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# Pilot plant study on the extractive distillation of toluene-Methylcyclohexane mixtures using NMP and the ionic liquid [hmim][TCB] as solvents

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## Abstract

The separation of the close-boiling point mixture: toluene – methylcyclohexane can be carried out by extractive distillation using the ionic liquid 1-hexyl-3-methylimidazolium tetracyanoborate ([hmim][TCB]), reported as promising solvent for the separation of this mixture. However, the polar nature of ionic liquids causes the formation of two liquid phases which can be overcome with high solvent-to-feed ratios (S/F) resulting in high liquid phase viscosities that cause mass transfer limitations. Experiments in an extractive distillation pilot plant were performed with the objective of firstly exploring different operating conditions and secondly to compare the mass transfer efficiencies produced by [hmim][TCB] and the reference organic solvent *N*-methyl-2-pyrrolidone. Pure viscosity, density and surface tension data as well as ternary viscosity and density data of toluene –

methylcyclohexane - [hmim][TCB] were measured to compute the mass transfer efficiency. From pilot plant experiments it was found that all the studied operating conditions did not form two-liquid phases. However, the high solvent-to-feed ratios increased the liquid phase viscosities and consequently the use of this ionic liquid produces Height Equivalent to a Theoretical Plates (HETPs) twice as high as the reference solvent NMP causing slightly lower top purities and a longer required distillation column for a required separation.

*Keywords: Extractive distillation, pilot plant, ionic liquids, toluene, methylcyclohexane*

## Nomenclature

$E_{ov}$	Tray efficiency
$HETP$	Height equivalent to a theoretical plate, m
$H_L$	Height of transfer unit in the liquid phase, m
$H_V$	Height of transfer unit in the vapor phase, m
$H_{ov}$	Overall height of transfer unit, m
$k_L$	Liquid side mass transfer coefficient, $m\ s^{-1}$
$k_V$	Vapor side mass transfer coefficient, $m\ s^{-1}$
$\bar{k}$	Average mass transfer coefficient, $m\ s^{-1}$
$N'_L$	Number of transfer units in the liquid phase

$N_v$	Number of transfer units in the vapour phase
$N_{ov}$	Overall number of transfer units
$T$	Temperature, K
$u_L$	Superficial velocity of liquid, $\text{m s}^{-1}$
$u_v$	Superficial velocity of vapor, $\text{m s}^{-1}$

### **Greek letters**

$\alpha$	Relative volatility
$\Lambda$	Stripping factor
$\eta$	Dynamic viscosity, $\text{mPa s}$
$\sigma$	Surface tension, $\text{mN m}^{-1}$
$\delta$	Chilton – Colburn averaging parameter

## 1 Introduction

In the petrochemical industry, the separation of toluene and methylcyclohexane is challenging by normal fractional distillation due to the proximity of their boiling points. Extractive Distillation (ED) is used to efficiently separate this complex mixture by means of adding a high boiling point solvent at the top of the column which is commonly of an organic nature. These organic solvents show several drawbacks such as flammability, high toxicity and high volatility which results in solvent losses. Additionally, they are required in large amounts to achieve a proper separation. The normally used solvent to separate this mixture is *N*-methyl-2-pyrrolidone (NMP) [1]. Recently, several studies regarding ionic liquids (ILs) as replacement of conventional organic solvents have been published [2-8] due to their excellent properties such as negligible vapor pressure and high selectivity. The ionic liquid **1-hexyl-3-methylimidazolium tetracyanoborate ([hmim][TCB])** has been proposed as a novel solvent for this mixture [9] as the produced relative volatilities are around three times higher than the currently used organic solvent NMP. To our knowledge, no other ionic liquid has been proposed to separate this mixture by ED.

Nevertheless, high viscosity is an important disadvantage of ILs when used as solvents because this could bring a decrease in mass transfer efficiency. In our previous studies [2,10] the decrease in mass transfer efficiency with solvent viscosity in ED using ionic liquids has been studied for the water – ethanol mixture.

Besides that, the separation of this mixture with [hmim][TCB] as solvent is challenging because the IL shows limited solubility in the toluene –

methylcyclohexane mixture [9] and the formation of two liquid phases becomes an issue. This is caused by the mixing of an ionic liquids which is of polar nature with a nonpolar mixture. To overcome the formation of two liquid phases high solvent-to-feed (S/F) ratios are required, which would cause a significant increase of the liquid phase viscosity, result in mass transfer limitations and finally yield a longer ED column to achieve the desired purity. In our previous study [10], pilot plant tests were successfully used to evaluate the mass transfer efficiency decrease with the increase of liquid-phase viscosities. Therefore, comparisons of the mass transfer efficiency performance between NMP and [hmim][TCB] in the ED of toluene – methylcyclohexane mixture can be carried out using pilot plant experiments.

Thus, the objective of this work is to compare the produced mass transfer efficiencies of two solvents: NMP and [hmim][TCB] in the extractive distillation of toluene – methylcyclohexane mixtures in an pilot plant equipped with Mellapak<sup>®</sup> 750Y structured packing at several operating conditions (continuous operation) that allow to have one liquid phase. To achieve this, the physical and transport properties: density, viscosity and surface tension are measured for pure [hmim][TCB] as well as density and viscosity of the ternary mixture, all at various temperatures. Next, the liquid phase resistances when using both solvents are quantified by calculating the height of transfer units and distribution ratios. Finally, in this work the mass transfer efficiency is characterized through the Height Equivalent to a Theoretical Plate (HETP) obtained under these challenging operating conditions. To our knowledge, this is the first study where the performance of

this new promising ionic liquid is studied in a pilot plant and for this aromatic – aliphatic mixture.

### 1.1 Background of toluene – methylcyclohexane separation with [hmim][TCB]

Table 1 shows the produced relative volatilities by both solvents. It is observed that [hmim][TCB] produces three times higher relative volatilities than the reference solvent. On the other hand, the separation of toluene – methylcyclohexane using [hmim][TCB] requires operating parameters to avoid the two-phase region as mentioned above.

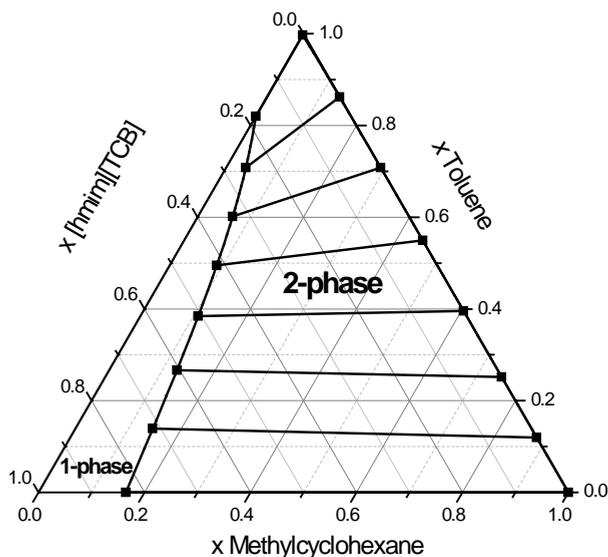
**Table 1.** Relative volatilities at a S/F in mass basis obtained by the use of different solvent and calculated at 70% w/w toluene<sup>a</sup>.

$\alpha$			
Solvent	S/F = 5	Model	Source of binary parameters
NMP	2.83	NRTL	ASPEN <sup>®</sup> Plus
[hmim][TCB]	9.42	UNIQUAC	[9]

<sup>a</sup> This concentration falls into the one-phase region in Figure 1

Figure 1 shows in a ternary diagram the single and two liquid phase regions. The polar nature of this ionic liquid causes a poor solubility in the aliphatic – aromatic mixture. The solubility of methylcyclohexane in [hmim][TCB] is limited to a mole fraction of 0.16 while the toluene solubility in [hmim][TCB] is 0.82 at the indicated temperature. The temperature does not have a significant influence on the solubility for this

system [9]. Figure 1 indicates that to reach the single liquid phase region, first high S/F ratios and second low reflux ratios are required due to the strongly increased relative volatility. The latter is to overcome the poor solubility of [hmim][TCB] in methylcyclohexane in comparison to toluene. Having two liquid phases inside the ED column would lead to column instability because the solvent has to mix with toluene and methylcyclohexane to increase the relative volatility. Besides that, if the operation exceeds the miscibility limit, the solvent will not produce the expected effect and it will increase the liquid holdup inside the column causing flooding or a drop in capacity. [11]



**Figure 1.** Ternary diagram for the system Toluene – Methylcyclohexane – [hmim][TCB] at the equilibrium temperature. Concentrations are expressed in mole fractions.

On the other hand, these high S/F ratios will certainly cause increased viscosities inside the ED column resulting in a reduction of the mass transfer efficiency. However, in our previous works [2,10] we have concluded that the viscosity of the solvents does not affect the mass transfer efficiency of the extractive distillation process as long as the solvent produces sufficiently high relative volatilities. Therefore, overall, an improved mass transfer efficiency is expected when using [hmim][TCB].

## 2 Experimental

### 2.1 Materials

For the pilot plant tests, pure toluene and methylcyclohexane were purchased to prepare the feed stream. 1-hexyl-3-methylimidazolium tetracyanoborate was obtained from Merck GmbH ( $\geq 98\%$ ) and used without further purification. *N*-methyl-2-pyrrolidone was purchased from Applichem GmbH ( $\geq 98\%$ ) and used without further purification. For the analysis of the liquid samples taken from the pilot plant and the determination of viscosity and surface tension, analytical grade chemicals were used. Toluene was purchased from Sigma Aldrich ( $\geq 99.8\%$ ). For the Gas Chromatography analysis analytical grade acetone (99.9 %) as diluent and ethylbenzene (99.9 %) as internal standard were used. For the density, viscosity and surface tension measurements analytical grade chemicals were used. Toluene was purchased from Sigma-Aldrich ( $\geq 99.9\%$ ) and

methylcyclohexane was purchased from Fluka ( $\geq 98\%$ ). The ionic liquid used in these experiments was the same as above.

## 2.2 Density measurements

To determine dynamic viscosities, density measurements are required. Densities of the pure [hmim][TCB] and the ternary mixture toluene – methylcyclohexane – [hmim][TCB] were measured from 298.15 to 328.15 K using an Anton Paar DMA-5000 densimeter. Samples were prepared in an Erlenmeyer flask with a NS top to minimize the water uptake and filled with ionic liquid, toluene and methylcyclohexane. The reached concentration was obtained for a Mettler Toledo AT200 high precision balance ( $\pm 0.0001$  g). Finally the mixture was stirred for 10 minutes. The measured ternary compositions cover the one liquid phase region where the extractive distillation of this mixture takes place. Density was obtained directly from the densimeter with an accuracy of  $5 \times 10^{-6} \text{ g} \cdot \text{cm}^{-3}$ . A complete description of the density measurements is given elsewhere [12,13].

## 2.3 Viscosity measurements

The kinematic viscosity of the pure [hmim][TCB] and the ternary system toluene – methylcyclohexane – [hmim][TCB] were measured from 298.15 to 328.15 K with an automatic and PC-controlled viscosimeter Lauda iVisc with

Ubbelohde capillary viscometers from Schott (DIN). Three capillary diameters were used: 0.84, 0.95 and 1.13 mm (referenced at Schott-Geräte GmbH). The dynamic viscosity of the ternary system toluene – methylcyclohexane – NMP was not measured since this organic solvent is not viscous and the ternary viscosity can be obtained using a mole-average mixing rule without losing accuracy. The accuracy of the viscosity measurements was 0.2%. Details of the viscosity measurements can be found elsewhere [12,13].

#### **2.4 Surface tension measurements**

The surface tension of [hmim][TCB] was measured at 298.15 K with a Kruss K11 tensiometer using a ring of 9.545 mm radius certified by Kruss GmbH. The equipment resolution is 0.1 mN/m and 0.1 K. The surface tension was measured three times with a reproducibility of 2%. Additional details of the experimental procedure can be found elsewhere [12].

#### **2.5 The pilot plant and operating conditions**

The extractive distillation column used for this study is schematically shown in **Figure 2**. This column contains Mellapak<sup>®</sup> 750Y structured packing provided by Sulzer<sup>®</sup> as separating media. The column is equipped with an electrical thermosyphon reboiler, a vertical condenser with an internal funnel which provides reflux and finally three liquid distributors for avoiding maldistribution. Two feed lines provide the column with solvent and toluene – methylcyclohexane mixture. Additionally, to measure the concentration

profiles and the liquid-phase temperatures, six liquid circular collector basins are installed inside the packing whose collect liquid and allow inserting thermocouples. Furthermore, liquid samples can be withdrawn at the distillate stream and at the reboiler. Additional information about the pilot plant can be found elsewhere [10].

The pilot plant is operated in continuous mode and to maintain the ED pilot plant running in the miscible region is necessary to know the operating conditions beforehand. By using the equilibrium model in ASPEN<sup>®</sup> Plus Radfrac with UNIQUAC parameters from literature it is possible to estimate suitable process parameters, which are listed in Table 2. As observed from Table 2 only one S/F ratio is studied because a further increase of this parameter appeared to make the pilot plant very difficult to operate and by reducing S/F the liquid-liquid immiscibility region would be entered. It is worth noting that, equilibrium calculations are insufficient to represent the real process of this pilot plant since they do not take into account the heat and mass transfer limitations.

**Table 2.** Operating conditions

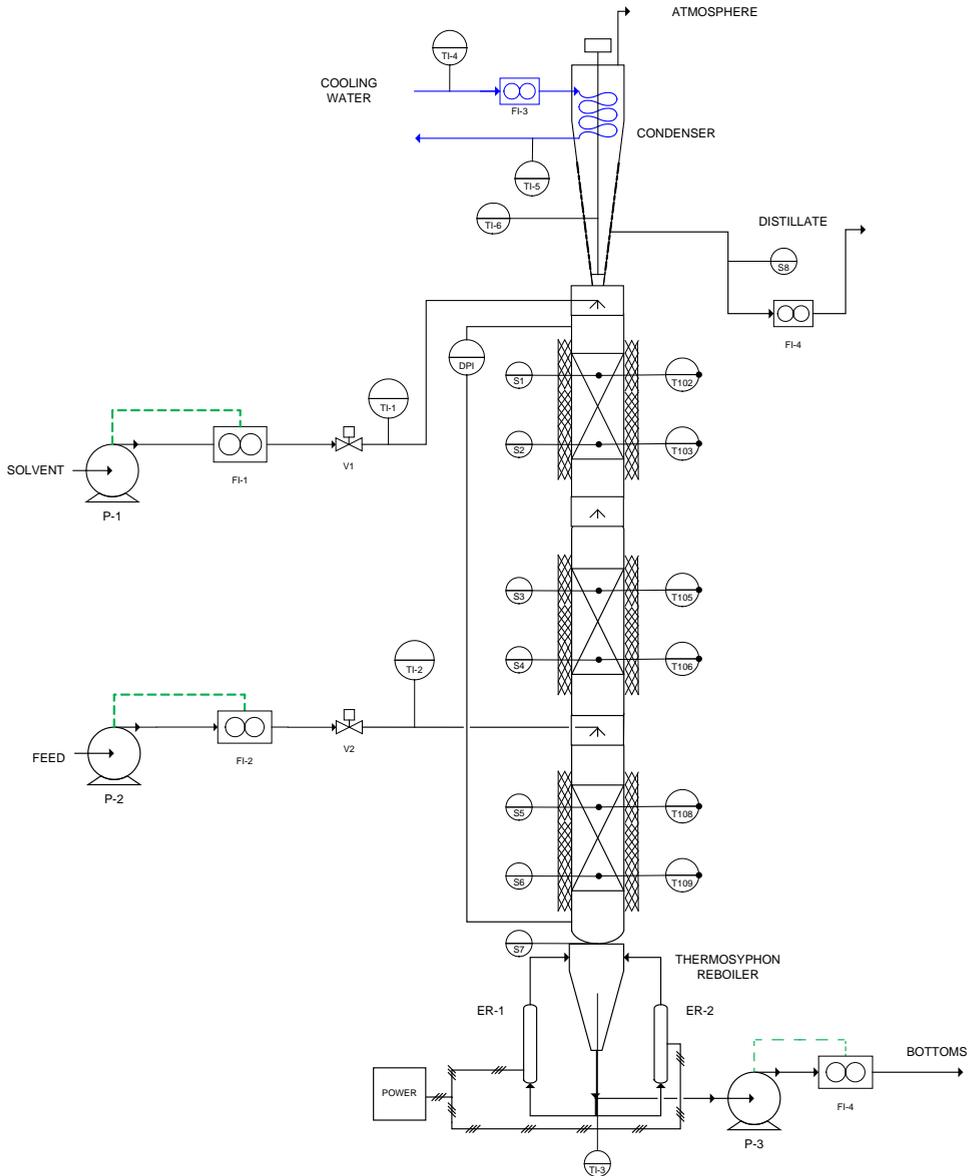
Variable	Value
Feed flow rate [kg h <sup>-1</sup> ]	2
Toluene concentration at feed [wt%]	70
Feed temperature [°C]	90
Solvent temperature [°C]	100
Solvent-to-feed ratio (mass)	5

Case studies	Solvent	Reboiler duty [kW] <sup>a</sup>	Distillate rate [kg h <sup>-1</sup> ]
Case I.a	NMP	50%	0.3
Case I.b	[hmim][TCB]	50%	0.3

Case II	[hmim][TCB]	50%	0.6
Case III	[hmim][TCB]	30%	0.3

<sup>a</sup> 100% = 2.04 [kW]



**Figure 2.** Scheme of the extractive distillation pilot plant.

## **2.6 Analysis of the samples taken from the pilot plant**

After the pilot plant reaches steady state (approximately 1 hour), a small volume (~ 0.5 ml) of liquid sample was taken out of the collector basins, reboiler and condenser using a glass syringe in order to not disturb the compositions profiles inside the column. These liquid samples were stored in Gas Chromatography (GC) vials and analyzed after allowing them to cool down to room temperature. To determine the toluene and methylcyclohexane content in the sample, GC analysis was used. 0.1 ml of sample was mixed with 0.05 ml of ethylbenzene (internal standard) and 1 ml of acetone as a diluent. The analyses of the samples were carried out with a Varian 430 gas chromatograph equipped with a Supelco Nukol<sup>®</sup> Fused silica capillary column (50 m x 0.32 mm x 0.45 mm). After sample injection, the ionic liquid is collected in a cup-liner in order to not disrupt the analysis [14,15]. The GC analyses were carried out in triplicate. The variation of the GC analysis is <2% and the inaccuracy <2%. Since the ionic liquid could not be analyzed in a GC, the concentration is determined by a mass balance.

## **2.7 Mass transfer efficiency evaluation**

The mass transfer efficiency in a packed column is expressed by the Height Equivalent to a Theoretical Plate:

$$HETP = H_{OV} \frac{\ln(\Lambda)}{\Lambda - 1} \quad 1$$

where the overall height of a transfer unit is calculated as:

$$H_{OV} = H_V + \Lambda H_L \quad 2$$

which is composed of the height of a transfer unit in the vapor phase,  $H_V$  and the height of a transfer unit in the liquid phase,  $H_L$  by the stripping factor,  $\Lambda$ . Both originate from the resistance. The height of the transfer units is defined as:

$$H_L = \frac{u_L}{k_L a} \quad 3$$

$$H_V = \frac{u_V}{k_V a} \quad 4$$

where,  $k_L$  and  $k_V$  are the binary mass transfer coefficients in the liquid and vapor phase respectively. Equations 1 through 4 are the basis for the comparisons between both solvents. The mass transfer coefficients are calculated using correlations for structured packing which in turn require physical and transport properties. Previously, it was established that liquid viscosities, surface tension and infinite dilution diffusion coefficients have to be accurately provided to use the mass transfer correlations when using ionic

liquids [10]. However, the transport properties can be predicted by means of Wilke-Chang model without losing accuracy in the mass transfer calculations.

The Bravo et al [16] mass transfer correlation has been chosen. The main assumption in this correlation is that the surface provided by the packing is completely wetted and the change of interfacial area for mass transfer as function of surface tension is not considered. For aqueous systems, this assumption brings large deviations as demonstrated previously [10]. However, in this work, the components of the ternary mixture have relatively low surface tensions that would enhance the degree of wetting of the packing surface approaching to the complete wetting. Several studies confirm this fact. For instance Tsai et al. [17] measured the changes in effective area with surface tension in chemical absorption using Mellapak® 250Y and 500Y. Reductions in surface tension of the system enhance the effective area for mass transfer. Additionally, Ataki and Bart [18] determined that viscosity exhibits an effect on degree of wetting of Rombopak® structured packing. Highly viscous forces increase the degree of wetting of the packing surface. For these reasons it is considered a valid approach to estimate the mass transfer in this low surface tension and viscous system by the Bravo et al. [16] mass transfer correlation.

### **2.7.1 Computation of the *HETP* values**

The mass transfer efficiency (*HETP*) in this work is determined from the liquid phase compositions and liquid temperatures obtained directly from the pilot plant. Additional information such as liquid and vapor molar flow rates

are obtained from equilibrium simulations in ASPEN Plus<sup>®</sup>. The method to calculate the *HETP* value is extensively described elsewhere [19].

Firstly, using the experimental liquid phase compositions and temperatures, it is possible to calculate the physical and transport properties at the liquid phase required by the Bravo et al. [16] mass transfer correlation which are ternary viscosities, densities and the binary diffusion coefficients. The first two properties are obtained by using the models presented here. The diffusion coefficients at infinite dilution are predicted by means of Wilke-Chang equation and then the binary diffusion coefficients in the ternary mixture are calculated by the Kooijmann – Taylor mixing rule [20] .

Next, to calculate the binary mass transfer coefficients at the liquid phase, the previously calculated diffusion coefficients are required. Besides that, the information regarding to the packing geometry has to be provided. These are, total surface area (Mellapack<sup>®</sup> 750 Y), equivalent diameter and the packing perimeter. Additionally, the liquid velocity through the packing is calculated using the liquid molar flow rate. With all this information, the binary mass transfer coefficients can be determined as described in Bravo et al. [16].

At the vapor phase, the toluene – methylcyclohexane – solvent concentrations are determined by means of bubble point calculations using thermodynamic parameters obtained from literature [9]. From those points, it is possible to calculate binary diffusion coefficients through the Wilke – Lee equation [21]. The vapor velocity is calculated from the vapor molar flow

rates obtained previously and thus it is possible to calculate the binary mass transfer coefficients.

Since this is a ternary mixture, three binary diffusion coefficients at the liquid and three at the vapor phase are obtained from the above calculations. These coefficients lead to three *HETP* profiles per solvent. In order to provide better understanding in the comparisons between the ionic liquid [hmim][TCB] and the reference solvent NMP only one *HETP* profile per solvent should be calculated. Therefore, average mass transfer coefficients  $\bar{k}$  are obtained using a Chilton-Colburn averaging parameter as follows:

$$\bar{k} = \frac{\sum_{i=1}^{nc-1} \sum_{j=i+1}^{nc} (x_i + \delta) (x_j + \delta) k_{ij}}{(x_i + \delta)(x_j + \delta)} \quad 5$$

Where,  $x$  is the molar fraction,  $k_{ij}$  is the binary mass transfer coefficient at the liquid or vapor phase and the averaging parameter  $\delta$  is kept as default at  $10^{-4}$ . With this, liquid and vapor height of transfer unit are obtained. Finally, using the mole fractions in the liquid and vapor phase and the liquid and vapor molar flow rates, the stripping factor ( $\Lambda$ ) required in equation 1 is obtained. This gives directly the *HETP* from equation 1.

### 3 Results

#### 3.1 Analysis of the experimental density, viscosity and surface tension measurements

The measured density values are presented in **Tables 3** and 4 for the pure [hmim][TCB] and the ternary mixture respectively. Values of the pure [hmim][TCB] are compared with data of NMP data from literature.

**Table 3.** Densities ( $\rho$ ) and viscosities ( $\eta$ ) as function of temperature of the pure solvents.

$T$ [K]	$\rho$ [g cm <sup>-3</sup> ]		$\eta$ [mPa s]	
	NMP <sup>a</sup>	[hmim][TCB]	NMP <sup>a</sup>	[hmim][TCB]
298.15		0.9905		47.83
303.15	1.0234	0.9869	1.51	37.42
308.15	1.0193	0.9833	1.41	29.89
313.15	1.0148	0.9797	1.33	24.33
318.15	1.0101	0.9762	1.21	20.11
323.15		0.9726		16.89
328.15		0.9691		14.28
333.15		0.9656		12.30
338.15		0.9622		10.68
343.15		0.9587		9.34

<sup>a</sup> Values obtained from Ref.[22]

It is observed that, the densities of the pure ionic liquids are not much different from the reference organic solvent. On the other hand, **Table 3** shows that the pure [hmim][TCB] viscosity is around 25 times higher than the organic solvent at  $T = 298.15$  K and at higher temperatures this ratio reduces to around 10. **As a result, the mixture liquid phase viscosity is higher when using the ionic liquid compared to that using NMP as solvent, which is observed by the ternary viscosity data presented in Table 4.**

**Table 4.** Densities,  $\rho$  [ $\text{g cm}^{-3}$ ], and dynamic viscosities,  $\eta$  [mPas], of the ternary mixture toluene(1) – methylcyclohexane (2) - [hmim][TCB](3) at several temperatures.

$x_1$	$x_2$	$T = 298.15 \text{ K}$		$T = 308.15 \text{ K}$		$T = 318.15 \text{ K}$		$T = 328.15 \text{ K}$	
		$\rho$	$\eta$	$\rho$	$\eta$	$\rho$	$\eta$	$\rho$	$\eta$
0.6042	0.0251	0.9497	7.317	0.9424	5.590	0.9348	4.411	0.9274	3.596
0.4855	0.0439	0.9580	11.089	0.9506	8.151	0.9433	6.251	0.9359	4.953
0.0392	0.1279	0.9759	36.245	0.9688	23.506	0.9617	16.290	0.9546	11.857
0.2784	0.0859	0.9690	19.837	0.9618	13.733	0.9546	10.054	0.9475	7.698
0.0000	0.1074	0.9818	41.252	0.9746	26.395	0.9676	18.053	0.9605	13.040

Secondly, surface tension data is necessary to demonstrate the validity of using the Bravo et al. [16] mass transfer coefficient. To our knowledge no surface tension data has been published before for [hmim][TCB]. Table 5 gives the obtained surface tension for [hmim][TCB]. It is observed that the measured surface tension of [hmim][TCB] is slightly higher than the reference solvent NMP. Therefore, no differences in mass transfer efficiency are expected to originate from this physical property. Besides that, the surface tension of this ionic liquid is lower than that of water, which confirms that the IL would yield a higher degree of packing surface wetting. Therefore, the Bravo et al. mass transfer coefficient can be used to determine mass transfer efficiency.

**Table 5.** Pure component surface tension at  $T = 298.15 \text{ K}$

Component	$\sigma$ [mN m]
Toluene	27.76 <sup>a</sup>
Methylcyclohexane	23.29 <sup>b</sup>
NMP	40.06 <sup>c</sup>
[hmim][TCB]	40.3 <sup>d</sup> $\pm$ 0.1 <sup>e</sup>

<sup>a</sup> Values obtained from literature at  $T = 297.76 \pm 0.05 \text{ K}$  [23].

<sup>b</sup> Values obtained from literature at  $T = 298.15\text{K}$  [24]

<sup>c</sup> Values obtained from literature  $T = 297.76 \pm 0.05\text{K}$  [23].

<sup>d</sup> Measured in this work. Measuring temperature  $T = 296.12$  <sup>a</sup> Values obtained from literature <sup>c</sup>

<sup>e</sup> Standard deviation.

### *Correlation of the experimental viscosity data*

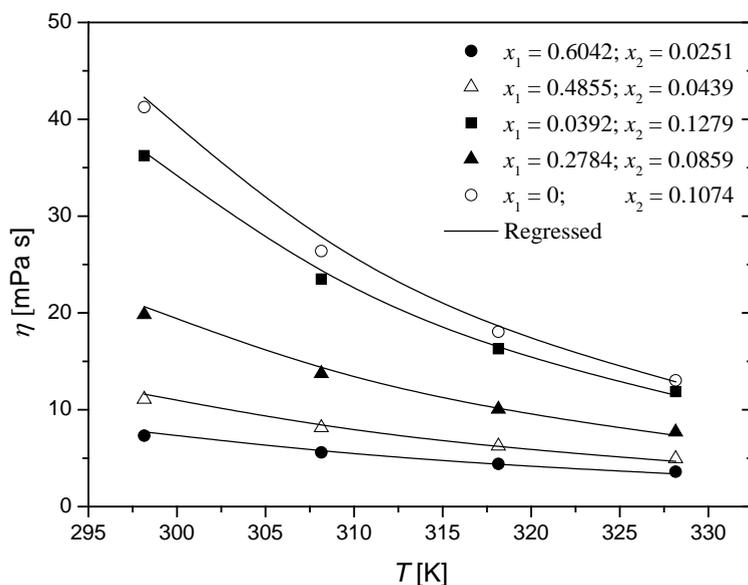
To calculate ternary viscosity as function of any ternary concentration and temperature, a model is necessary. The Eyring-Patel-Teja model was used to correlate the experimental data [25]. The model needs of parameters that are obtained by regressing experimental data and minimizing the relative difference between the experimental data and the calculated value. **A Margules type mixing rule (GM2)** in combination with the mentioned model are used to correlate de experimental data [13]. The obtained parameters are given in **Table 6**.

**Table 6.** Parameters obtained from experimental data regression  $l_{i,j}$  in Eyring-Patel-Teja model.

Interaction parameter	GM2
$l_{12}$	0
$l_{21}$	0.8071
$l_{13}$	0.1462
$l_{31}$	0.0077
$l_{23}$	0.6531
$l_{32}$	-0.3519
$\%ADD^a$	2.54

$$^a \text{ ADD [\%]} = 100/n_{\text{exp}} \sum_{i=1}^{n_{\text{exp}}} |\eta_{\text{mix,exp}} - \eta_{\text{mix,calc}}| / \eta_{\text{mix,exp}}$$

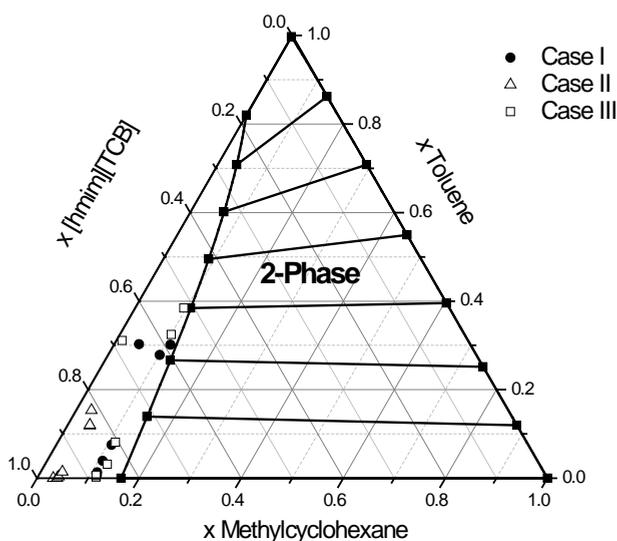
Figure 3 shows the experimental and regressed ternary dynamic viscosities as function of temperature. It is observed that the Model represents the changes in viscosity as function of concentration and temperature well. The average deviation is below 3%. This model along with the regresses parameters from Table 6 are used to calculate the viscosities inside the column once the compositions are determined.



**Figure 3.** Regression of the experimental data of ( $x_1$  toluene +  $x_2$  methylcyclohexane +  $x_3$ [hmm][TCB]) with the Eyring-Patel-Teja model between  $T = 298.15$  K and  $T = 328.15$  K.

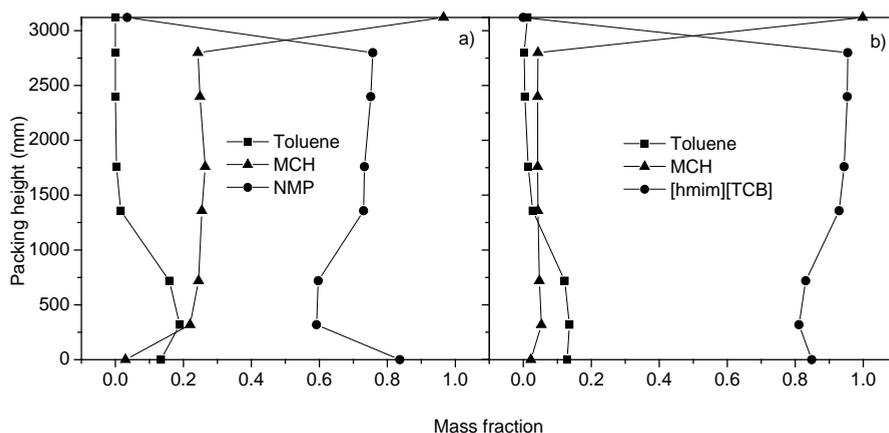
### 3.2 Experimental pilot plant profiles

Figure 4 shows the ternary diagram containing the experimental concentration profiles along the ED pilot-plant for the runs with [hmim][TCB] as solvent. In this figure is demonstrated that the proposed experimental conditions allowed the operation of the ED pilot-plant in the one-phase region. From all the experimental cases given in Table 2, Case II is the farthest away from the two phase boundary because more vapor of methylcyclohexane is withdrawn from the column when increasing the distillate rate decreasing the methylcyclohexane concentration over the column.

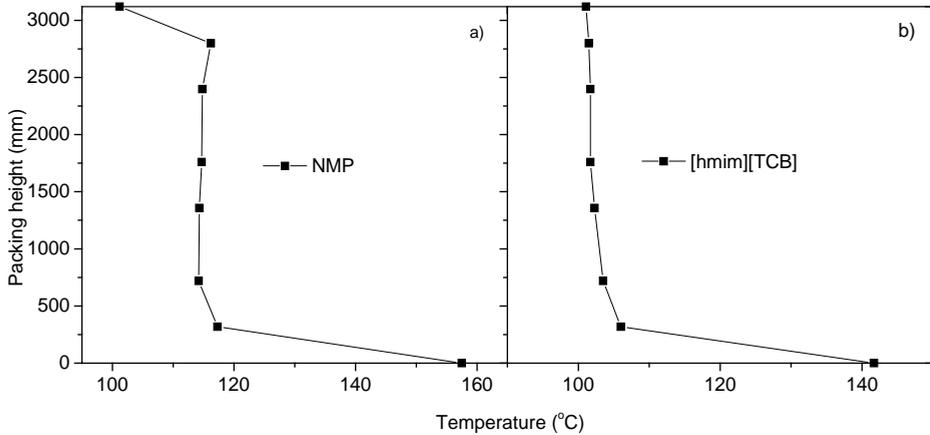


**Figure 4.** Experimental concentration profiles located inside the ternary diagram. Concentrations are expressed in mole fractions.

Figures 5 to 8 show the experimentally obtained concentration and temperature profiles over the column at the respective operating conditions shown in Table 2. First, NMP and [hmim][TCB] are compared (cases I.a and I.b respectively). Figure 5 and 6 show the concentration and temperature profiles respectively. As a consequence of  $S/F = 5$ , high (60-90 wt%) solvent concentrations are observed in Figure 5 for both cases I.a and I.b. This produces a viscous liquid phase inside the column. Differences between solvents are observed in the solvent concentration where [hmim][TCB] is present in even higher concentrations than NMP due to its negligible vapor pressure. For both cases, the toluene concentration is very low in the two concentration points below the condenser.



**Figure 5.** Concentration profiles (mass fractions) for the ED of toluene – methylcyclohexane using a) NMP (case I.a) and b) [hmim][TCB] (case I.b) as solvents. The operating conditions are detailed in Table 2.

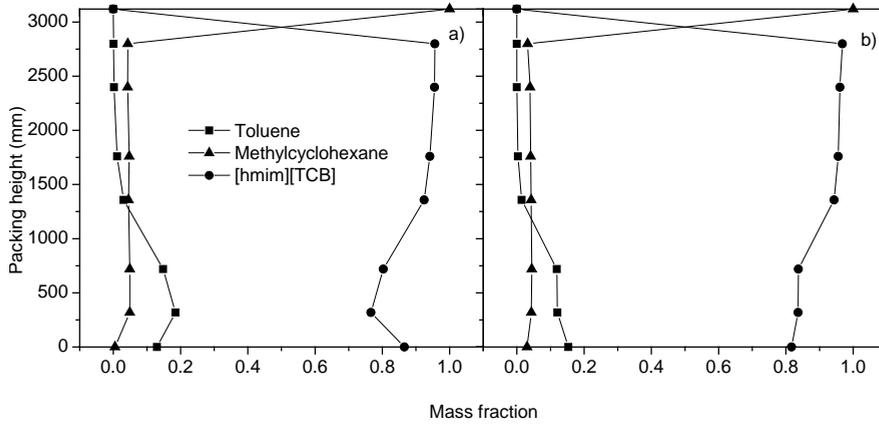


**Figure 6.** Experimental temperature profiles obtained from the pilot plant for the ED of toluene – methylcyclohexane using a) NMP (case I.a) and b) [hmim][TCB] (case I.b) as solvents.

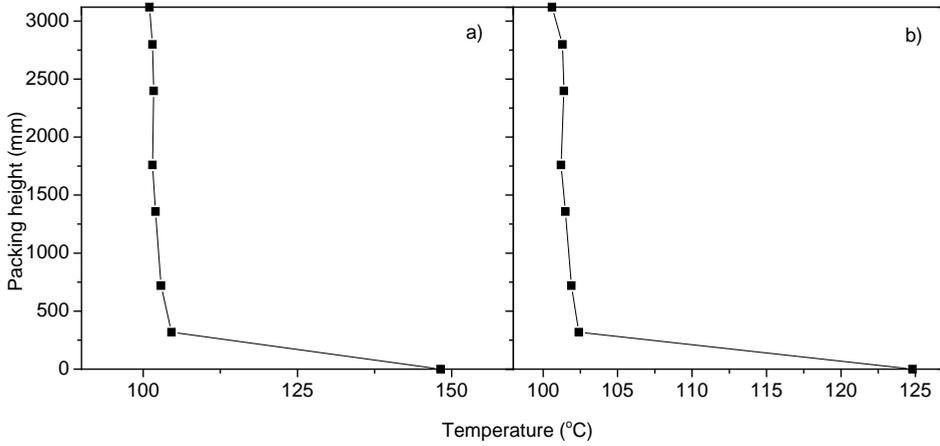
Figure 6 shows the temperature profiles over the column for both solvents. As expected, higher temperatures are obtained when applying NMP. This is because NMP is partially vaporized and its boiling point influences the temperature profiles. This phenomenon is also observed in our previous work [10] where the profiles containing the ionic liquids showed lower temperatures than those of the conventional solvent ethylene glycol for the separation of ethanol/water.

After these runs, two additional cases are studied to decrease the reflux ratio which is the other important operating parameter. In case II the distillate rate is increased keeping the rest of the operating variables constant. In case III the reboiler duty is reduced to decrease the reflux ratio. However, in both

cases the  $L/V$  ratio is increased influencing the mass transfer efficiency of the process. Figure 7 shows the concentration profiles of a) case II and b) case III. No significant differences are observed between both cases. Here, in both cases the  $L/V$  ratio is increased. Basically, no significant differences are observed in Figure 8 when compared to Figure 5.b. The concentrations profiles are very similar to Case I because the  $S/F$  ratio is the predominant operating variable. However, the differences appear in the temperature profiles. As expected, lower temperatures are obtained when reducing the reboiler duty because less vaporizable liquid passes from the liquid to the vapor phase. This decreases the boiling point of the mixture.



**Figure 7.** Experimental concentration profiles for the ED of toluene – methylcyclohexane obtained from the pilot plant for a) case II and b) case III. The operating conditions are detailed in Table 2.



**Figure 8.** Experimental temperature profiles from the pilot plant for the ED of toluene – methylcyclohexane for a) case II and b) case III. The operating conditions are detailed in Table 2.

### *Top purities*

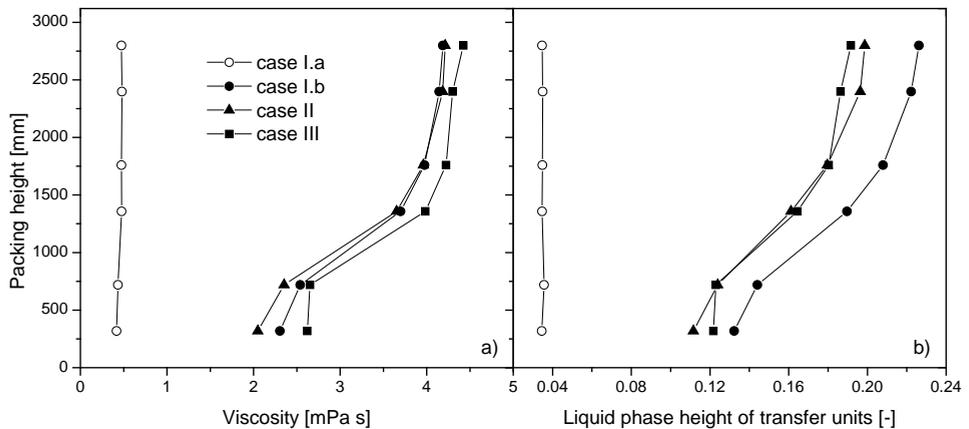
The top purity of the produced methylcyclohexane is compared between NMP and [hmim][TCB] on a solvent-free basis. Table 7 summarizes the top purities for cases I.a, I.b and II. Basically, in all the experimental runs the toluene mass fraction is small, therefore a good separation is achieved. However, slightly better purities are achieved when NMP is used. Even though, the ionic liquid produced higher relative volatilities and thus better separations, this solvent shows higher liquid phase viscosities than NMP since high S/F ratios are required. This latter effect could have a more significant impact on the separation than relative volatilities. This means that, when using [hmim][TCB] as solvent a longer extractive distillation column could be needed to achieve a desired methylcyclohexane purity in spite of the higher produced relative volatilities. Another important point is that, when using [hmim][TCB] no solvent concentrations is obtained at the top of the column because this solvent exhibits no vapor pressure which is one of the advantages of ionic liquids over organic solvents.

**Table 7.** Experimental top purities in a solvent free basis.

Case studies	Solvent	Toluene $w_1$	Methylcyclohexane $w_2$
Case I.a	NMP	0	1
Case I.b	[hmim][TCB]	0,0082	0,9918
Case II	[hmim][TCB]	0,0034	0,9966

## Mass transfer

Figure 9.a and 9.b show the viscosity profiles and the liquid phase height of transfer unit profiles respectively for all four experimental cases. The liquid phase viscosities were calculated from the experimental concentration profiles in the ED pilot plant using the above developed Eyring-Patel-Teja model.

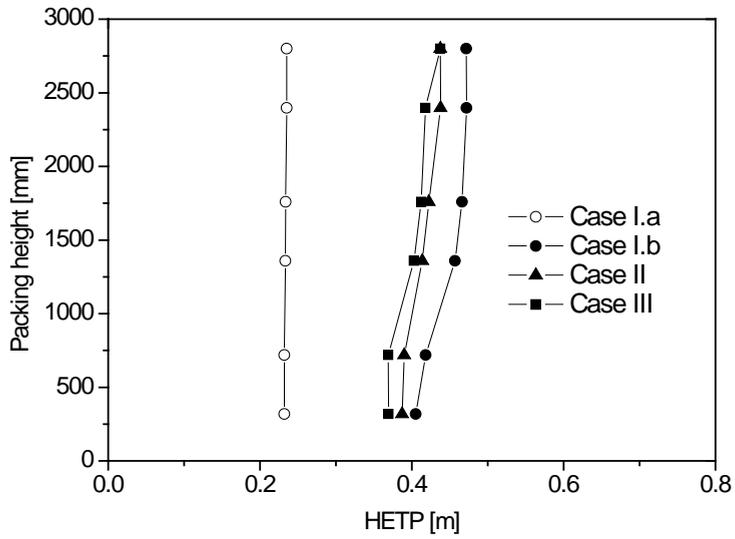


**Figure 9.** Calculated liquid phase viscosity and liquid phase height of transfer unit profiles for the ED of toluene – methylcyclohexane for all the studied cases.

In Figure 9.a, the influence of [hmim][TCB] on the liquid viscosity can be clearly observed. While the separation of the toluene – methylcyclohexane mixture with NMP (Case 1.a) shows low viscosities, the one with [hmim][TCB] exhibits high values reaching 4 mPa s in the rectifying section. This behavior is observed for all the cases where the IL is involved with

small differences between them. Next, the liquid phase height of transfer unit profiles in the liquid phase for all the cases are presented in [Figure 9.b](#). The effect of viscosity on these profiles is clearly noticed since they follow the same trend as [Figure 9.a](#). Case I.b shows the highest values because of the differences in vapor-liquid ratios. The large differences between NMP and the IL in [Figure 9.b](#) illustrate the need to study the mass transfer efficiency profiles in more detail.

Figure 10 shows the calculated *HETP* profiles over the ED pilot plant for all the cases. It can be observed that the effect of the solvent viscosity on the mass transfer efficiency is significant. As previously noticed, the high viscosities produced inside the pilot plant by the high *S/F* ratios when using [hmim][TCB], resulted in a decrease of mass transfer efficiency with regard to the reference solvent NMP even though the use of the IL as solvent produced much higher relative volatilities. As a result the *HETP* when using [hmim][TCB] is about twice as high as the *HETP* when using NMP and this is reflected in the top purities.



**Figure 10.** Calculated *HETP* profiles for the ED of toluene – methylcyclohexane for all studied cases.

## 4 Conclusions

Extractive distillation pilot plant experiments were carried out for evaluating the mass transfer efficiency decrease when using an ionic liquid as solvent for the separation of toluene and methylcyclohexane.

Viscosities of the pure [hmim][TCB] are 25 time higher than the NMP at 298.15K. On the other hands, the densities and the surface tension of [hmim]TCB] are similar to the reference solvent.

In general, all the proposed operating conditions were favorable for the separation of this mixture avoiding the formation of two liquid phases inside the column.

High viscosities were observed as a consequence of the high solvent-to-feed ratios and the viscosity of the ionic liquid.

High solvent-to-feed ratios and low reflux were required to avoid forming two liquid phases leading to attractive relative volatilities ( $\alpha = 9.42$  at S/F ratio 5) and high liquid phase viscosities. The top purities of methylcyclohexane in a solvent free basis are higher than those showed when [hmim][TCB] is used as solvent.

High mass transfer efficiencies were expected due to the high relative volatilities. However, the use of the IL as solvent exhibited lower mass transfer efficiencies for all the studied cases. The *HETPs* when using [hmim][TCB] were almost as twice as high as with NMP.

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