

Intensified extractive distillation process for the separation of n-heptane-toluene mixture using the ionic liquid 1-Ethyl-4-methylpyridinium Bis(trifluoromethanesulfonyl)imide

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Abstract

Ionic liquids (ILs) have emerged in recent years as promising green solvents to replace conventional solvents. This work aims to the separation of n-heptane-toluene mixture by extractive distillation using ionic liquid (IL) to enhance the performance of the process. The ionic liquid [4EMPy] [NTF₂], "1-ethyl-4-methylpyridiniumBis(trifluoromethanesulfonyl)imide", was proposed due to its high selectivity compared to the conventional solvent "Sulfolane". The calculation of the VLE of n-heptane-toluene mixture in the presence of the solvent was performed using the NRTL activity coefficient model. The effect of the concentration of the IL showed that the relative volatility of n-heptane (1) to toluene (2) in the presence of [4EMPy] [NTF₂] increases at a smaller solvent concentration compared to Sulfolane. The best operating conditions for the extractive distillation process were determined to recover n-heptane with a high purity of 99.9 mol. %. It was found that the ionic liquid [4EMPy] [NTF₂] is more efficient than sulfolane for separating n-heptane/toluene close boiling point mixture even it is used in small amounts and it is less energy consuming.

Keywords: n-heptane/toluene, close boiling point, NRTL, [4EMPy] [NTF₂], extractive distillation, energy consumption

I. INTRODUCTION

The separation of aromatic-aliphatic hydrocarbon mixtures is one of the most difficult separations in the chemical and petrochemical industries due to their close boiling points and the formation of azeotropes. These types of separations were first studied 42 years ago in a European project [32].

The separation of toluene from n-heptane mixture is an aromatic-aliphatic separation. This separation is useful for the production of low aromatic fuels which are widely recommended nowadays [3].

Research has shown that this mixture can be separated by extractive distillation or by azeotropic distillation [7, 8, 14, 26, 28].

The currently used organic solvents for n-heptane/toluene separation such as sulfolane [5, 4, 6, 16, 39], N-methyl pyrrolidone (NMP) [16], N-formyl morpholine (NFM), and ethylene glycol [1, 34, 39] 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. Recently, ionic liquids as a new kind of "green" solvents have been proposed for being a potential solvent for separation process [9, 10, 12, 20, 22-24, 38, 40] and as a substituent of the organic solvents due to their high separation ability, negligible vapor pressure, relative low melting point and recyclability [31, 36, 37]. Many studies have demonstrated the great ability of these new class of solvents to separate complex mixtures by extractive distillation [7, 8, 14, 17-19, 26, 28].

In this work, to evaluate the thermodynamic and the energy efficiency of the extractive distillation process of the close-boiling



point mixture n-heptane/toluene using IL¹-ethyl-4-methylpyridinium Bis (trifluoromethanesulfonyl) imide [4EMPy][NTF₂], the sensitivity analysis of the key operating parameters of the process was performed using Aspen Plus software V.10.

II. METHODS

Physical and thermodynamic properties of the ionic liquid [4EMPy][NTF₂] were estimated, such as critical properties using an extended group contribution method, which is based on the well-known concepts of Lydersen and Joback and Reid [2], and vapor pressure using the Antoine equation [29]. The standard enthalpy of vaporization was predicted with Verevkin's method [33] and the heat capacity was correlated with a group contribution method developed by Sattari and al. [30].

The ionic liquid molecule [4EMPy][NTF₂] was introduced into Aspen Plus with the properties listed in Tab. 1.

The thermodynamic behavior of the n-heptane/toluene mixture in the presence of sulfolane and [4EMPy][NTF₂] ionic liquid was studied. The Non-Random two liquids NRTL model was used to calculate the vapor-liquid equilibrium based on the experimental data of the n-heptane (1) - toluene (2) system in the presence of the organic solvent sulfolane and the ionic liquid [4EMPy][NTF₂] [15, 21, 25, 35] using Aspen plus software v10.

Table 1. Physical properties of the ionic liquid [4EMPy][NTF₂]

Properties	Mw (g/mol)	T _b (K)	T _c (K)	P _c (bar)
[4EMPy][NTF ₂]	402.3	806.12	1465.08	25.88

In distillation, the separation efficiency of two constituents is often denoted by a quantity called the relative volatility α_{ij} which define the ease of separation of a given mixture

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} = \frac{\gamma_i P_i^0}{\gamma_j P_j^0} \quad (1)$$

Where x is the mole fraction in the liquid phase, y is the mole fraction in the vapor phase, γ is the activity coefficient, and P_i^0 is the vapor pressure of the pure component.

The solvent is introduced to increase the relative volatility as far from unity as possible. Since the ratio of P_i^0 / P_j^0 is constant at small temperature changes, the added solvent enhances the relative volatility as the ratio γ_i / γ_j changes in the presence of the solvent, this ratio is called selectivity S_{ij} [19]:

$$S_{ij} = \left(\frac{\gamma_i}{\gamma_j} \right)_s \quad (2)$$

III. RESULTS AND DISCUSSION

A. Calculation of vapor - liquid equilibrium for n-heptane-toluene-solvent system

The regression of the NRTL binary interaction parameters was done without considering the temperature dependence. The regressed parameters are grouped in Tab. 2.

Table 2. Regressed binary interaction parameters of NRTL model

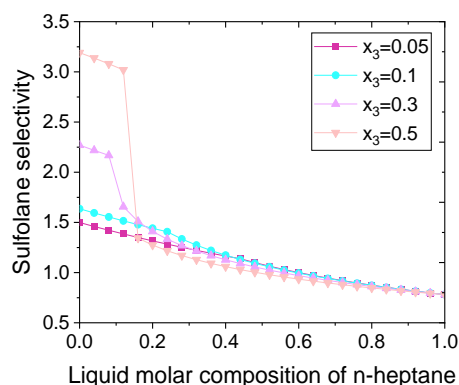
Component i	Component j	A _{ij}	A _{ji}	α
n-heptane	Toluene	-33.2	153.8	0.3
n-heptane	Sulfolane	1329.7	934.6	0.3
Toluene	Sulfolane	889.0	17.7	0.3
n-heptane	[4EMPy][NTF ₂]	944.1	741.9	0.4
Toluene	[4EMPy][NTF ₂]	363.0	-399.2	0.4

1) Effect of the solvent concentration on the selectivity of sulfolane and [4EMPy][NTF₂]

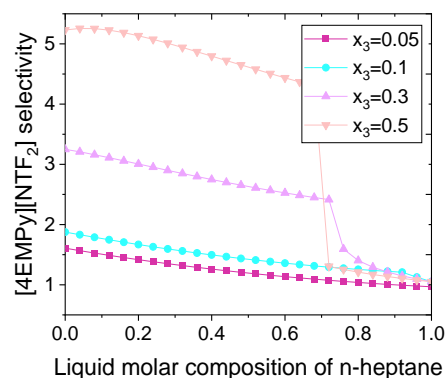
Figure 1 (a) and (b) respectively show the variation of the selectivity of sulfolane and the ionic liquid [4EMPy][NTF₂] as a function of the mole fraction of n-heptane in the pseudo-binary mixture.

It can be seen from Fig. 1 that the selectivity reaches its maximum value at infinite dilution of n-heptane in toluene, which confirms that sulfolane and [4EMPy][NTF₂] are selective solvents with respect to toluene.

From Fig.1 we notice that, the selectivity is proportional to the solvent mole fraction (x_3) in the mixture. The ionic liquid [4EMPy][NTF₂] have a high selectivity toward toluene (Fig. 1 (b)) compared to sulfolane (Fig. 1 (a)), thus, for a solvent fraction of 0.5, the selectivity of sulfolane and [4EMPy][NTF₂] are respectively equals to 3.2 and 5.2.



(a)



(b)

Figure 1. Variation of selectivity as a function of the n-heptane mole fraction in the pseudo binary mixture, (a): sulfolane, (b): [4EMPy][NTF₂]

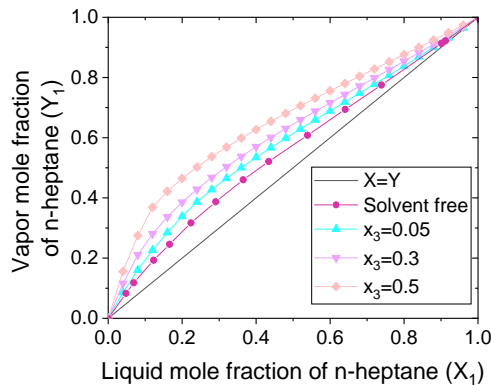
2) *Effect of the solvent concentration on the relative volatility of n-heptane to toluene in the presence of sulfolane and [4EMPy] [NTF₂]*

A relative volatility close to unity means that separation of the two component is likely to be difficult, whereas a relative volatility greater than unity means that few equilibrium stages are required for separation. For a binary system, equation (1) can be rearranged to give:

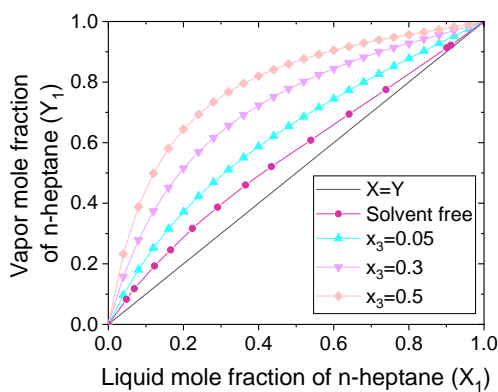
$$y_i = \frac{\alpha_{ij}x_i}{1+(\alpha_{ij}-1)x_i} \quad (3)$$

The vapor-liquid equilibrium curves are plotted in Fig. 2 at different solvent concentrations, from which it can be seen that in the absence of the solvent, the relative volatility of n-heptane is very close to unity over the composition range from 0.8 to 1. The vapor-liquid equilibrium curve moves away from the diagonal as the mole fraction of the solvent (x_3) increases.

The relative volatility of n-heptane to toluene increases notably in the presence of [4EMPy] [NTF₂] (Fig. 2 (b)) compared to sulfolane (Fig. 2 (a)) for the same solvent concentrations. As a result, the ionic liquid [4EMPy] [NTF₂] is more efficient for n-heptane/toluene separation in comparison with the organic solvent sulfolane.



(a)



(b)

Figure 2. Effect of the solvent molar fraction of sulfolane (a) and [4EMPy][NTF₂] (b) on the relative volatility of n-heptane

B. Simulation of the extractive distillation process for the separation of n-heptane-toluene mixture

The simulated process flowsheet, as presented in Fig. 3, consists of two columns, an extractive distillation column for the separation of the n-heptane/toluene mixture using a heavy entrainer and a recovery column for the solvent regeneration. In extractive distillation column, the entrainer is fed continuously above the main feed mixture, bringing an additional extractive section in the column, between the stripping and the rectifying sections [11]. N-heptane is recovered at the top of the extractive distillation column, and the mixture toluene + entrainer removed at the bottom is sent to the regeneration column. At the bottom of the regeneration column, the solvent is recovered with a high purity, and then recycled back to the extractive distillation column. The rigorous simulation of the extractive distillation process was carried out using Aspen plus V.10. The operating pressure of the extractive distillation process was set to 1 atm, the feed is assumed to be in the boiling liquid state and the solvent feed temperature was fixed to 25°C. The molar feed flow rate (F) was set to 100 kmoles/hr and the mixture was chosen for an equimolar composition. The n-heptane purity in the distillate of the extractive distillation column and the solvent purity at the bottom of the regeneration column must be higher than 99.9 mol%.

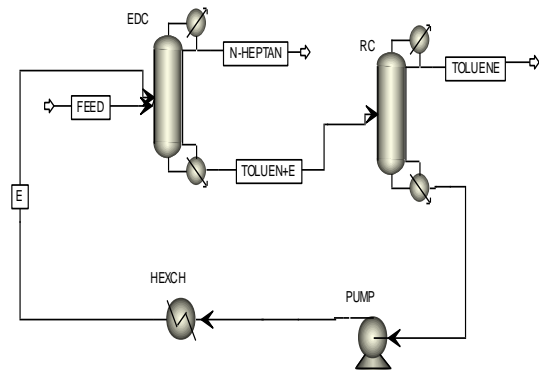
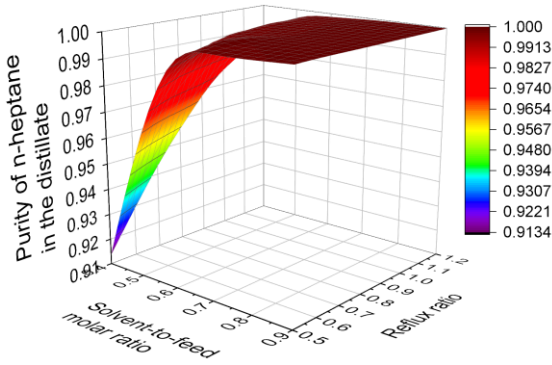


Figure 3. Extractive distillation process flowsheet for separating n-heptane from toluene using either sulfolane or [4EMPy] [NTF₂] as an entrainer

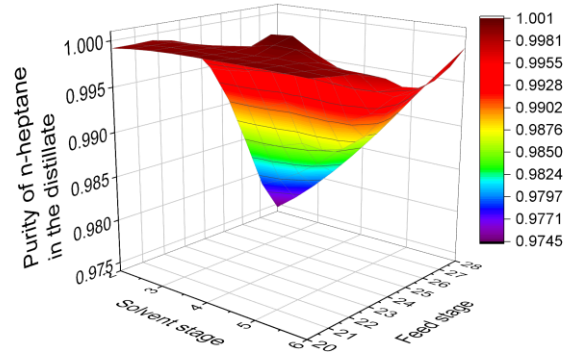
1) *Sensitivity analysis of extractive distillation column using sulfolane and [4EMPy] [NTF₂] as solvents*

3.2.1.1 *Effect of solvent-to-feed molar ratio and reflux ratio on the n-heptane purity*

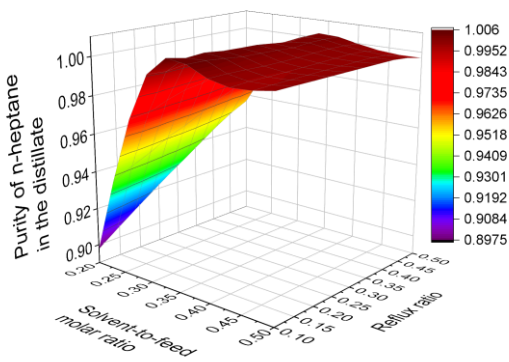
The reboiler heat duty as a function of the solvent-to-feed molar ratio and reflux ratio at fixed purity of n-heptane is represented in Fig. 6 (a) and (b). It was shown that the reboiler duty is proportional to both solvent rate and reflux ratio. The best operating parameters of F_E/F and R are determined by minimizing the energy consumed in the reboiler (Q_R) of the extractive distillation column.



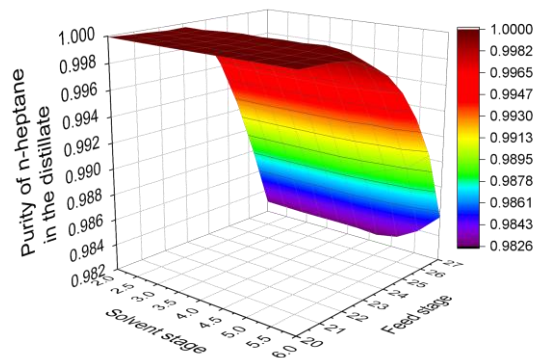
(a)



(a)



(b)



(b)

Figure 4. Effect of solvent-to-feed molar ratio and reflux ratio on the n-heptane purity in the distillate using Sulfolane (a) and [4EMPy] [NTF₂] (b)

Figure 5. Effect of solvent stage and feed stage on the n-heptane purity in the distillate using Sulfolane (a) and [4EMPy] [NTF₂] (b)

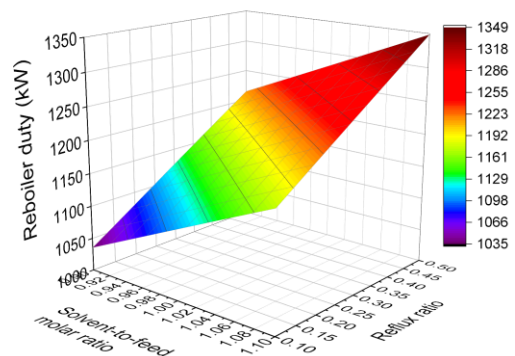
b) Effect of the solvent feed stage and the main feed stage on the n-heptane purity

The effects of solvent feed stage and feed stage of initial mixture on the purity of n-heptane in the distillate using sulfolane and [4EMPy] [NTF₂] are represented in Fig. 5 (a) and (b). We notice from Fig. 5 (a) that the high purity of n-heptane can be reached in column with extractive sections of 17, 16, 15 and 14 stages. It can be noted from this analysis that the minimum and the maximum number of stage in the extractive section allowing to obtain a purity higher than 99.9 mol. % using sulfolane are 14 and 17 stages respectively, the best feed stage is N_F=20 and the entrainer stage can be chosen from 3 to 6 stages from the top of the column.

When using the ionic liquid [4EMPy] [NTF₂] (Fig. 5 (a)), the purity of n-heptane reaches its maximum for the entrainer feed stage from 2 to 6, and mixture feed stage from 20 to 22. This means that the minimum and the maximum number of stage in the extractive section to achieve purity greater than 99.9 mol. % are 14 and 19 stages respectively.

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

The reboiler heat duty as a function of the solvent-to-feed molar ratio and reflux ratio at fixed purity of n-heptane is represented in Fig. 6 (a) and (b). It was shown that the reboiler duty is proportional to both solvent rate and reflux ratio. The best operating parameters of F_E/F and R are determined by minimizing the energy consumed in the reboiler (Q_R) of the extractive distillation column.



(a)

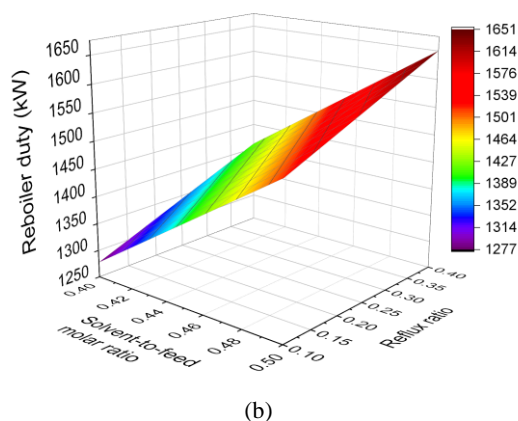


Figure 6. Effect of the solvent-to-feed molar ratio and the reflux ratio on the reboiler duty using sulfolane (a) and [4EMPy] [NTF₂] (b)

2) Design parameters for the extractive distillation column using sulfolane and [4EMPy] [NTF₂]

The best operating parameters for the extractive distillation column were determined by the sensitivity analysis for a feed containing 50 mol. % of n-heptane to recover n-heptane in the distillate with a high purity of 99.97 mol. %. The total number of stages was fixed to 30 stages. The operating parameters of the extractive distillation column using sulfolane and [4EMPy] [NTF₂] are displayed in Tab.3.

Table 3. Design parameters of the extractive distillation column using Sulfolane and [4EMPy] [NTF₂]

Parameters	Solvent	
	Sulfolane	[4EMPy][NTF ₂]
Number of stages	30	30
N _E	5	3
N _F	22	20
F _E /F	1	0.33
R	0.2	0.06
n-heptane purity in mol. %	99.97	99.97
Q _R (kW)	1149.53	1078.55
Bottom temperature (°C)	123.38	133.13

For the both solvents sulfolane and [4EMPy] [NTF₂], the separation requires 17 stages in the extractive section to get a purity of n-heptane of 99.97% in the distillate for the same total number of stages of the extractive distillation column. In addition, [4EMPy] [NTF₂] needs less stages in the rectifying section compared to sulfolane and more stages for the stripping section, this means that the separation of n-heptane from toluene is easy when using the ionic liquid and that the affinity of [4EMPy] [NTF₂] for toluene is higher than that of sulfolane. It is also noted that the extractive distillation column using [4EMPy] [NTF₂] consumed less solvent flow rate for low reflux ratio and is less energy consuming.

3) Design parameters for the regeneration column using sulfolane and [4EMPy] [NTF₂]

The separation of toluene from the solvent was achieved in a distillation column. The pressure of the regeneration column of sulfolane was set to 1 atm, however, the [4EMPy] [NTF₂] ionic liquid is regenerated at a vacuum pressure to avoid decomposition of the ionic liquid [9]. The thermal decomposition temperature for

the pyridinium ionic liquids is between 510-720 K, according to Jacob and al. The decomposition temperature of the used IL is not mentioned, nevertheless, it may be equal to or slightly less than the [BMPy] [NTF₂] which is 670 K [13], for this purpose, the bottom temperature of the regeneration column using [4EMPy] [NTF₂] should not exceed 396.85 °C. The operating parameters of the regeneration column using sulfolane and [4EMPy] [NTF₂] are represented in Tab. 4.

Table 4. Design parameters of the solvent regeneration column using Sulfolane and [4EMPy] [NTF₂]

Parameters	Solvent	
	Sulfolane	[4EMPy][NTF ₂]
Pressure (bar)	1.013	0.1
Number of stages	6	4
Feed stage	3	3
R	0.4	0.12
Solvent purity in mol. %	99.97	99.97
Q _R (kW)	1650.41	1597.07
Bottom temperature (°C)	286.26	323.48

It can be seen from Tab. 4, that the separation of toluene from the ionic liquid [4EMPy] [NTF₂] to be regenerated required less number of stages, reflux ratio and less energy consumption compared to sulfolane to get the same solvent purity.

IV. CONCLUSION

In this work, the extractive distillation process for the separation of n-heptane-toluene mixture using [4EMPy] [NTF₂] ionic liquid and sulfolane was investigated. The vapor-liquid equilibrium of the n-heptane-toluene close boiling point mixture in the presence of different concentrations of solvent was calculated by the NRTL model using Aspen plus software. The binary interaction parameters of the model were regressed from the VLE experimental data.

The thermodynamic study show that the ionic liquid [4EMPy] [NTF₂] have a high selectivity for toluene compared to sulfolane. Furthermore, this ionic liquid is more efficient for n-heptane-toluene separation comparing to sulfolane because it increases the relative volatility of n-heptane even at low amounts

The rigorous simulation of the extractive distillation process shows that the extractive distillation column using [4EMPy] [NTF₂] requires lower values of solvent-to-feed molar ratio and reflux molar ratio compared to sulfolane to get a high purity of 99.97 mol. % of n-heptane.

Finally, we conclude that extractive distillation using the ionic liquid [4EMPy] [NTF₂] is feasible and even very advantageous compared to the conventional process using sulfolane, as well as, the solvent flow rate and the overall energy consumption using the ionic liquid [4EMPy] [NTF₂] can be reduced up to 67% and 4.44% respectively. Thereby, extractive distillation using ionic liquids can be considered as a potential energy saving technology for separating a close-boiling point mixtures if a suitable ILs with a high selectivity are chosen to replace the organic solvents which are in most cases toxic, more volatile and not easily recyclable.

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