Extractive Distillation of Ethanol-Water Using Ionic Liquids as Entrainers

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Abstract

In recent years, ionic liquids (ILs) have received considerable attention for their use in chemical industry and are considered to be an alternative to conventional entrainers in extractive distillation, because of their ability to selectively separate azeotropic/close boiling mixtures [1, 2].

In this work, an extractive distillation process was investigated, comparing the imidazoliumbased ionic liquids (1-ethyl-3-methylimidazolium acetate), [EMIM][OAc] and (1-ethyl-3-methylimidazolium dicyanamide), [EMIM][DCA] with ethylene glycol (EG) organic solvent for ethanol dehydration. These ionic liquids were proposed with the aim of obtaining a higher selectivity than EG traditional solvent.

The thermodynamic behavior of the ethanol/water mixture in the presence of the solvent was studied using Simulis Thermodynamics software; ionic liquids were created as new components, with the required thermodynamic and physical property parameters. The experimental data for ethanol/water/ethylene glycol mixture were fitted with the non-random two-liquid (NRTL) activity coefficient model to determine the binary interaction parameters, while, binary interaction parameters for ionic liquids were obtained from the literature.

The vapor liquid equilibrium (VLE) behavior of ethanol-water in the presence of [EMIM][DCA] showed that this ionic liquid enhances the relative volatility of ethanol and allows to eliminate the ethanol-water azeotrope. The main operating conditions of anhydrous ethanol production have been determined to achieve a high distillate purity of 99.9 mol% in ethanol. It has been found that the [EMIM] [DCA] ionic liquid is very effective for the separation of ethanol-water azeotropic system even at low concentrations and less energy consuming compared to the conventional benchmark solvent EG.

Introduction

Bioethanol and biodiesel have received increasing attention as excellent alternative fuels and have virtually limitless potential for growth. As bioethanol is part of biofuels, the main challenge facing its production is the separation of high purity ethanol.

Over the years, many technologies have been proposed to separate ethanol/water mixture [3–11]. Among others, extractive distillation is an energy-efficient technology that allows the separation of this complex azeotropic mixture [12–15]. This separation technology implies the addition of a high boiling solvent as separating agent at the top of the extractive distillation column. This solvent has a major affinity with the component to be “extracted” that is obtained at the bottom of the column along with the solvent. The interaction between the solvent and one of the components are mainly hydrogen bonding. In turn, the solvent has less affinity with the component to be obtained at the top of the column [12].

The currently used organic solvents for water–ethanol separation such as glycols [12, 13, 1620] show some disadvantages. Although, their boiling point is high, they still have some volatility that eventually pollutes the top product and large amounts of solvent or high reflux ratios are needed to obtain the desired product purity. This volatility makes them difficult to contain in the process. Recently, ionic liquids have been proposed as potential replacement of these organic solvents due to their high separation ability, non-detectable vapor pressure, relative low melting point and recyclability. Many studies have demonstrated the great ability of these new class of solvents to separate complex mixtures by extractive distillation [21–23]. In extractive distillation column, the entrainer is fed at a different location than the main mixture, bringing an additional extractive section in the column, between the stripping and the rectifying sections [24]. The basic principle is that the extractive entrainer interacts differently with the components of the original mixture and thereby alters their relative volatility. These interactions occur predominantly in the liquid phase and the entrainer is introduced above the original mixture feed point to ensure that the entrainer remains in appreciable concentration in the liquid phase in the column section below [25]. In this way, it is possible to obtain one pure component at the top of one column and the other, together with the solvent at the bottom, which may be separated easily in a secondary distillation column, due to a high boiling point of the solvent. The solvent doesn’t need to be vaporized in the extractive distillation process. The success of an extractive distillation process relies on the choice of an extractive agent whose selection criteria are related to thermodynamics (selectivity and boiling point) and to process operation (minimal entrainer-feed flow rate ratio, low corrosion, price, toxicity, and high thermal stability) [26].

Methods

The thermodynamic behavior of ethanol/water azeotropic mixture in the presence of ethylene glycol and ionic liquids was studied using Simulis Thermodynamics software v2.0.14. Physicochemical and thermodynamic properties of ionic liquids were estimated, such as critical properties and vapor pressure [27], standard enthalpy of vaporization [28] and heat capacity [29].

The ethanol/water mixture forms a positive azeotrope at atmospheric pressure, the composition of the azeotrope is 89.43 mol% of ethanol corresponding to a minimum boiling temperature of 78.15°C (according to DECHEMA database). The NRTL activity coefficient model was used to calculate the vapor liquid equilibrium of this strongly polar mixture, where the vapor phase is assumed to be ideal. The binary interaction parameters of ethanol-water-ethylene glycol system were regressed from the VLE experimental data, while, binary interaction parameters of ethanol-ILs and water-ILs systems were obtained from the literature.

Table 1 Binary interaction parameters regressed for ethanol-water-ethylene glycol system using the NRTL model.

Binary	A_{ij}	A_{ji}	α	RMS
Ethanol- water	-138.796	1332.722	0.28	0.0051
Ethanol- ethylene glycol	1298.18	74.064	0.3	0.081
Water- ethylene glycol	52.685	-37.91	0.3	0.054

Figure 1 Regression of the VLE experimental data by the NRTL model for ethanol-water, ethanol-ethylene glycol and water-ethylene glycol systems.

Table 2 Binary interaction parameters of the NRTL model for Ethanol-ILs and Water-ILs systems.

Component i	Component j	A_{ij}	A_{ji}	α	Reference
Ethanol	[EMIM][OAc]	-1426.4	-965.94	0.4	[30]

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j}$$

$$= \frac{\gamma_i P_i^0}{\gamma_j P_j^0}$$

Water	[EMIM][OAc]	-1505.8	-1109.3	0.4	[31]
Ethanol	[EMIM][DCA]	7034.1	-2054.2	0.75	
Water	[EMIM][DCA]	9557	-2613	0.827	

The ease of separation of a given mixture with key components i and j is given by the relative volatility:

The solvent is introduced to change the relative volatility as far away from unity as possible.

Since the ratio of $\frac{P_i^0}{P_j^0}$ is constant for small temperature changes, the only way that the

γ^i/γ_j , This ratio, relative volatility is affected is by introducing a solvent which changes the ratio in the presence of the solvent, is called selectivity S_{ij} [12]:

$$S_{ij} = \left(\frac{\gamma_i}{\gamma_j} \right)_s$$

The methodology of this work consists in determining at first the effect of the solvent concentration on the VLE of the ethanol-water system, more precisely on the displacement of the azeotropic point until its disappearance. Then, determine the solvent concentration range allowing to facilitate the separation and to increase the relative volatility of ethanol. The solvent-to-feed ratio necessary for each case of mixture (from 20 mol% to 80 mol% of ethanol) found by Simulis thermodynamics were validated by simulation using ProsimPlus.

The separation of the ethanol/water mixture containing 20 mol% to 80 mol% of ethanol was carried out in an extractive distillation column. As an entrainer, a conventional solvent "Ethylene Glycol" and two Ionic Liquids, namely 1-ethyl-3-methylimidazolium acetate, [EMIM][OAc] and 1-ethyl-3-methylimidazolium dicyanamide, [EMIM][DCA], have been applied. The structures of the ionic liquids used in this work are as the following:

1-ethyl-3-methylimidazolium acetate

1-ethyl-3-methylimidazolium

dicyanamide

The process flowsheet consists of two columns, an extractive distillation column for the separation of the ethanol/water mixture and a recovery column for solvent regeneration. In the extractive distillation column, the solvent is fed continuously in a given location of the column different from that of the ethanol-water mixture, making it possible to create an extractive section in which the attraction of the water molecules by the solvent takes place and therefore, the relative volatility of ethanol will be increased. Ethanol is obtained at the top of the extractive distillation column, and the water + entrainer mixture removed at the bottom is sent to the regeneration column. At the bottom of the regeneration column, when the solvent is recovered with a satisfactory purity, it is recycled back to the extractive distillation column.

Figure 2 Extractive distillation process flowsheet with a heavy entrainer [32].

Unusual extractive distillation processes exist: the process with ionic liquid entrainers [1] behaves like any heavy entrainer extractive distillation process.

The rigorous simulation of the extractive distillation column was carried out using ProSimPlus simulator version 2.0.14.

The design parameters of the separation process such as: reflux molar ratio (R), feed stage (N_F), solvent stage (N_E) and solvent-to-feed molar ratio (F_E/F) were evaluated. The operating pressure of the extractive distillation column is set at 1 atm and the feed is assumed to be in the boiling liquid state.

The sensitivity analysis was performed to visualize the effect of the solvent-to-feed ratio (F_E/F) and reflux ratio (R) on the purity of ethanol. The purity of ethanol in the distillate must higher than 99.9 mol%. The energy consumption on the reboilers has been optimized by choosing the appropriate pair (F_E/F , R).

Results

1. Feasibility of the Extractive Distillation Process

The choice of a suitable entrainer affects the feasibility and efficiency of extractive distillation process. The entrainer should interact differently with the mixture components, causing their relative volatilities to either increase or reduce, and thereby ease the separation. But entrainer selection and extractive process design require a detailed knowledge of thermodynamic properties of the mixture to be separated: the residue curve map topology and the equivolatility and equidistribution curves [27].

For the separation of a minimum boiling azeotropic mixture A-B, one should add a heavy entrainer E that forms no new azeotrope. Following Serafimov's classification of ternary diagrams. The corresponding ternary mixture Ethanol-Water-Entrainer exhibits a single azeotrope and a single distillation region. It belongs to the (1.0-1a) class [33], in which occurrence among all azeotropic ternary mixtures amounts to 21.6% [34]. The product withdrawn by extractive distillation is a saddle, or intermediate boiling point in the distillation region.

Figure 3 Residue curves map of ethanol-water with a heavy entrainer (ethylene glycol).

Filled circles in residue curves map represent stable node [SN] corresponding to the component with the highest boiling temperature in the diagram, empty circles represent unstable node [UN], lowest boiling temperature node, and empty down triangles represent residue curve saddle points [S], intermediate boiling points.

The residue curves map of ethanol-water with a heavy entrainer illustrate the case when the univolatility is located at A-E side, therefore, A is the expected product in the distillate because it is the most volatile in the region ABE where it is connected to E by a residue curve of decreasing temperature from E to A.

2. Vapor - Liquid Equilibrium (VLE) for ethanol –water-solvent system

□ Effect of solvent on the VLE of ethanol – water system

In order to find the minimal entrainer amount for breaking the ethanol-water azeotrope, the variation of the activity coefficients of ethanol and water and the evolution of the relative volatility of ethanol were studied as a function of solvent-to-feed ratio.

Table 3 Displacement of the azeotropic point as a function of solvent-to-feed molar ratio (F_E/F).

Solvent	Ethylene Glycol			[EMIM][DCA]		
F_E/F	0	0.02	0.05	0	0.001	0.002
$x_{EtOH_{azeo}}$	0.9	0.95	1	0.9	0.95	1
γ_1	1.0058	1.0043	1.0044	1.0052	1.007	1.002
γ_2	2.24	2.26	2.2	2.27	2.24	2.2
α_{12}	1.023	1.013	1.039	1.008	1.024	1.04

The solvent increases the relative volatility of ethanol as far away as possible from unit and decreases the activity coefficient of water, then, brings the ethanol-water system closer to ideality and ultimately facilitates separation.

For the ionic liquid [EMIM][DCA], the azeotrope completely disappears from a solvent-to-feed ratio of 0.002, this value of minimal solvent amount is very low compared to that of the ethylene glycol organic solvent, therefore, [EMIM][DCA] is more selective for ethanol-water separation than ethylene glycol.

Figure 4 Effect of solvent-to-feed ratio on the relative volatility of ethanol,
(a) Ethylene glycol, (b) [EMIM][DCA].

Figure 4 shows the effect of the solvent-to-feed ratio (F_E/F) on the VLE behavior of ethanolwater. It is noticed that for EG, the ease of separation is always proportional to F_E/F , while for [EMIM][DCA], a value of F_E/F greater than 10% will have a negative effect on the separation, from these results, it can be noted that the [EMIM][DCA] ionic liquid is very efficient for ethanol dehydration even if it is added in very small quantities.

3. Extractive distillation process simulation

□ Sensitivity analysis results of extractive distillation column using EG and [EMIM][OAc] as solvents

a) Effect of solvent-to-feed molar ratio and reflux ratio on the ethanol purity

The effect of solvent-to-feed ratio (F_E/F) and reflux ratio (R) on the ethanol composition was studied in order to determine the best operating parameters which lead to a high purity of products. Rigorous simulation results presented in (Fig.5) shows that the reflux ratio is inversely proportional to solvent-to-feed ratio. For a feed containing 80 mol. % of ethanol, it is necessary to increase the F_E/F and to decrease the reflux ratio to have a purity of ethanol higher than 99.9 mol. %. This relation is valid for the ethylene glycol organic solvent (Fig.5 (a)), as well as for the [EMIM][OAc] ionic liquid (Fig.5 (b)). It is also noticed from (Fig.5) that extractive distillation column using [EMIM][OAc] as entrainer consumes less of solvent quantity than using EG, and required a lower reflux ratio.

Figure 5 Effect of solvent-to-feed ratio and reflux ratio (R) on the molar composition of ethanol in distillate using ethylene glycol (a), using [EMIM][OAc] (b).

b) Effect of solvent-to-feed molar ratio and reflux ratio on the reboiler duty

The study of solvent-to-feed ratio and reflux ratio parameters sensitivity on the reboiler duty indicates that the heat quantity supplied to the reboiler increases as the two parameters increase for a given purity. It is therefore a question of choosing the appropriate pair (F_E/F , R) which involves the lowest energy consumption on the reboiler. It is noticed from (Fig.6) that extractive distillation using [EMIM][OAc] is less energy consumption than using EG.

Figure 6 Effect of solvent-to-feed ratio and reflux ratio (R) on the reboiler duty using ethylene glycol (a), using [EMIM][OAc] (b).

c) Effect of number of stages in extractive section on ethanol molar composition

It is important to increase the number of stages in the extractive section because it represents the most important part of the extractive distillation column, this section must be as large as possible in order to increase the contact time between the ethanol/water mixture and the solvent then to improve the efficiency of separation. The theoretical total number of stages of the

extractive distillation column was set to 30 stages, the solvent tray (N_E) using EG and [EMIM][OAc] was set respectively to 5 and 2. Decreasing the number of stages in the extractive section will have a negative effect on the ethanol purity. Figure 7, indicates that the optimal values of the number of stages of the extractive section for ethylene glycol and [EMIM][OAc] are respectively 23 and 22 stages.

Figure 7 Effect of the number of stages in the extractive section on the molar composition of ethanol in distillate using ethylene glycol (a), using [EMIM][OAc] (b).

- Optimal operating parameters for the extractive distillation column in the presence of EG, [EMIM][OAc] and [EMIM][DCA] as solvents

The parametric sensitivity study allowed to choose the best operating parameters of the extractive distillation column. The parameters were calculated for a feed containing 20 mol. % to 80 mol. % of ethanol, the ethanol purity was set to 99.97 mol. % and the total number of stages was fixed to 30 stages. The results are summarized in table 4. It can be seen that the F_E/F and the energy consumed at the reboiler increase when the molar fraction of ethanol in the feed is higher. The relationship between the reflux ratio and the molar composition of ethanol in feed is inversely proportional; this remains valid also for ionic liquids. Extractive distillation column using [EMIM][OAc] and [EMIM][DCA] ionic liquids as solvents requires low values of reflux ratio compared to that using ethylene glycol due to the high boiling point of these ionic liquids compared to EG. Extractive distillation column using [EMIM][DCA] requires higher values of reflux ratio compared to that using [EMIM][OAc] because [EMIM][DCA] is used in very small quantities compared to [EMIM][OAc]. The energy consumed at the reboiler using ionic liquids is lower than using ethylene glycol; therefore, ionic liquids are more selective than ethylene glycol for the ethanol dehydration. Extractive distillation column using [EMIM][DCA] it is less energy consumption than using [EMIM][OAc], as a result, [EMIM][DCA] remains the best entrainer for ethanol/water

separation, this can be explained by the high selectivity of this ionic liquid for water, the dicyanade anion is more electronegative (N^-) than the acetate anion (O^-), which allows it to retain water molecules more easily.

Solvent	Ethylene glycol N_E $= 5 / N_F = 26$			[EMIM][OAc] $N_E = 2 / N_F = 25$			[EMIM][DCA] $N_E = 5 / N_F = 25$		
$X_{F,EtOH}$	F_E/F	R	$Q_B(kW)$	F_E/F	R	$Q_B(kW)$	F_E/F	R	$Q_B(kW)$
20%	0.26	2.2	798.84	0.1	1.35	604.94	0.01	1.5	581.48
40%	0.55	1.6	1346.89	0.24	0.5	882.44	0.013	0.71	787.81
50%	0.55	1.2	1416.56	0.26	0.42	1038.03	0.014	0.62	925.41
60%	0.65	1	1579.11	0.28	0.35	1184.33	0.016	0.57	1072.05
80%	0.76	0.9	2020.33	0.325	0.2	1521.06	0.02	0.5	1357.34

Table 4 Operating parameters and energy consumption at the reboiler of the extractive distillation column using EG, [EMIM][OAc] and [EMIM][DCA].

□ Composition profiles in the extractive distillation column

Figure 8 shows the molar composition profiles of ethanol, water and solvent in the liquid phase along the extractive distillation column, where it is noticed that The molar composition of ethanol increases considerably from the feed stage (N_F) to the entrainer stage (N_E) to reach a maximum value in the condenser. The molar composition of water is maximum in the stripping section and the concentration of the solvent is kept constant along the extractive section.

(8) (b)

Figure 8 Composition profiles in the extractive distillation column using ethylene glycol (a), using [EMIM][DCA] (b).

□ Temperature profile in the extractive distillation column

According to Figure 9, it is noted that the temperature in the rectification section is close to the boiling temperature of ethanol, since in this section ethanol is predominant in the liquid phase. The extractive section is characterized by a constant temperature, while in the stripping section, the temperature begins to increase to reach a maximum value which is that of the reboiler.

Figure 9 Temperature profile in the extractive distillation column using EG, [EMIM][OAc] and [EMIM][DCA].

The temperature in the reboiler of the extractive distillation column increases when using ionic liquids. The extractive distillation column using [EMIM][DCA] as a solvent is less energy consumption than using [EMIM][OAc].

□ Optimal operating parameters for the solvent regeneration column

Table 5 presents the operating parameters of the recovery column for ethylene glycol, [EMIM][OAc] and [EMIM][DCA]. The molar composition of the solvent in the residue of the regeneration column was set to 99.98 mol %.

Table 5 Operating parameters and energy consumption at the reboiler of the extractive distillation column using EG, [EMIM][OAc] and [EMIM][DCA].

Solvent	Ethylene glycol N = 8 / N _F = 4		[EMIM][OAc] N = 7 / N _F = 2		[EMIM][DCA] N = 7 / N _F = 3	
X _{F,EtOH}	R	Q _B (kW)	R	Q _B (kW)	R	Q _B (kW)
20%	1.6	2461.56	0.1	1193.62	0.01	951.76
40%	0.45	1184.33	0.4	1393.33	0.01	731.73
50%	0.5	1046.16	0.5	1254.00	0.01	613.53
60%	0.65	961.40	0.7	1244.71	0.01	495.91
80%	0.8	1555.89	2.4	1193.62	0.03	265.31

It is observed from Tab. 5 that the recovery column of the ionic liquids requires less number of stages and consumes less energy compared to ethylene glycol regeneration column.

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