OAc}]^- > [\text{Cl}]^- > [\text{N}(\text{CN})_2]^- > [\text{BF}_4]^-$, similarly with the water the order is $[\text{OAc}]^- \approx [\text{Cl}]^- > [\text{N}(\text{CN})_2]^- > [\text{BF}_4]^-$. Verma and Banerjee (2010) investigated 240 ionic liquids that result from the combination of 10 cations and 24 anions and their effect in the system ethanol-water. They found that the ILs with the smallest anions and cations have the strongest interaction with water and are, in consequence, the more suitable to be used as entrainers. The cation with best results was imidazolium, while $[\text{Cl}]^-$, $[\text{OAc}]^-$, and $[\text{Br}]^-$ were the best anions. For this reason, $[\text{emim}][\text{Cl}]$ and $[\text{emim}][\text{OAc}]$ are considered interesting prospects to use as entrainers in industrial applications. This is also true for the system isopropanol-water (Ma et al., 2019).

An increasing number of studies (Hou, Huang, Wang, & Bai, 2011; Quijada-Maldonado, van der Boogaart, Lijbers, Meindersma, & de Haan, 2012; Zhang et al., 2007) have determined that $[\text{emim}][\text{OAc}]$ improves the separation of ethanol and water by enhancing the relative volatility. Dong, Dai, and Lei (2018) indicated the potential of the IL because of its low toxicity, low melting point, low viscosity, and biodegradability. After analyzing the quaternary system methanol-ethanol-water- $[\text{emim}][\text{OAc}]$ and the two resulting

ternary systems, they concluded that both methanol and ethanol can be obtained as pure light components in an extractive distillation process. This is because the IL breaks the ethanol-water azeotrope, showing a salt-out effect for the ethanol. They also carried out the rigorous equilibrium stage model of the extractive distillation process to compare the IL with the conventional entrainer ethylene glycol. It was found that it is required 25% less amount of entrainer when using the IL as well as 6% less for each condenser and reboiler heat duties.

In addition, Quijada-Maldonado, Meindersma, and de Haan (2014) estimated the relative volatilities of the mixture water-ethanol, at different solvent-to-feed ratios for three ILs, [emim][Cl], [emim][OAc], and [emim][DCA], and the organic solvent ethylene glycol (EG). They proved that EG does not have a significant effect on the relative volatility in contrast with the ILs. Amongst these, [emim][Cl] has the greatest effect, followed by [emim][OAc]. However, the first presents very high liquid phase viscosity which can limit the mass transport inside the column. For this reason, in both rectifying and stripping sections [emim][OAc] showed the highest tray efficiency.

Furthermore, [mim][Cl] is conformed of one of the most favorable anions for the separation of ethanol and water, and of the shortest alkyl chain. Therefore, it has the potential to enhance the separation of these components (Shen et al., 2011). The same happens with [bmim][Cl], that although the length of the chain is longer, still has a strong salting-out effect (Zhao, Dong, Li, Meng, & Wang, 2006). Ramírez-Corona et al. (2015) proposed a design method based on tray-by-tray calculations for ethanol-water distillation using these ILs as solvents, demonstrating the ability of these ILs to produce high-purity ethanol and validating the methodology with rigorous simulations. Similarly, Ramírez-Corona, Schramm-Flores, Reyes-Lombardo, and Jiménez-Gutiérrez (2019) studied the dynamic behavior and controllability of the extractive distillation system using the same entrainers.

3 Methodology

3.1 Vapor-Liquid Equilibrium Model

In order to describe the vapor-liquid equilibrium (VLE), vapor phase was assumed to be ideal, while the liquid phase non-ideality was predicted using the thermodynamic model

NRTL (Renon & Prausnitz, 1968), to estimate the activity coefficients, as expressed in Equation (1),

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{G_{ij} x_j}{\sum_k G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_k \tau_{kj} G_{kj} x_k}{\sum_k G_{kj} x_k} \right) \quad (1)$$

where $\ln \gamma_i$ is the activity coefficient of component i , x_i denotes the liquid-phase mole fraction of component i , and the interaction parameters, τ_{ij} and G_{ij} , are defined by Equation (2),

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT}, \quad G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (2)$$

The binary interaction parameters of the mixture water-ethanol-IL were taken from the literature and are presented in Table 1. For [emim][OAc], the data was retrieved from Ge et al. (2008), where it was reported at a pressure of 100 kPa. Δg_{12} and Δg_{21} , in J/mol, were set as $3698.8 + 4.2758T(K)$ and $-2216.0 + 6.7055T(K)$, respectively, and α_{12} to 0.4 (Y. T. Tang, Huang, & Chien, 2003). Additionally, the values of α_{13} and α_{23} were established as 0.3. For [mim][Cl] and [bmim][Cl] the parameters were reported at atmospheric pressure by Shen et al. (2011) and Geng, Zhang, Deng, Ge, and Ji (2010), respectively.

Table 1

NRTL correlation parameters for the system water (1) - ethanol (2) - IL (3) recovered from Ge et al. (2008) for [emim][OAc], Shen et al. (2011) for [mim][Cl], and Geng et al. (2010) for [bmim][Cl]

ij	α_{ij}	Δg_{ij} (J/mol)	Δg_{ji} (J/mol)
water + ethanol	0.4000	$3698.8 + 4.2758(T/K)$	$-2216.0 + 6.7055(T/K)$
water + [emim][OAc]	0.3000	-14357.000	-8789.900
ethanol + [emim][OAc]	0.3000	-12775.000	-8266.200
water + ethanol	0.3008	5615.836	-511.560
water + [mim][Cl]	0.4297	362.357	-6692.568
ethanol + [mim][Cl]	0.3009	3332.725	-3602.459
water + [bmim][Cl]	0.3000	-5270.600	-7372.200
ethanol + [bmim][Cl]	0.3000	-2449.900	-6457.300

The saturated vapor pressures, P_1^{sat} and P_2^{sat} were evaluated with the Antoine equation and P_3^{sat} was assumed negligible. VLE calculations were done at six concentrations of IL (x_{IL}): 0, 0.05, 0.10, 0.15, 0.20, 0.30. The non-ideal behavior of the mixture was fitted to the empirical model for relative volatility presented by Doherty and Malone (2001), as shown in Equation (3). The parameters α_{21} and β were adjusted to minimize the sum of squared error (SSE) of the composition of ethanol in the vapor phase, y_2 .

$$y_2 = \frac{\alpha_{21}x_2}{1 + x_2(\alpha_{21} - 1)} + \beta x_2(1 - x_2) \quad (3)$$

3.2 Design Method of Distillation Columns

The system behaves as a pseudo-binary mixture, therefore the McCabe-Thiele method was used for the estimation of the minimum reflux ratio for the design of the distillation columns, under the assumption of constant molar flows (McCabe, Harriott, & Smith, 2001). The representation of the process for the extractive distillation system is presented in Figure 1, based on the case study given by Ramírez-Corona et al. (2015). In this study, it is proposed the separation of ethanol and water mixture that enters the system as saturated liquid at 25°C. The feed is composed of 80 mol% water and 20 mol% ethanol, and the feed rate is 1000 kmol/h. It is desired to achieve a purity of 99.5 mol% of the distillate product and recover 95% of the ethanol that enters the system. The solvent is added into the reflux stream and fed to the top of the column. The reflux ratio was set as 1.5 times the minimum reflux ratio.

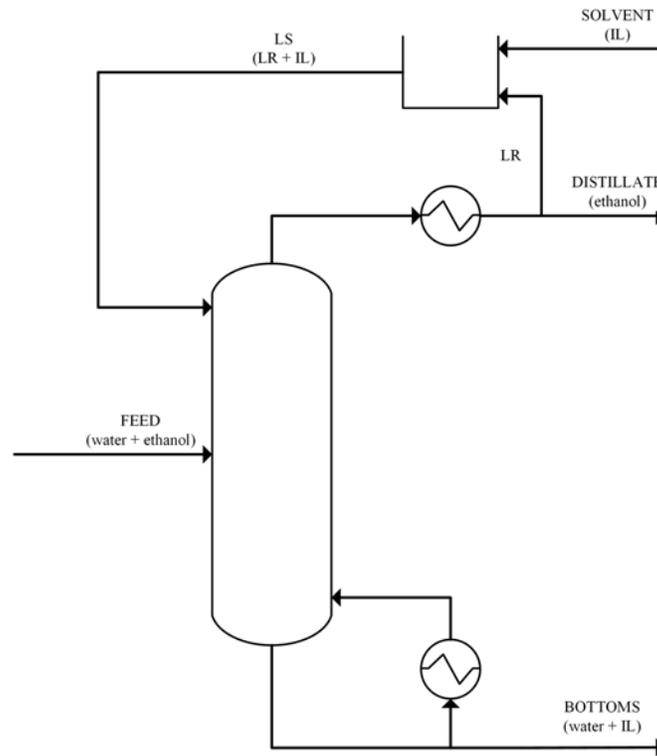


Figure 1. Process flowsheet for the extractive distillation of ethanol

As mentioned in the literature review, the amount of solvent increases relative volatility, thus, facilitating the separation. Therefore, the analysis was performed at different molar fractions of IL in the solvent feed stage. This was evaluated by Equation (4), also taken from Ramírez-Corona et al. (2015), where LR identifies the reflux rate,

$$x_{IL} = \frac{IL}{IL + LR} \quad (4)$$

The calculations with this method are performed at a solvent-free basis. The material balance for ethanol in the rectifying section is given by Equation (5) and the material balance for the stripping section is given by Equation (6), as presented by Ramírez-Corona et al. (2015) in their methodology description,

$$y_{n+1,2} = \frac{LR}{V} x_{n,2} + \frac{D}{V} x_{D,2} \quad (5)$$

$$y_{n,2} = \frac{\bar{L}}{\bar{V}} x_{n+1,2} - \frac{B}{\bar{V}} x_{B,2} \quad (6)$$

where D and B denote the distillate and bottoms molar flows, respectively, $x_{n,2}$ stands for the liquid-phase composition of the second component in stage n , $y_{n,2}$ represents the vapor-phase composition of ethanol in stage n , $x_{D,2}$ denotes the composition of the second component in the distillate product and $x_{B,2}$ the composition in the bottoms.

The McCabe-Thiele graphical method was combined with the stage-by-stage calculations with the relative volatility model to estimate the equilibrium stages and analyze the composition profiles. For this reason, the design of the extractive distillation system was done following a hybrid methodology.

3.3 Energy Consumption Evaluation

To evaluate the energy consumption of the extractive distillation columns, the heat duties of the total condenser and of the partial reboiler were estimated through the energy balance in steady state described in Equation (7),

$$F \sum_i z_i \int_{T_{ref}}^{T_F} Cp_i dT + IL \int_{T_{ref}}^{T_{IL}} Cp_{IL} dT - D \sum_i x_{D,i} \int_{T_{ref}}^{T_D} Cp_i dT - B \sum_i x_{B,i} \int_{T_{ref}}^{T_B} Cp_i dT + Q_R - Q_C = 0 \quad (7)$$

where Q_R represents the reboiler heat duty, Q_C represents the condenser heat duty, T_{ref} stands for the reference temperature for the evaluation of the heat capacity as function of temperature, and the subindices F , D and B denote feed, distillate, and bottoms flows, respectively. Q_C is calculated with Equation (8),

$$Q_C = V \sum_i y_i \lambda_i \quad (8)$$

where y_i stands for the mole fraction of component i in the vapor flow that enters the condenser and λ_i denotes the heat of vaporization of component i . Poling, Prausnitz, and O'Connell (2001) report the values of this property, which are 38.56 kJ/mol and 40.66 kJ/mol, for ethanol and water.

So as to simplify the energy balance, the value of the reference temperature was set to the value of the temperature of the bottoms product, because this is the only flow that has all three components. To evaluate the heat capacity, the parameters of the polynomial expression were also taken from Poling et al. (2001) as shown in Table 2.

Table 2

Parameters for TRC polynomial equation for C_p/R retrieved from Poling et al. (2001)

Component	a_0	a_1	a_2	a_3	a_4
water	4.3950	-4.19E-03	1.41E-05	-1.56E-08	6.32E-12
ethanol	4.3960	6.28E-04	5.55E-05	-7.02E-08	2.69E-11

The experimental data of the heat capacity of [emim][OAc] is reported in Štejfa, Rohlíček, and Červinka (2020) and for [bmim][Cl] in Hu, Soriano, Leron, and Li (2011). The heat capacity data of these ILs behaves linearly. For this reason, and to estimate the heat capacity as a function of temperature, a linear regression was obtained from the experimental information, as presented in Figure 2 and Figure 3, for each IL. For the first IL, the coefficients of the polynomial are $a_0 = 218.8$ and $a_1 = 0.3533$, and for the second they are $a_0 = 106.82$ and $a_1 = 0.6711$.

On the other hand, there is not enough information of this property for [mim][Cl], so it was approximated to next similar molecule [emim][Cl]. Yang, Zhu, Liu, Lv, and Luo (2019) report the regression parameters for the specific heat capacity equation with three terms, $a_0 = 8.734$, $a_1 = -3.058 \times 10^{-02}$ and $a_2 = 5.087 \times 10^{-5}$.

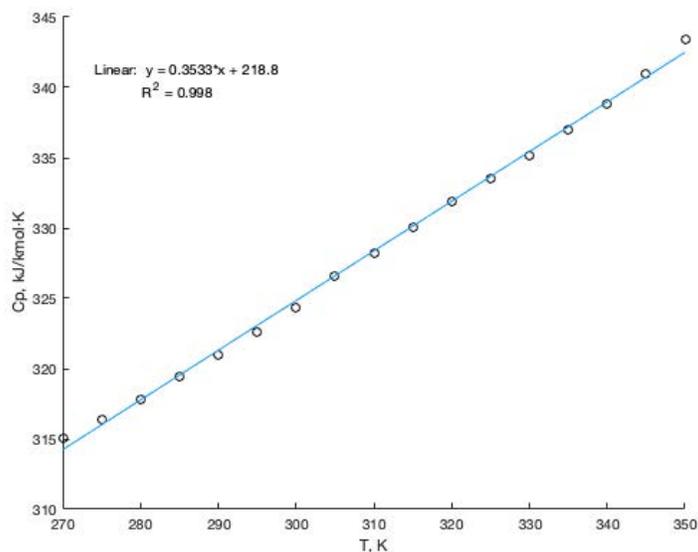


Figure 2. Linear regression of heat capacities of [emim][OAc] reported by Štejfa et al. (2020)

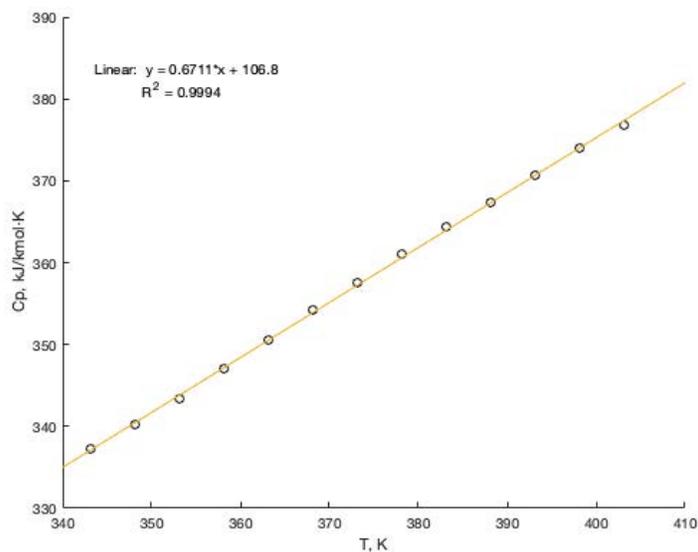


Figure 3. Linear regression of heat capacities of [bmim][Cl] reported by Hu et al. (2011)

4 Results and Discussion

VLE for the pseudo-binary system water-ethanol-[emim][OAc] has been determined at constant pressure of 100 kPa and different IL concentrations. In Figure 4, it can be observed the effect the IL has on the azeotropic system water-ethanol. All data are plotted on a solvent-

free basis, x'_2 . As the composition of solvent increases, the azeotrope breaks and the deviation on ideality becomes less significant, until practically having an ideal behavior, above molar concentrations of 0.15. This proves that [emim][OAc] has a significant effect in increasing the relative volatility of the system and is a suitable entrainer for ethanol dehydration. This result is consistent with previous studies by Ge et al. (2008), Gutiérrez, Meindersma, and de Haan (2012), and Lei et al. (2014). Nevertheless, at low IL concentrations an inflection point is still present around ethanol composition of 90%, which may difficult the separation. For instance, at 0.05 the separation is not feasible since the number of stages in the rectifying section tends to infinity. The same can be said about the effect of the other two ionic liquids, which VLE is shown in Figure 5 and 6 at atmospheric pressure.

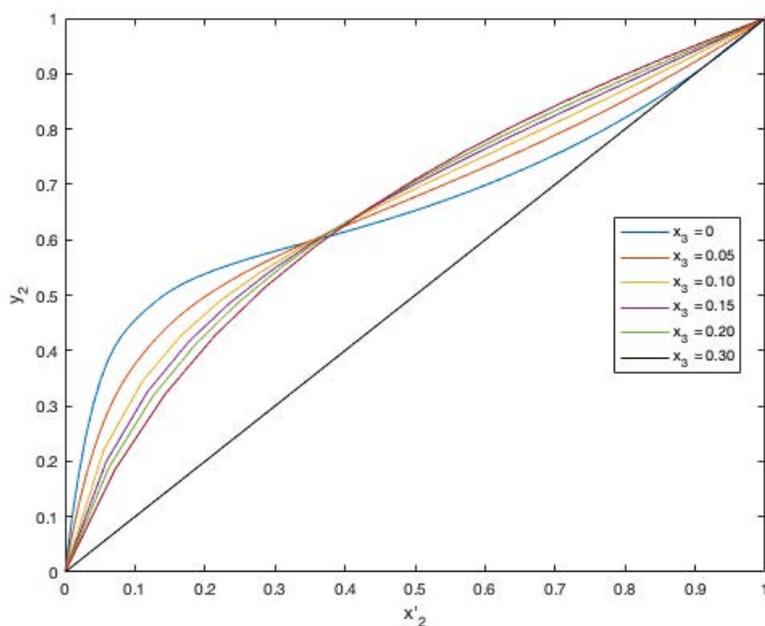


Figure 4. Effects of [emim][OAc] concentration on the water-ethanol VLE

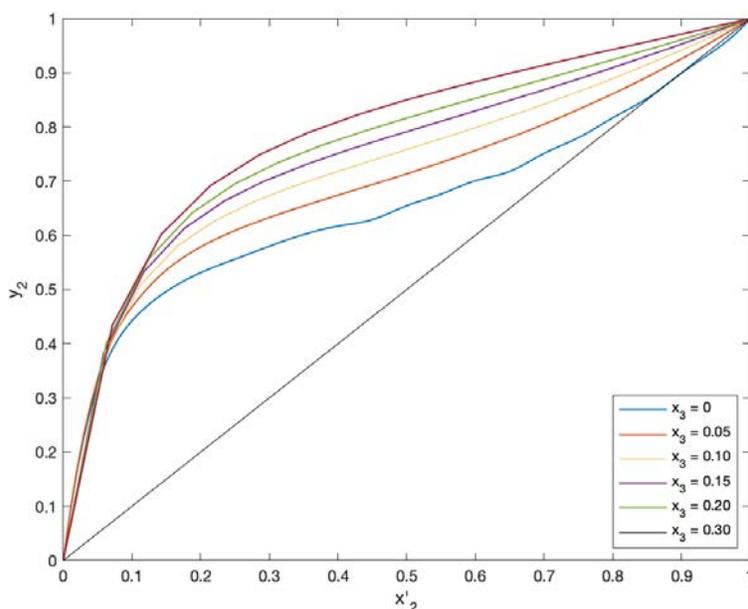


Figure 5. Effects of $[mim][Cl]$ concentration on the water-ethanol VLE

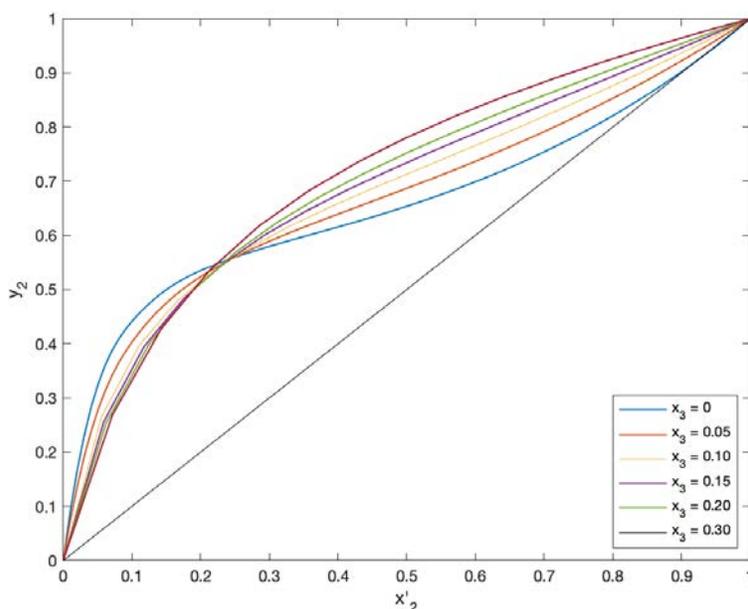


Figure 6. Effects of $[bmim][Cl]$ concentration on the water-ethanol VLE

Table 3 reports the parameters achieved when the empirical model of relative volatility was fitted for the VLE data predicted with the thermodynamic model NRTL. Likewise, Figure 7, Figure 8 and Figure 9 illustrate how the model can describe accurately the y - x relation for the non-ideal solution with each IL. As the equilibrium curve moves further from the

azeotrope with the addition of IL, the prediction improves and the value of the parameter β approaches to zero, because that term of the equation characterizes the non-ideality. It is important to notice that the values of the parameters vary considerably in each case, although components and conditions are the same, except for [mim][Cl] that have quite similar values.

Table 3

Adjusted parameters for the relative volatility empirical model

IL composition	[emim][OAc]			[mim][Cl]			[bmim][Cl]		
	α_{21}	β	SSE	α_{21}	β	SSE	α_{21}	β	SSE
0.05	6.775	-0.768	2.14E-03	10.023	-0.780	2.12E-03	7.694	-0.786	1.87E-03
0.10	5.131	-0.568	1.10E-03	10.170	-0.604	1.62E-03	6.478	-0.602	1.37E-03
0.15	4.240	-0.423	5.56E-04	10.265	-0.474	1.14E-03	5.749	-0.458	9.30E-04
0.20	3.699	-0.317	2.77E-04	10.306	-0.375	7.49E-04	5.299	-0.345	6.00E-04
0.30	3.101	-0.183	6.84E-05	10.259	-0.240	2.83E-04	4.870	-0.188	2.14E-04

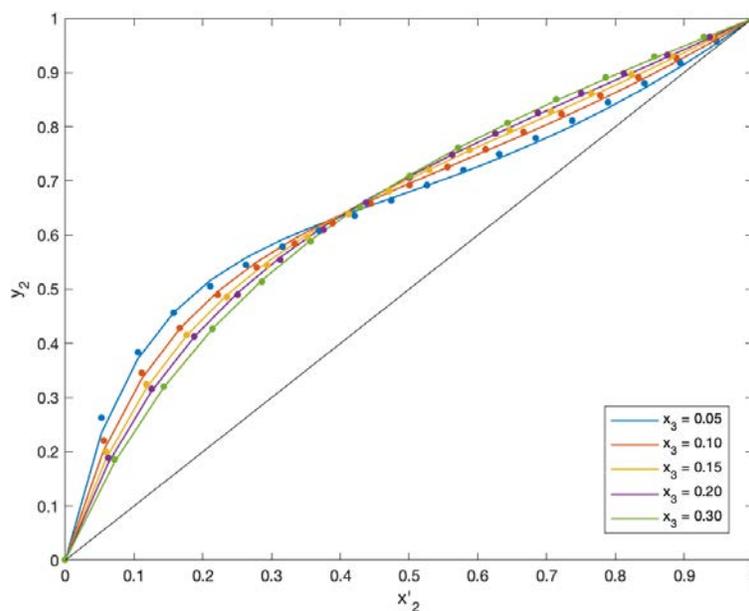


Figure 7. Empirical relative volatility model fitted to NRTL predicted VLE at different [emim][OAc] concentrations

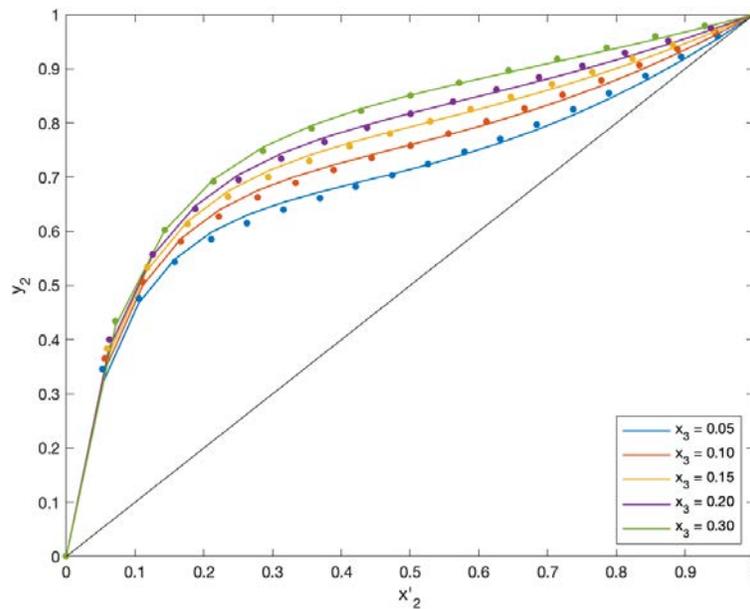


Figure 8. Empirical relative volatility model fitted to NRTL predicted VLE at different [mim][Cl] concentrations

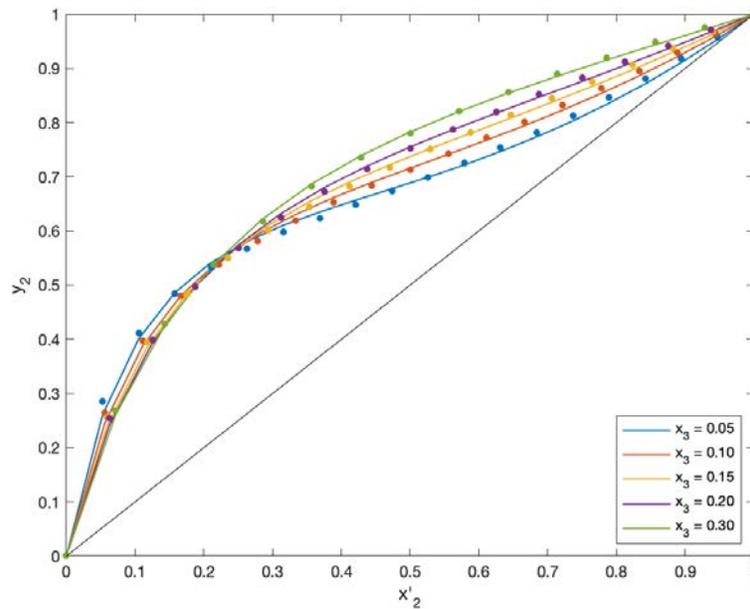


Figure 9. Empirical relative volatility model fitted to NRTL predicted VLE at different [bmim][Cl] concentrations

Based on these results, the design of the distillation columns has been performed at $x_{IL} = (10, 15, 20, 30) \%$. The results of the design variables for the extractive distillation processes

using [emim][OAc] as solvent, at the four mole fractions, are summarized in Table 4. For every design it was possible to achieve a product with 99.5 mol% purity. The distillate rate is the same (190.95 kmol/h) for all four processes because it was a design specification. All IL is recovered in the bottoms stream because it is nonvolatile, then, the distillate stream is composed of ethanol and a small fraction of water.

In contrast, the molar flow of entrainer that is used for the separation depends on the reflux flowrate, which changes in every design. Apart from the first case, the minimum reflux ratio increases with the IL composition, thus the reflux flow rate in each case increases as well. This causes that the required entrainer flow rate is significantly larger from system to system, being the last flow rate almost four times the first. It is also worth noting that as the concentration increases, the operating line at minimum reflux ratio intersects the equilibrium curve at the same point as the feed line, like a nearly ideal binary system. On the other hand, at 0.10, the equilibrium curve still has an inflection in the equilibrium curve, hence the minimum reflux ratio does not follow the pattern and the operating line at minimum reflux ratio presents a pinch point at high ethanol concentrations.

Table 4

Design variables for the water-ethanol separation by extractive distillation using [emim][OAc] as entrainer

Variable	IL composition			
	0.10	0.15	0.20	0.30
Ethanol purity	99.5%	99.5%	99.5%	99.5%
Entrainer flow rate, kmol/h	85.532	116.890	179.178	341.965
Minimum reflux ratio	2.688	2.313	2.502	2.786
Reflux ratio	4.031	3.469	3.753	4.179
Reflux flow rate (LR), kmol/h	769.79	662.37	716.71	797.92
Theoretical stages	39	27	22	20
Feed stage	35	21	16	13

The equilibrium stages were calculated with the relative volatility model and incorporated to the diagram $x'y$. Figure 10 presents the design of the extractive distillation column with an IL concentration of 0.10 and 0.30, the most diluted and the most concentrated systems. It can

be observed that as more solvent is present in the column, the theoretical stages are required are less. This is in agreement with findings in the literature (Ramírez-Corona et al., 2015). This can be explained by the fact that the entrainer increases the relative volatility of the system, enhancing the separation of ethanol and water. The number of stages relates as well with the minimum reflux ratio, because the larger reflux flow rates the fewer the number of stages is. From the first case to the last, it can be seen a reduction in the number of stages of almost half, from 39 to 20 stages. Besides, there is an important reduction from case 1 to case 2.

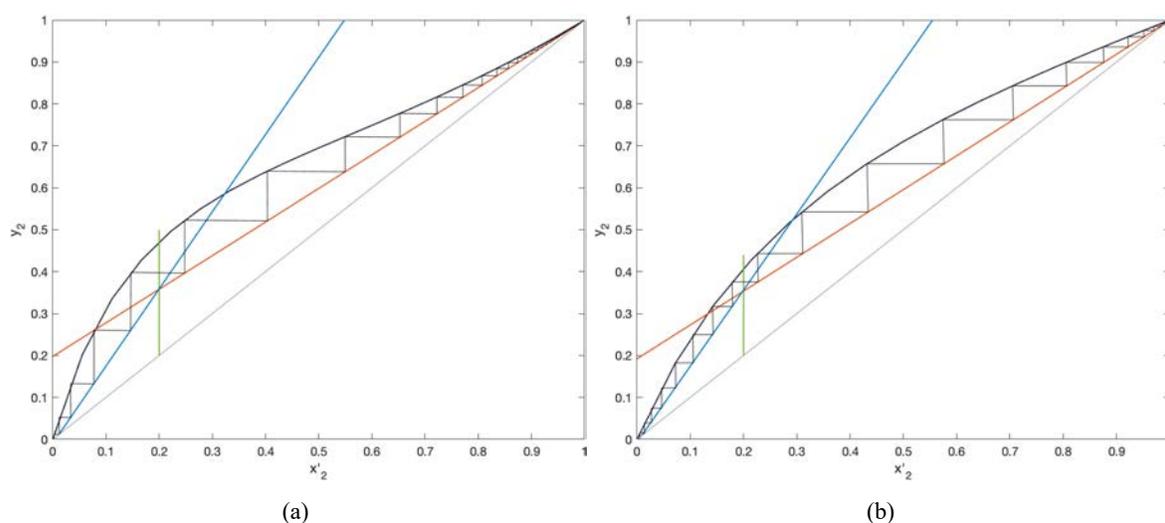


Figure 10. McCabe-Thiele construction for the pseudo-binary system water – ethanol with [emim][OAc], at (a) $x_{IL} = 0.10$ and (b) $x_{IL} = 0.30$

It is also interesting to note how the feed tray location changes. For IL fractions of 10% and 15%, the rectifying section consists of most of the stages. Consequently, the feed stage location is almost at the bottom of the column. These results are also similar to those reported by Zhu et al. (2016). At high concentrations of ethanol, it is still difficult to separate it from water. Therefore, the stages are many, but the difference in the composition between each other is practically none.

This can also be observed in the vapor composition profiles included in Figure 11, [emim][OAc] is not included in the graphs because its vapor composition of remains zero in

all the column. The first two profiles are very wide until a few stages in proximity with the feed tray, demonstrating that the change in compositions at the top of the column is not significant between stages.

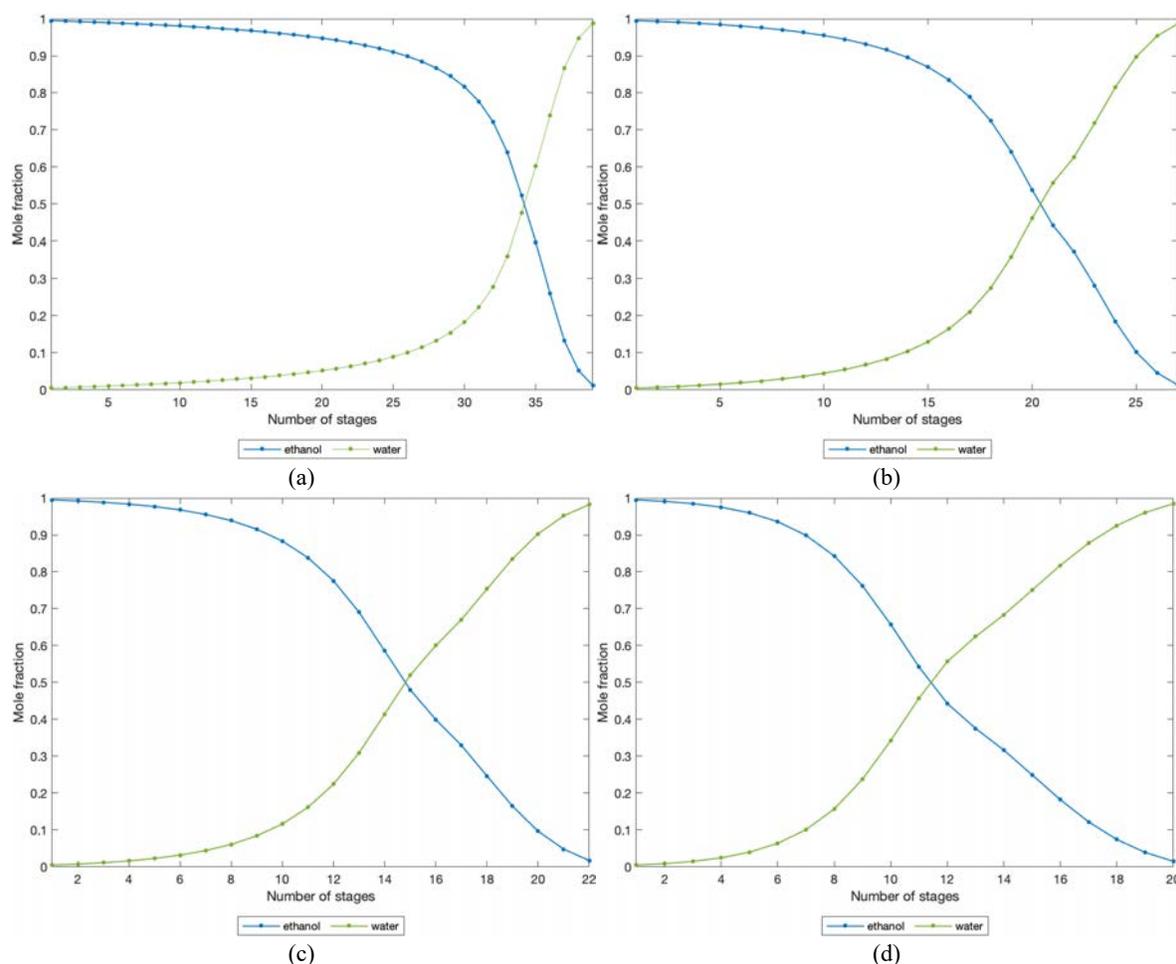


Figure 11. Composition profiles of the extractive distillation columns for water-ethanol assisted with IL at different concentrations: (a) $x_{IL} = 0.10$, (b) $x_{IL} = 0.15$, (c) $x_{IL} = 0.20$, (d) $x_{IL} = 0.30$

On the other hand, Table 5 and Table 6 contain the design variables for the solvents [mim][Cl] and [bmim][Cl]. For these entrainers the minimum reflux ratios are smaller than for the previous IL, thus the entrainer flow rates are quite smaller as well. The difference in the reflux happens because of the effect the ILs have in the VLE of the mixture, as the equilibrium curve is wider for these cases.

The values for the minimum reflux ratio and the entrainer flow rate for the cases of the ionic liquids with the chlorine anion were taken from Ramírez-Corona et al. (2015). This has the objective of comparing the results obtained using this simplified methodology of stage-by-stage calculations with the relative volatility model against the design method detailed in their paper, which is similar to the Boundary Value Method (BVM). The number of stages obtained with the relative volatility model is close to those reported in the mentioned study, especially for high IL molar fraction. For low concentrations of [mim][Cl], the number of stages increases significantly since the VLE still presents an inflection point, thus the model estimates small changes between each stage. This can be observed in Figure 12a where the stages in the rectifying section are almost imperceptible. It is important to notice in Figure 12b that there is an error in the stage calculation, meaning the model has problems predicting equilibrium compositions in that zone.

Table 5

Design variables for the water-ethanol separation by extractive distillation using [mim][Cl] as entrainer

Variable	IL composition			
	0.10	0.15	0.20	0.30
Ethanol purity	99.5%	99.5%	99.5%	99.5%
Entrainer flow rate, kmol/h	44.00	40.80	54.00	83.00
Minimum reflux ratio	1.350	0.800	0.750	0.670
Reflux ratio	2.025	1.200	1.125	1.005
Reflux flow rate (LR), kmol/h	386.68	229.15	214.82	191.91
Theoretical stages	59	42	20	13
Feed stage	56	39	16	9
Theoretical stages in Ramírez-Corona et al. (2015)	24	24	18	17
Feed stage in Ramírez-Corona et al. (2015)	22	21	15	14

For the case of [bmim][Cl], there is an increment for IL concentration of 0.10 because it also presents an inflection point, as seen in Figure 13a. However, for the remaining concentrations the number of stages is almost equal. In all cases, the number of stages in the stripping section

changes by only one stage or does not have any variation. This means that the simplified methodology proposed in this paper gives a good approximation for the design of distillation columns assisted with ionic liquids.

Table 6

Design variables for the water-ethanol separation by extractive distillation using [bmim][Cl] as entrainer

Variable	IL composition			
	0.10	0.15	0.20	0.30
Ethanol purity	99.5%	99.5%	99.5%	99.5%
Entrainer flow rate, kmol/h	80.00	91.50	112.00	186.00
Minimum reflux ratio	2.500	1.800	1.550	1.500
Reflux ratio	3.750	2.700	2.325	2.250
Reflux flow rate (LR), kmol/h	716.08	515.58	443.97	429.65
Theoretical stages	36	24	19	15
Feed stage	32	20	14	10
Theoretical stages in Ramírez-Corona et al. (2015)	29	24	18	17
Feed stage in Ramírez-Corona et al. (2015)	27	21	15	14

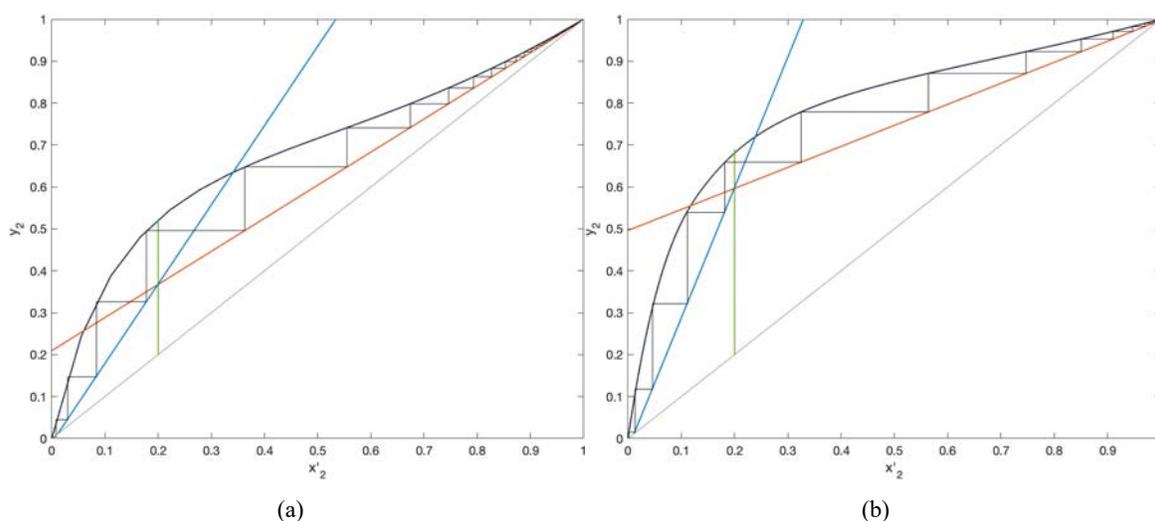


Figure 12. McCabe-Thiele construction for the pseudo-binary system water – ethanol with [mim][Cl], at (a) $x_{IL} = 0.10$ and (b) $x_{IL} = 0.30$

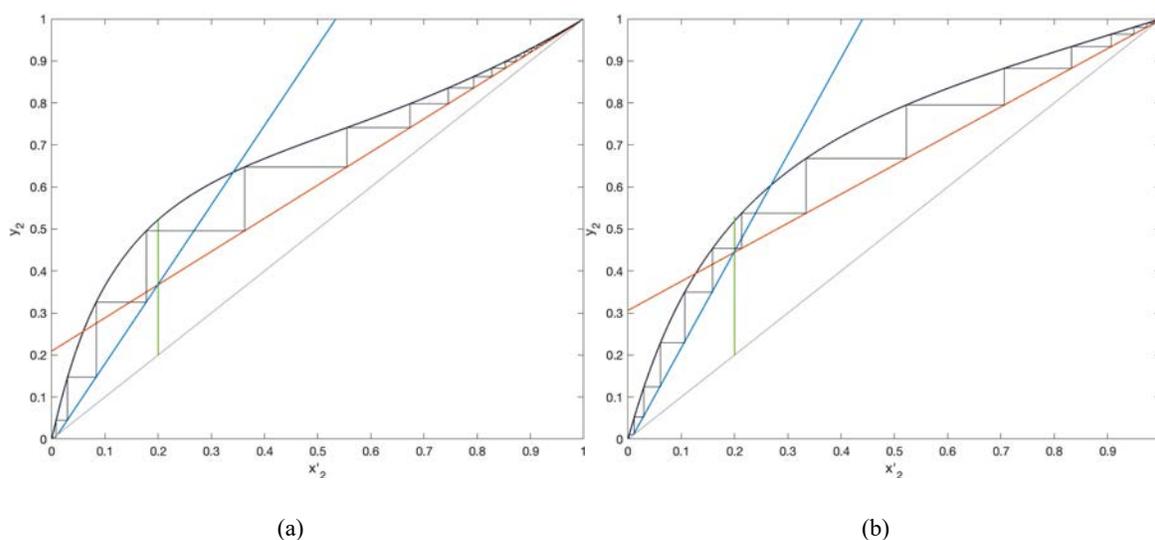


Figure 13. McCabe-Thiele construction for the pseudo-binary system water – ethanol with [bmim][Cl], at (a) $x_{IL} = 0.10$ and (b) $x_{IL} = 0.30$

Another aspect to consider is the energy consumption of the distillation systems. The results of the condenser heat duty and the reboiler heat duty depending on the amount of entrainer used in the process are compared in Table 7. Reboiler and condenser heat duties are almost equal because the feed is a saturated liquid, and it satisfies the McCabe-Thiele assumptions. As expected, the largest heat duties are present at high IL concentrations for [emim][OAc], since the largest reflux ratios were obtained there. The contrary happens with the chlorine ionic liquids. The increment in energy consumption is due to an increase in reflux ratio and in boil up (Quijada-Maldonado et al., 2014).

There is also an increment in the bottoms temperature since the mole fraction of the solvent in this stream grows, which also affects the heat duty of the reboiler. The temperature of the distillate remains 351 K for any concentration of solvent as there are no variations in the conditions of this flow within each case. All systems that have the lowest IL concentration have the highest energy consumption. This is because the minimum reflux ratio was larger due to an inflection in the equilibrium curve, as previously discussed. Therefore, it is important to consider the VLE when performing the current analyses.

Table 7*Energy results for the water-ethanol separation by extractive distillation with ionic liquids*

IL	IL composition	Variables		
		TB, K	QC, kJ/h	QR, kJ/h
[emim][OAc]	0.10	377.42	3.71E+07	4.07E+07
	0.15	380.86	3.29E+07	3.71E+07
	0.20	387.95	3.50E+07	4.05E+07
	0.30	406.61	3.81E+07	4.86E+07
[mim][Cl]	0.10	372.22	2.23E+07	2.55E+07
	0.15	372.01	1.62E+07	1.94E+07
	0.20	372.90	1.57E+07	1.90E+07
	0.30	375.08	1.48E+07	1.86E+07
[bmim][Cl]	0.10	374.13	3.50E+07	3.84E+07
	0.15	376.74	2.73E+07	3.09E+07
	0.20	378.53	2.45E+07	2.85E+07
	0.30	385.25	2.39E+07	2.93E+07

One downside for the [emim][OAc] is that the best separation is achieved with an IL concentration of 30%, which is also the one with the highest heat duties and requires a large molar flow of the solvent. Nonetheless, when compared with extractive distillation with ethylene glycol as entrainer, azeotropic distillation and pressure swing distillation, the heat duties for extractive distillation assisted with ionic liquids are the lowest (Lei et al., 2014). Furthermore, the number of stages is significantly smaller at higher solvent concentrations.

Although deeper analysis is needed to determine the optimal IL concentration fed into the distillation column, the results of the designs elaborated demonstrate that: (1) a feasible design can be obtained from low concentrations like 15%, (2) a very interesting approach may be achieved at concentrations around 20% and 30%; and (3) the relative volatility model can be used for the design of extractive distillation columns with ILs, especially when there are not inflection point in the equilibrium curve.

5 Conclusion

This paper has proposed a simplified methodology for the design of extractive distillation columns for the separation of ethanol and water assisted by the ionic liquids [emim][OAc],

[mim][Cl], and [bmim][Cl]. The non-ideality of the liquid phase was predicted with the NRTL thermodynamic model, and the parameters were obtained from the literature. Then, the vapor-liquid equilibria data was fitted to the empirical model for relative volatility for non-ideal mixtures, which was later applied for the estimation of number of stages and the composition profiles. The design variables at various IL concentrations were estimated using the McCabe-Thiele method in combination with the relative volatility model.

This study provides further evidence for the design of extractive distillation systems assisted with ionic liquids, in particular [emim][OAc], [mim][Cl], and [bmim][Cl]. Because of their high selectivity, the ionic liquids break the azeotrope of the system and enhance its relative volatility. At IL concentrations above 0.10 the equilibrium curve does not present an inflection point and has a nearly ideal behavior; thus, a feasible column design can be achieved to obtain a high-purity product. With an increment in IL concentration, the minimum reflux increases and the temperature at the bottom rises, as well. Therefore, the condenser and reboiler heat duties increase with the IL molar fraction. On the contrary, the number of stages required for the separation is smaller.

Additionally, the results were compared with those reported in the literature, which were developed with the Boundary Value Method. Demonstrating that the relative volatility model can be used to perform the stage-by-stage calculations, if there is not a significant inflection point in the equilibrium. Directions for future work include validation of the results by rigorous simulation, as well as process optimization and process control analysis of extractive distillation systems assisted with ionic liquids.

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