We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Mass Transfer in Extractive Distillation when Using Ionic Liquids as Solvents

Esteban Quijada-Maldonado,
Wytze G. Meidersma and André B. de Haan

Abstract

Mass transfer efficiency study in extractive distillation with ionic liquids for the mixtures water-ethanol and toluene-methylcyclohexane has been carried out in this work. Ionic liquids for the separation of these mixtures overcome the performance of the common volatile organic solvents. However, these also showed higher viscosities. A rated-based analysis was performed in order to quantify the effect of the solvent viscosity and relative volatility on mass transfer efficiency. In addition to this, an experimental analysis of the mass transfer efficiency was carried out experimentally in an extractive distillation pilot plant. The results indicated that, high liquid viscosities of ionic liquids should not affect the mass transfer efficiency negatively if the produced relative volatilities are sufficiently higher than those produced by organic solvents. However, when the ionic liquid showed very high viscosities or this solvent was present in large concentrations inside the column, the mass transfer efficiency decreases no matter how high the relative volatility is.

Keywords: extractive distillation, ionic liquids, rate-based model, mass transfer efficiency

1. Introduction

Azeotropic and close boiling point mixtures cannot be separated by normal fractional distillation. Extractive distillation (ED) is an energy efficient technology that enables the separation of these complex mixtures by using a high boiling point solvent added at the top of the column. With this, the activity coefficients at the liquid phase are modified improving the

relative volatiles. As a result, high purity products are obtained at the top of the distillation column with low energy demand. **Figure 1** depicts a common extractive distillation process including the solvent recovery column.

An important parameter in the ED process is the solvent-to-feed ratio which is defined by the ratio of the solvent added to the column and the feed stream added to the column on mass basis:

$$S/F = \text{solvent feed stream/feed stream} \tag{1}$$

The common solvents used in industry are normally of organic nature such as ethyleneglycol for separating water and ethanol [1–3], phthalic anhydride [4], *N*-methyl-pyrrolidone (NMP) and sulfolane [5–7] for the separation of aromatic from aliphatic and 1,3 butadiene from C_4 hydrocarbons, 1,2 propanediol [8, 9], 1,4 butanediol [10] or dimethyl sulfoxide [11] for the dehydration of tetrahydrofuran among other separations. These organic solvents show several drawbacks. Since the solvent is added at the top of the column and the organic solvents are volatile, they reduce the product purity. Besides this, large amounts of solvent are required to achieve certain separation. Lately, a new class of solvents called ionic liquids have been proposed as a novel solvent for ED due to their properties such us negligible vapor pressure and high selectivity in separation processes. Therefore, a non-volatile solvent is added to the column producing free solvent products in the condenser. Lately, many works have been published regarding the separation of azeotropes and close boiling point mixtures using ionic liquids as solvent, most of them are related to vapor-liquid equilibrium evaluation of ionic liquids for improving relative volatilities [12–22]. Here, it has been demonstrated that, in general, ionic liquids can produce better relative volatilities than organic solvents [22–25]. This advantage results in less solvent needed to perform the separation which brings less operational cost, or an ED column with less separation stages or a decrease in capital cost with regard a conventional ED column operating with organic solvents [26].
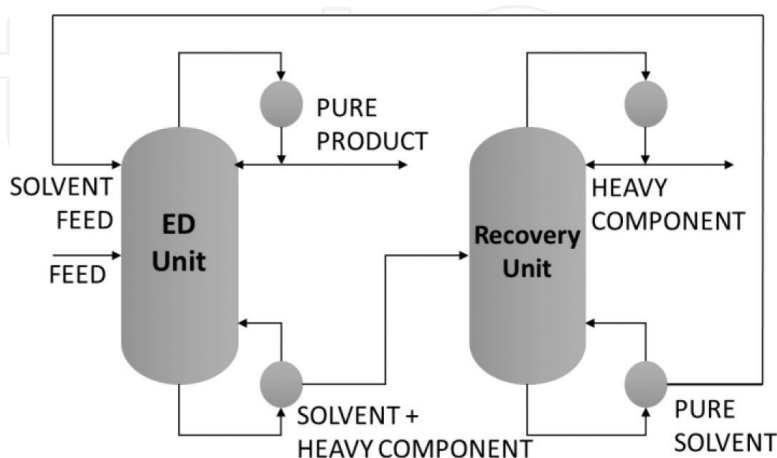

Figure 1. Scheme of a conventional extractive distillation unit and the solvent recovery step.

However, ionic liquids also show high viscosities. For example, one of the less viscous ionic liquids, 1-ethyl-3-metylimidazolium dicyanamide ([emim][DCA]), shows viscosities around 15 mPa·s at 298.15 K [27–30]. Nevertheless, ionic liquids containing halides as anion, such as chloride [I] or bromide [Br], exhibit much larger viscosities than the previous anion. For instance, the ionic liquid 1-octyl-3-methylimidazolium bromide ([omim][Br]) displays a viscosity of around 5000 mPa·s at 298.15 K [31] while 1-octyl-3-methylimidazolium chloride ([omim][Cl]) a value of 20.000 mPa·s at 298.15 K [32, 33]. These viscosity values could bring a decrease in mass transfer efficiency when using ionic liquids in extractive distillation.

Because of this, an ED column with more separation stages due to the mass transfer limitations will be required masking the above gained advantages provided by ionic liquids. However, a good point is that, the viscosity of ionic liquids drastically decreases with increasing the temperature [27] and since ED is a thermal separation process, the real mass transfer effects of ionic liquid on the separation need to be evaluated.

Therefore, the main aim of this work is to evaluate the decrease in mass transfer throughout the mass transfer efficiency concept when using ionic liquids in the extractive distillation of two important cases: separation of water ethanol and methylcyclohexane-toluene mixtures. The first represents the industrial case of dehydration of ethanol and the second the separation of aromatics from aliphatic in the petrochemical industry. On the other hand, the mass transfer efficiency will be evaluated using rate-based modeling or non-equilibrium stage modeling [34] since, on contrary of the equilibrium model, this one considers a real separation stage which is limited by the mass transfer. Therefore, the effect of the viscosity of ionic liquids of mass transfer efficiency would be quantified by this model. Finally, an experimental evaluation of the decrease in mass transfer efficiency is performed in an ED pilot plant equipped with structured packing.

2. Ionic selection for water: ethanol and toluene: methylcyclohenene separation

As it was mentioned above, ionic liquids show better performance than organic solvents in terms of vapor–liquid equilibrium. Therefore, the selection of the ionic liquids for a certain case study is based on the increase in relative volatility. The work of Ge et al. [23] shows an experimental selection of ionic liquids for water-ethanol separation. On the other hand, Gutierrez-Hernandez et al. [25] carried out a selection of ionic liquids for methylcyclohexane-toluene separation based on liquid-liquid extraction experiments. Nevertheless, the high viscosities of ionic liquids could limit the mass transfer in the ED column. **Table 1** contains experimentally determined relative volatilities and viscosities for both case studies.

It can be observed in **Table 1** that the selected ionic liquids for the separation of the water-ethanol mixture, 1-ethyl-3-methylimidazolium chloride ([emim][Cl) and 1-ethyl-3-methylimidazolium acetate ([emim][OAc]) showed higher produced relative volatilities than the conventional organic solvent ethylene glycol (EG). For the second case, the ionic liquid

Solvent	α		$\eta/mPa\ s$	
	S/F = 1	Ref.	T = 298.15 K	Ref.
Water-ethanol separation [35]				
[emim][Cl]	2.62	[23]	2597.69[a]	[36]
[emim][OAc]	2.24	[23]	132.9	[27]
[emim][DCA]	1.89	[23]	14.9	[27]
EG	1.83	Aspen®	16.6	[37]
Methylcyclohexane-toluene separation [38]				
	α		$\eta/\ mPa\ s$	
	S/F = 5	Ref	T = 298.15 K	Ref.
[hmim][TCB]	9.4	[25]	47.8	[38]
NMP	2.8	Aspen®	1.9	Aspen®

[a]extrapolated value from experimental data.

Table 1. Relative volatilities at a solvent-to-feed (S/F) ratio (mass basis) for different solvents and pure solvent viscosities (η) at T = 298.15 for both case studies.

1-hexyl-3-methylimidazolium tetracyanoborate ([hmim][TCB]) produced much higher relative volatilities than organic solvent. This is an indication that, a column with less separation stages or a less usage of solvent is expected to achieve a good separation. However, ionic liquids also show higher viscosity values than traditional solvents. Therefore, the mass transfer efficiency is expected to decrease.

3. Rate-based mass transfer efficiency analysis

To evaluate the effect of viscosity on mass transfer in the extractive distillation process with ionic liquids, it is necessary to use the concept of mass transfer efficiency. The most used mass transfer efficiency model is the Murphree Tray Efficiency [39]. However, this calculation requires the vapor composition per tray and this would not reflect the decrease in mass transfer due to viscosity in the liquid phase. The concept of efficiency that represents the changes in liquid phase viscosity is the tray efficiency defined from the point efficiency assuming that there is no concentration gradient in the axial direction [34, 40], this is:

$$E_{OV} = 1 - \exp(-N_{OV}) \qquad (2)$$

where E_{OV} is the tray efficiency and N_{OV} is the overall number of transfer units which is calculated from the number of transfer units in the vapor phase (N_V) and in the liquid phase (N_L) as follows:

$$\frac{1}{N_{OV}} = \frac{1}{N_V} + \frac{\Lambda}{N_L} \qquad (3)$$

where Λ is the stripping factor calculated from an activity coefficient model [23]. When using packing as internal in an ED column the mass transfer efficiency can be determined using the concept of height equivalent to a theoretical plate:

$$HETP = H_{OV} \frac{\ln(\Lambda)}{\Lambda - 1} \tag{4}$$

where H_{ov} is overall height of transfer units calculated from transfer height id the vapor phase (H_V) and in the liquid phase (H_L) as follows:

$$H_{OV} = H_V + \Lambda H_L \tag{5}$$

Equations (2)–(5) describe the changes in efficiency with physical properties, vapor-liquid equilibrium and the column internals. These equations are used to compare the mass transfer efficiency performance of the different solvents studied in this work. The number of transfer units and the height of transfer units are calculated using the mass transfer correlations depending on the column internal. This work is focused on two internals to evaluate the changes in mass transfer efficiency with viscosity: sieve trays and structured packing. For the case of sieve trays, AIChE mass transfer correlation calculates the number of transfer units in the liquid phase [41]:

$$N_L = 19700 \, (D_L)^{0.5} (0.4 \, F_S + 0.17) \, t_L \tag{6}$$

where t_L is the liquid phase residence time, F_S the superficial factor, and D_L the Fick diffusion coefficient. This last transport property accounts for the decrease in mass transfer efficiency due to the high liquid phase viscosity and it is calculated using the Wilke-Chang correlation [42]:

$$D_{12} = 7.4x \, 10^{-12} \frac{(\Phi \, M_{W,2})^{0.5} \, T}{\eta_2 \, V_1^{0.6}} \tag{7}$$

where $M_{W,2}$ is the molecular weight if the solvent, Φ is the association factor, T is the temperature, V_1 is the molar volume of the solute at its normal boiling point and η_2 is the viscosity of the solvent. To use this diffusion coefficient in the above correlation, a mixing rule has to be previously applied for concentrated solutions [34]. For the case of structured packings, Rocha mass transfer correlation describes well the height of transfer units in the liquid phase [43]:

$$H_L = \frac{u_L}{2a \left[\frac{D_L u_{Le}}{\pi S C_E} \right]^{0.5}} \tag{8}$$

where u_L is the superficial liquid phase velocity, a is the interfacial area per volume, u_{Le} is the effective liquid phase velocity, S is the side dimension of corrugation and C_E is a constant for surface renewal.

4. Simulation setup

ASPEN Plus® radfrac with the Rate-Sep package enables the use of the rate-based model to evaluate the effect of the solvent on the mass transfer efficiency in the ED process. This model needs physical and transport properties of both pure component and ternary mixture which were taken elsewhere [27, 37, 44]. Column internals are other parameters that have to be defined. Sieve trays and Mellapak® 250Y are the selected internals for this study. **Table 2** summarized the features of these internals. These internals will be used to analyze the separation of water-ethanol.

It is worth to mention that, vapor flow regimes inside the ED column could also affect mass transfer efficiency. However, to avoid this effect, these flow regimes were set constant at a value of flooding of 70%.

Sieve Tray	
Parameter	**Value**
Number of stages (real stages including reboiler and condenser)	22
Feed tray	12
Solvent feed	2
Mellapak® 205Y structured packing	
Parameter	**Value**
Packing height (m)	6
Feed point (m)	3
Packing material	Stainless steel

Table 2. Used column internal characteristics in the simulations for 100 kg/h of mixture and 50% wt ethanol as a base flow and feeding concentration respectively [35].

5. Experiments with an extractive distillation pilot plant

In this work, the analysis of mass transfer efficiency will be carried out also experimentally for the mixture toluene-methylcyclohexane to corroborate the results obtained from Aspen Plus®. For this purpose, a pilot-scale ED pilot plant was constructed at Eindhoven University of Technology, The Netherlands equipped with Mellapack® 750Y structured packing and that operates in continuous mode. The column diameter is 0.049 m and the packing material is stainless steel. Finally, the packing height is 3.12 m. To validate the rate-based model with experimental data from the pilot plant, collector basins and thermocouples were placed within packing segments to collect liquid samples a measure the concentration of all the component in the column at defined height of the column. **Figure 2**, shows a scheme of the constructed ED pilot plant. The experimental operating conditions are described in **Table 3**.
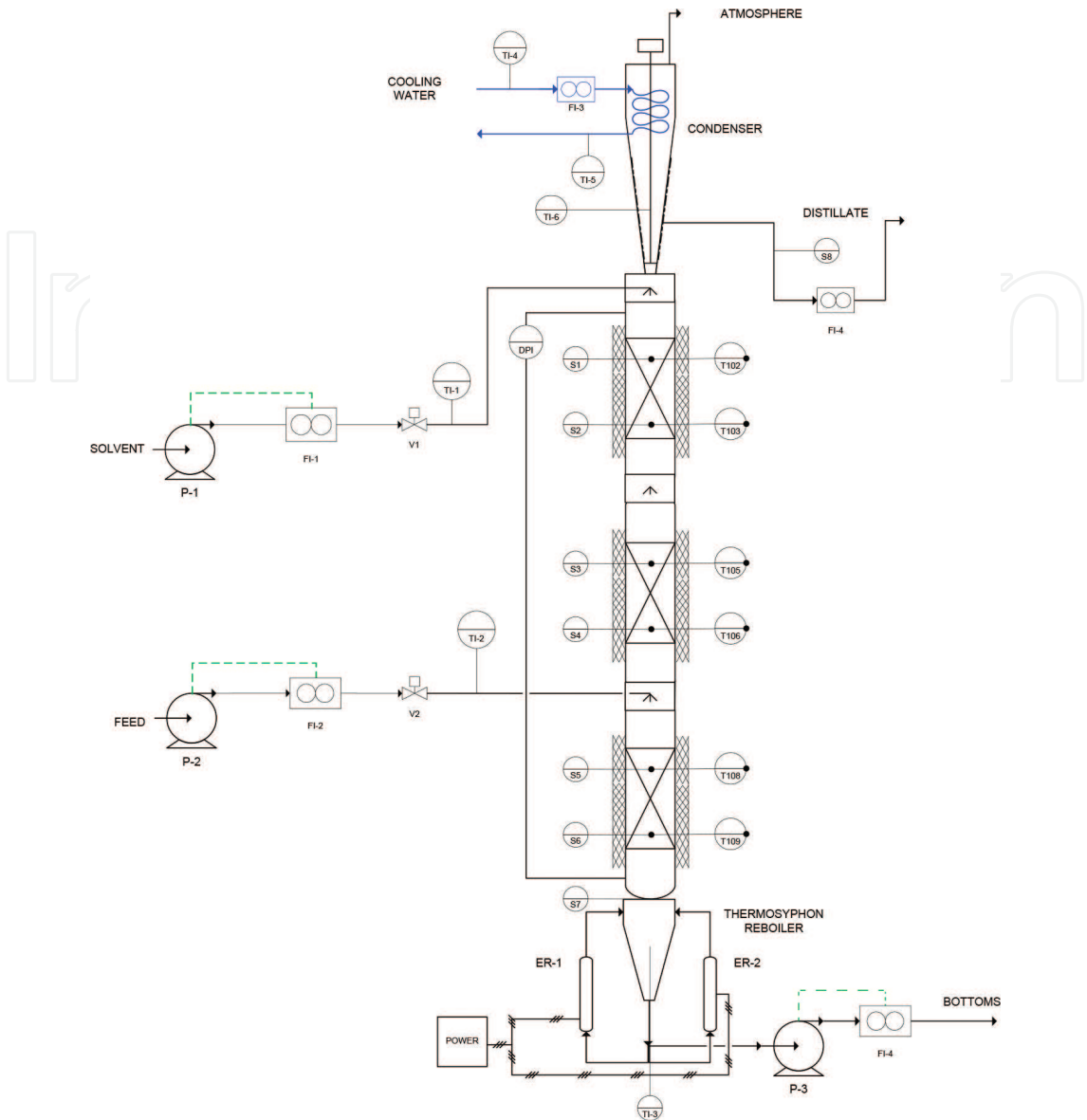
Figure 2. Scheme of the extractive distillation pilot plant at Eindhoven University of Technology [38].

Variable		Value	
Feed flow rate [kg h⁻¹]		2	
Toluene concentration at feed [wt%]		70	
Feed temperature [°C]		90	
Solvent temperature [°C]		100	
Solvent-to-feed ratio (mass)		5	
	Solvent	Reboiler duty [kW][a]	Distillate rate [kg h⁻¹]
	NMP	50%	0.3
	[emim][TCB]	50%	0.3

[a]100% = 2.04 [kW].

Table 3. Operating conditions [38].

6. Results and discussion

6.1. Mass transfer efficiency in sieve tray column

Figure 3 shows the generated relative volatility profile along the ED column that accounts for how good the separation is.

Before analysis these results, it has to be clarified that, the concentration of the solvent, either the organic solvent or the ionic liquids, is higher in the rectifying section than in the stripping section. It means from stage 2 to 12 in our ED column. This is because the solvent feed is at the top of the column and below the solvent is diluted by the feed stream at stage 12. Having mentioned this, it can be observed in **Figure 3** that the relative volatility profiles, in general, follow the same trend as **Table 1** where the ionic liquid [emim][Cl] showed the best values being the most promising solvent for water-ethanol, separation. In spite of these results, this ionic liquid would not be used in a real ED column due that it is a corrosive fluid [45] and the melting point is 87°C [46]. Anyhow, this ionic liquid will be kept for the analysis. Therefore, [emim][OAc] becomes the most promising ionic liquid which exhibits the second best relative volatilities. On the other hand, EG produces the lowest relative volatility values as indicated in **Table 1**.

Next, **Figure 4**, shows the viscosity profile at the liquid phase when using the different solvent. It is clearly seen that the increase in the liquid phase viscosity inside the ED column is directly influenced by the solvent viscosity. This explains why when using [emim][Cl] as the solvent the highest viscosity values are observed inside the column and the rest of the solvent follow the trend in **Table 1**. Therefore, the trend observed in this figure is as follows: [emim][Cl] > [emim][OAc] > [emim][DCA] > EG. In the stripping section the liquid viscosity drops for all four solvents as the solvent concentration is reduced by dilution with the feed stream.

As a summary, ionic liquids produced higher relative volatilities that the organic solvent, but higher viscosities as well. **Figure 5** shows the mass transfer efficiency profiles along the column for all solvents.

Figure 5 shows the tray efficiency profiles over the ED column calculated using Eq. (2). The rectifying section shows lower mass transfer efficiencies than the stripping section due to the effect of solvent viscosity. At S/F = 1, the mass transfer efficiency order is [emim][OAc] > [emim][DCA] > EG > [emim][Cl]. This order does not follow exactly the expected trend from **Figure 4**. Therefore, the viscosity is not the only important effect in calculating the mass transfer efficiency as observed in Eq. (2). Hence, the relative volatility values should play an important role as well. Ionic liquids are able to outperform the relative volatilities of the common organic solvents as it has previously mentioned. In **Table 1** it is observed that very good relative volatilities are produced by [emim][OAc]. This property enhances the mass transfer efficiency even though having relatively high viscosity. However, for then case of [emim][Cl], this ionic liquid shows the highest relative volatility and also it exhibits high viscosities. Here, due to the high viscosities this property is more important than
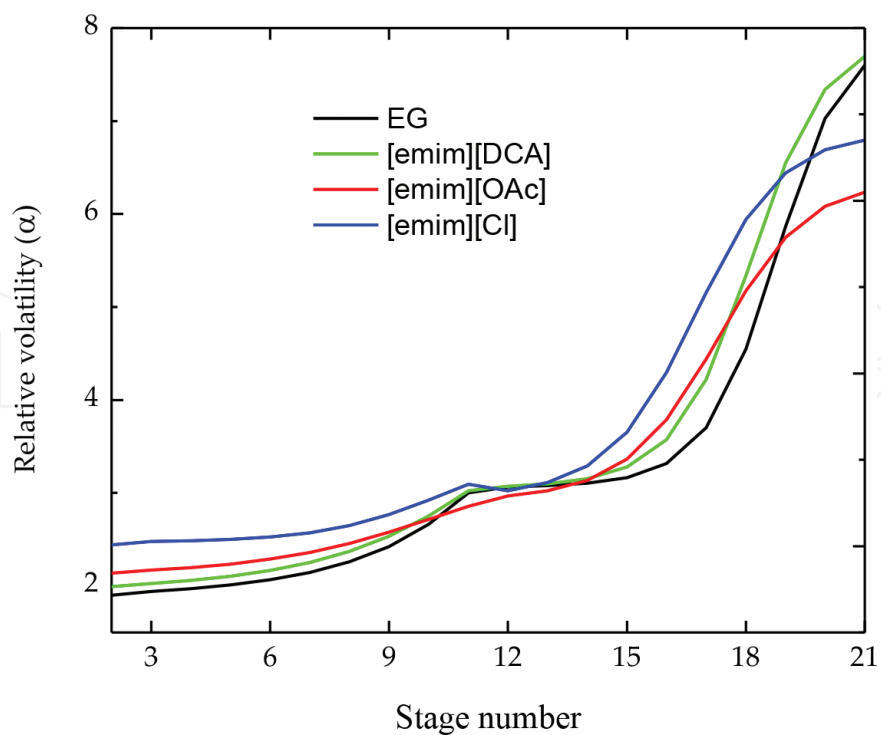
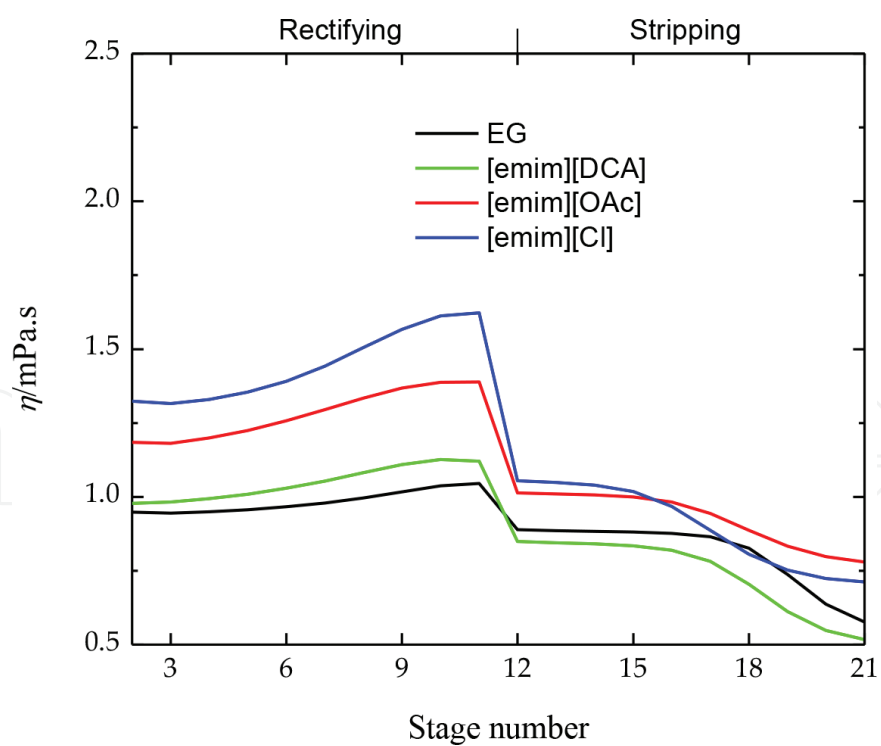**Figure 3.** Relative volatility profiles along the extractive distillation column for S/F = 1.

Figure 4. Viscosity profiles along the column for S/F = 1 formed when the different solvents are added to the column and D/F = 0.4 (mass basis) [35].
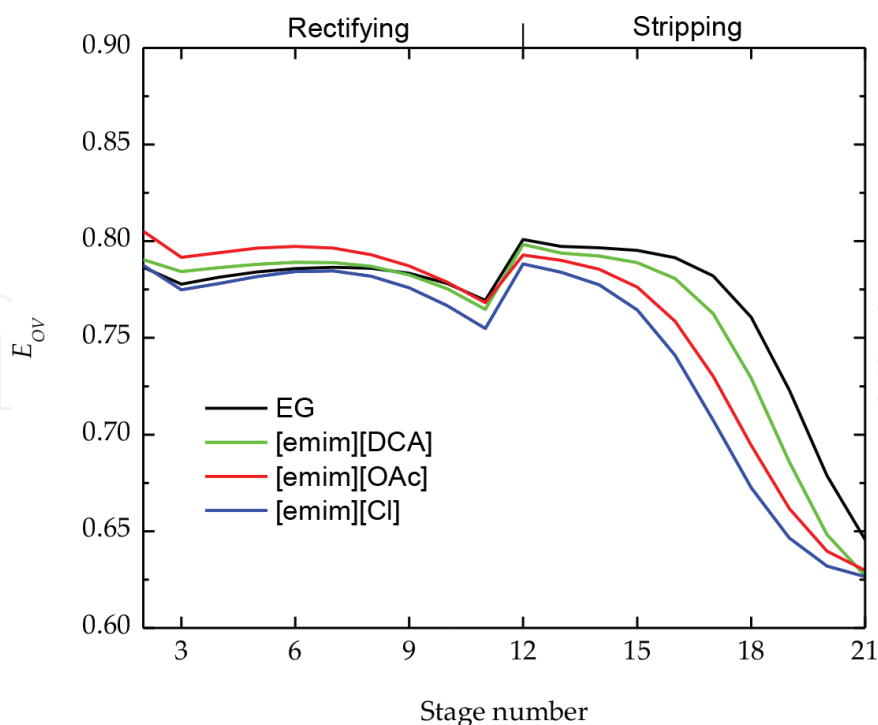
Figure 5. Tray efficiency profiles along the column for S/F = 1 calculated when the different solvents are added to the column and D/F = 0.4 (mass basis). The column is numbered from the top to the bottom [35].

relative volatility and becomes the limiting factor in mass transfer efficiency. Therefore, moderately high viscosities of ionic liquids in ED would not limit the mass transfer when combined with high values of relative volatility. However, the relative volatility does not enhance mass transfer efficiency sufficiently in the presence of a very viscous ionic liquid.

6.2. Mass transfer efficiency in Mellapack® 250Y structured packing

Figure 6 shows the generated Height Equivalent to a Theoretical Plate (HETP) profiles along the column for the same operating conditions as the sieve tray column.

For the structured packing, the values of mass transfer efficiency are represented the HETP, and here the lowest value means the most efficient case. The mass transfer efficiency order is [emim][OAc] > [emim][DCA] ≈ [emim][Cl] > EG in the rectifying section. The observation of these profiles does not produce different conclusions from sieve trays. However, two important points are observed here. Firstly, in contrast to sieve trays, more notorious difference in efficiency is shown here. This is explained by the fact that in packed columns the liquid and vapor flow are in countercurrent and the packing surface allows an intimate vapor-liquid contact. As a result, the packed distillation column operates closer to equilibrium than sieve trays, and thereby the effect of the relative volatility predominates over the increase in liquid phase viscosity. This is the reason why [emim][Cl] produces now better mass transfer efficiencies than EG on contrary to the case of the sieve tray column and this latter solvent presents the lowest mass transfer efficiency (highest *HETP*). It worth to mention that, the results obtained here were previously validated in a pilot plant where that developed rate-based model predicts the performance of the pilot plant within 10% error.
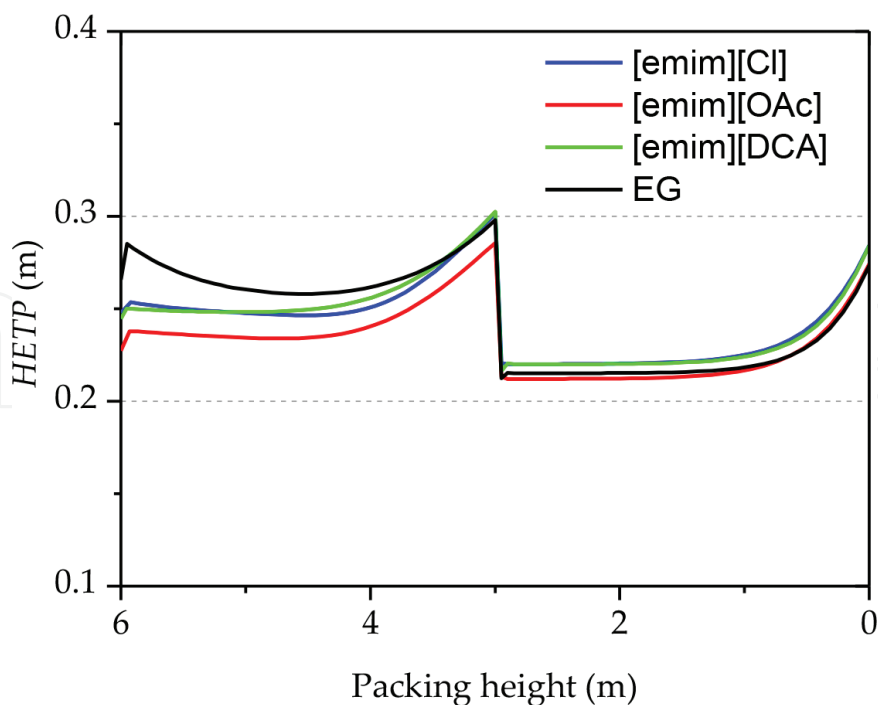
Figure 6. HETP profiles along the column for S/F = 1 (mass basis) calculated when the different solvents are added to the column and D/F = 0.4 (mass basis). The column is measured from the bottom (0 m) to the top (6 m) [35].

6.3. Experimental study of mass transfer efficiency in the system toluene-methylcyclohexane

The extractive distillation of toluene-methylcyclohexane is an interesting case because the ionic liquid [hmim]TCB] overcome by far the relative volatility of the conventional organic solvent NMP (see **Table 1**). In addition to this, the viscosity of the ionic liquid is not as high as [emim][OAc] for example. Therefore, one would not expect a decrease in mass transfer efficiency as it was concluded before. However, since this is a very nonpolar mixture and the ionic liquid is a solvent of a polar nature, phase split is expected when mixing. Nevertheless, the phase splitting can be solved by increasing the S/F ration at high values [25]. Due to this fact, there could be a decrease in mass transfer efficiency. **Figure 7** shows the ternary map indicating the one-phase region to operate.

As it can be observed in **Figure 7**, to reach the one-phase region, two conditions should be set: first, high concentration of [hmim][TCB] inside the column and high methylcyclohaxene distillate rates (or low reflux ratios) to keep its concentration as low as possible inside the column to avoid phase split. **Figure 8** shows the experimentally obtained liquid phase concentration profiles when NMP (**Figure 8a**) and [hmim][TCB] (**Figure 8b**) where the solvent, respectively.

It can be observed that, due to the high S/F ratios, high solvent concentration was developed inside the ED column for both cases NMP and [hmim][TCB]. However, when using the organic solvent, a little lower liquid phase solvent concentration is observed due to this solvent is volatile. High concentration will lead to high liquid phase viscosities. **Figure 9** shows the viscosity profiles inside the column and the Height Equivalent to a Theoretical Plate (HETP).
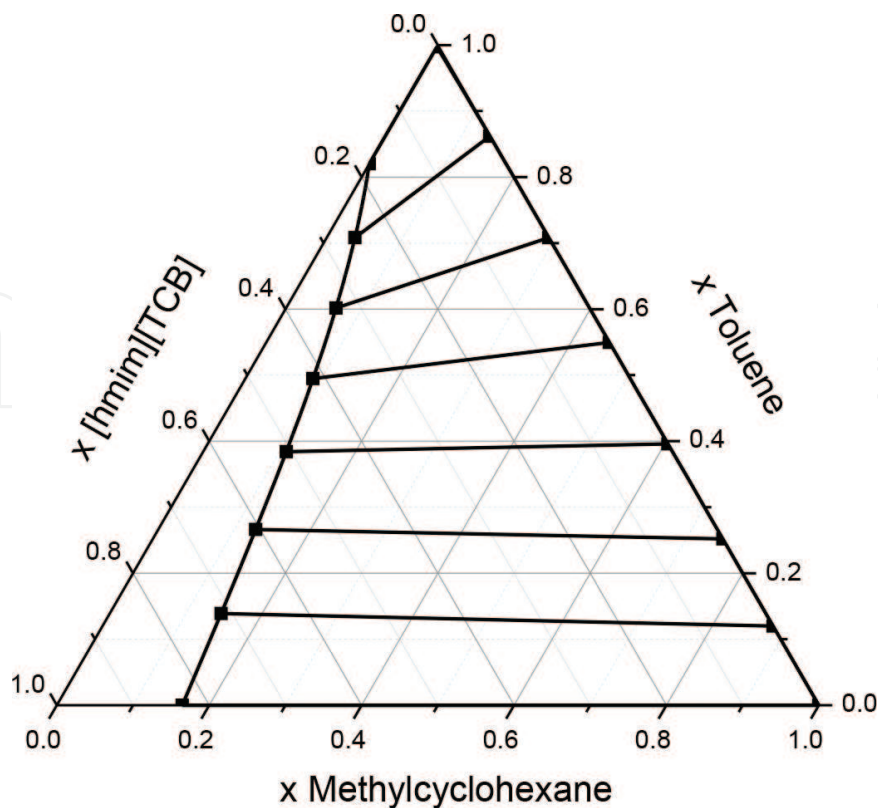
Figure 7. Ternary diagram for the system toluene-methylcylcohexane-[hmim][TCB] [38].

In **Figure 9a** it can be clearly observed the influence of the viscosity of [hmim][TCB] due to the high S/F ratios. While the separation of the toluene-methylcyclohexane mixture with NMP show low viscosities, [hmim][TCB] exhibit high values reaching the 4 [cP] in the rectifying section leading to a decrease in mass transfer efficiency as observed in **Figure 9b**. The impact of the liquid phase resistance on the mass transfer efficiency is significant even though the use of the first solvent produces much higher relative volatilities. The conclusions made in this
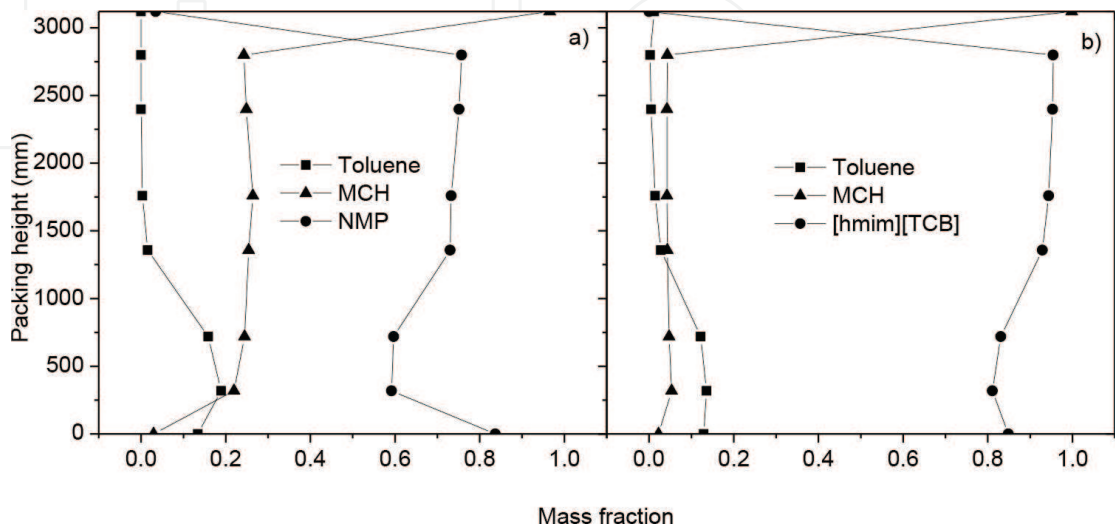

Figure 8. Concentration profiles (mass fractions) for the ED of toluene-MCH using (a) NMP and (b) [hmim][TCB] as solvents. For cases 1 and 2 [38].
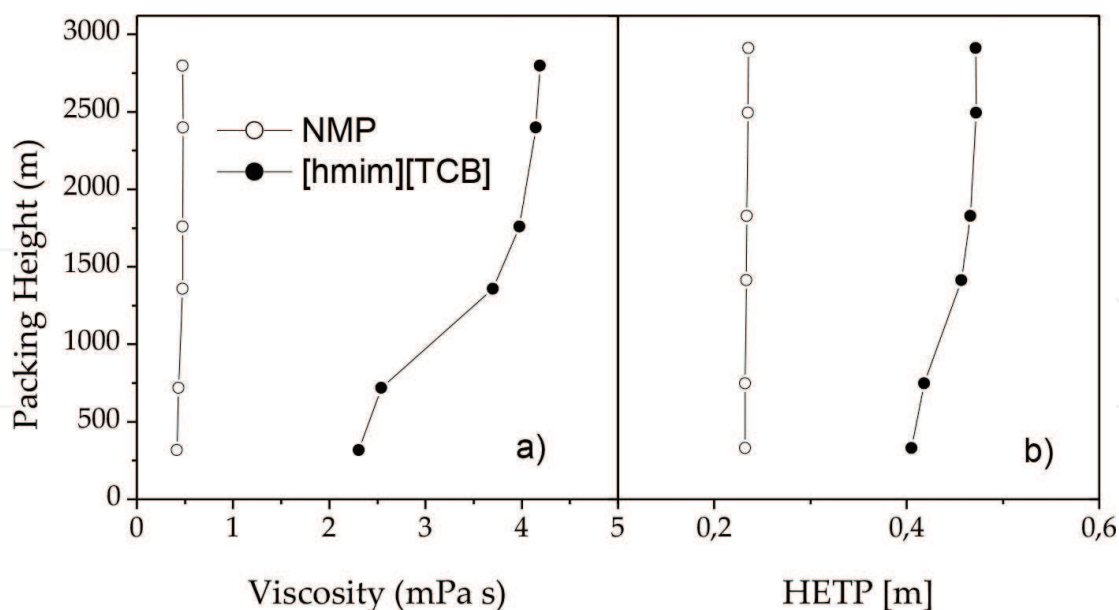
Figure 9. Liquid phase viscosity inside the ED column and HETP for the system toluene-methylcyclohexane using both solvent NMP and [hmim][TCB] [38].

work should be used in the selection of the ionic liquids for extractive distillation processes along with the studies on relative volatility.

7. Conclusions

In this study, the mass transfer efficiency of the extractive distillation with ionic liquids has been analyzed for the water ethanol mixtures using a developed rate-based model and in a pilot plant scale extractive distillation column.

The results from the rate-based indicated that the use of ionic liquids as solvents in ED is beneficial due to the increase in relative volatilities when compared to organic solvents.

The high viscosities of ionic liquids were reflected in the increase of que liquid phase viscosity inside the ED column. However, this viscosity did not decrease the mass transfer efficiency of the ED whereas the relative volatilities are high. On the other hand, when very high viscosities or high solvent to feed ratios are applied to the ED column, a decrease in mass transfer efficiency was observed even though having high relative volatilities.

Acknowledgements

Author details

Esteban Quijada-Maldonado[1]*, Wytze G. Meidersma[2] and André B. de Haan[3]

*Address all correspondence to: esteban.quijada@usach.cl

1 University of Santiago de Chile, Santiago, Chile

2 Eindhoven University of Technology, Eindhoven, The Netherlands

3 Delft University of Technology, Delft, The Netherlands

References

[1] Meirelles A, Weiss S, Herfurth H. Ethanol dehydration by extractive distillation. Journal of Chemical Technology and Biotechnology. 1992;**53**:181-188. DOI: 10.1002/jctb.280530213

[2] Ravagnani MASS, Reis MHM, Filho RM, Wolf-Maciel MR. Anhydrous ethanol production by extractive distillation: A solvent case study. Process Safety and Environmental Protection. 2010;**88**:67-73. DOI: 10.1016/j.psep.2009.11.005

[3] Benyahia K, Benyounes H, Shen W. Energy evaluation of ethanol dehydration with glycol mixture as entrainer. Chemical Engineering and Technology. 2014;**37**:987-994. DOI: 10.1002/ceat.201300872

[4] Berg L. Separation of benzene and toluene from close boiling nonaromatics by extractive distillation. AICHE Journal. 1983;**29**:961-966. DOI: 10.1002/aic.690290614

[5] Wang Q, Zhang BJ, He C, He CC, Chen QL. Optimal design of a new aromatic extractive distillation process aided by a co-solvent mixture. Energy Procedia. 2017;**105**:4927-4934. DOI: 10.1016/j.egypro.2017.03.984

[6] Kim YH, Kim SY, Lee B. Simulation of 1,3-butadiene extractive distillation process using N-methyl-2-pyrrolidone solvent. Korean Journal of Chemical Engineering. 2012;**29**:1493-1499. DOI: 10.1007/s11814-012-0075-3

[7] Jalali F, Saffari R. Simulation and optimization in 1,3-butadiene process from C4-CUT using genetic algorithm. in: Marquardt W, Pantelides C, editors. Computer Aided Chemical Engineering. 16th European Symposium on Computer Aided Process Engineering and 9th International Symposium on Process Systems Engineering. 21st ed. Elsevier; 2006. pp. 901-906. DOI: 10.1016/S1570-7946(06)80160-4

[8] Xu S, Wang H. Separation of tetrahydrofuran-water azeotropic mixture by batch extractive distillation process. Chemical Engineering Research and Design. 2006;**84**:478-482. DOI: 10.1205/cherd05050

[9] Deorukhkar OA, Deogharkar BS, Mahajan YS. Purification of tetrahydrofuran from its aqueous azeotrope by extractive distillation: Pilot plant studies. Chemical Engineering and Processing: Process Intensification. 2016;**105**:79-91. DOI: 10.1016/j.cep.2016.04.006

[10] Xu S, Wang H. A new entrainer for separation of tetrahydrofuran-water azeotropic mixture by extractive distillation. Chemical Engineering and Processing: Process Intensification. 2006;**45**:954-958. DOI: 10.1016/j.cep.2006.02.001

[11] Zhang Z, Huang D, Peng M, Sun D, Li W. Entrainer selection for separating tetrahydro-furan/water azeotropic mixture by extractive distillation. Separation and Purification Technology. 2014;**122**:73-77. DOI: 10.1016/j.seppur.2013.10.051

[12] Fang J, Liu J, Li C, Liu Y. Isobaric vapor-liquid equilibrium for the acetonitrile + water system containing different ionic liquids at atmospheric pressure. Journal of Chemical & Engineering Data. 2013;**58**:1483-1489. DOI: 10.1021/je3009792

[13] Li X, Shen C, Li C. Effect of alkanolammonium formates ionic liquids on vapour liquid equilibria of binary systems containing water, methanol, and ethanol. The Journal of Chemical Thermodynamics. 2012;**53**:167-175. DOI: 10.1016/j.jct.2012.05.001

[14] Zhao J, Dong C, Li C, Meng H, Wang Z. Isobaric vapor-liquid equilibria for ethanol-water system containing different ionic liquids at atmospheric pressure. Fluid Phase Equilibria. 2006;**242**:147-153. DOI: 10.1016/j.fluid.2006.01.023

[15] Khan I, Batista MLS, Carvalho PJ, Santos LMNB, Gomes JRB, Coutinho JAP. Vapor-liquid equilibria of imidazolium ionic liquids with cyano containing anions with water and ethanol. The Journal of Physical Chemistry. B. 2015;**119**:10287-10303. DOI: 10.1021/acs.jpcb.5b03324

[16] Tsanas C, Tzani A, Papadopoulos A, Detsi A, Voutsas E. Ionic liquids as entrainers for the separation of the ethanol/water system. Fluid Phase Equilibria. 2014;**379**:148-156. DOI: 10.1016/j.fluid.2014.07.022

[17] Gjineci N, Boli E, Tzani A, Detsi A, Voutsas E. Separation of the ethanol/water azeotropic mixture using ionic liquids and deep eutectic solvents. Fluid Phase Equilibria. 2016;**424**:1-7. DOI: 10.1016/j.fluid.2015.07.048

[18] Shen C, Li X, Lu Y, Li C. Effect of ionic liquid 1-methylimidazolium chloride on the vapour liquid equilibrium of water, methanol, ethanol, and {water+ethanol} mixture. The Journal of Chemical Thermodynamics. 2011;**43**:1748-1753. DOI: 10.1016/j.jct.2011.06.002

[19] Li W, Li L, Zhang L, Li H, Zhang T. Isobaric vapor-liquid equilibrium for 2-butanone + ethanol + phosphate-based ionic liquids at 101.3-kPa. Fluid Phase Equilibria. 2018;**456**:57-64. DOI: 10.1016/j.fluid.2017.10.001

[20] Cumplido M, Lladosa E, Loras S, Pla-Franco J. Isobaric vapor-liquid equilibria for extractive distillation of 1-propanol+water mixture using thiocyanate-based ionic liquids. The Journal of Chemical Thermodynamics. 2017;**113**:219-228. DOI: 10.1016/j.jct.2017.06.014

[21] Chen X, Yang B, Abdeltawab AA, Al-Deyab SS, Yu G, Yong X. Isobaric vapor-liquid equilibrium for acetone + methanol + phosphate ionic liquids. Journal of Chemical & Engineering Data. 2015;**60**:612-620. DOI: 10.1021/je5007373

[22] Jongmans MTG, Schuur B, de Haan AB. Ionic liquid screening for ethylbenzene/styrene separation by extractive distillation. Industrial and Engineering Chemistry Research. 2011;**50**:10800-10810. DOI: 10.1021/ie2011627

[23] Ge Y, Zhang L, Yuan X, Geng W, Ji J. Selection of ionic liquids as entrainers for separation of (water+ethanol). The Journal of Chemical Thermodynamics. 2008;**40**:1248-1252. DOI: 10.1016/j.jct.2008.03.016

[24] Pereiro AB, Araujo JMM, Esperanza JMSS, Marrucho IM, Rebelo LPN. Ionic liquids in separations of azeotropic systems—A review. The Journal of Chemical Thermodynamics. 2012;**46**:2-28. DOI: 10.1016/j.jct.2011.05.026

[25] Gutierrez JP, Meindersma W, de Haan AB. Binary and ternary (liquid+liquid) equilibrium for {methylcyclohexane (1)+toluene (2)+1-hexyl-3-methylimidazolium tetracyanoborate (3)/1-butyl-3-methylimidazolium tetracyanoborate (3)}. The Journal of Chemical Thermodynamics. 2011;**43**:1672-1677. DOI: 10.1016/j.jct.2011.05.029

[26] Lei Z, Li C, Chen B. Extractive distillation: A review. Separation and Purification Reviews. 2003;**32**:121-213. DOI: 10.1081/SPM-120026627

[27] Quijada-Maldonado E, van der Boogaart S, Lijbers JH, Meindersma GW, de Haan AB. Experimental densities, dynamic viscosities and surface tensions of the ionic liquids series 1-ethyl-3-methylimidazolium acetate and dicyanamide and their binary and ternary mixtures with water and ethanol at T = (298.15 to 343.15K). The Journal of Chemical Thermodynamics. 2012;**51**:51-58. DOI: 10.1016/j.jct.2012.02.027

[28] Larriba M, Navarro P, Garcia J, Saffari R, Rodríguez F. Liquid-liquid extraction of toluene from heptane using [emim][DCA], [bmim][DCA], and [emim][TCM] ionic liquids. Industrial and Engineering Chemistry Research. 2013;**52**:2714-2720. DOI: 10.1021/ie303357s

[29] Freire MG, Teles AR, Rocha MAA, Schröder B, Neves CMSS, Carvalho PJ, Evtuguin DV, Santos LMNB, Coutinho JAP. Thermophysical characterization of ionic liquids able to dissolve biomass. Journal of Chemical & Engineering Data. 2011;**56**:4813-4822. DOI: 10.1021/je200790q

[30] Neves CMSS, Kurnia KA, Coutinho JAP, Marrucho IM, Lopes JNC, Freire MG, Rebelo LP. Systematic study of the thermophysical properties of imidazolium-based ionic liquids with cyano-functionalized anions. The Journal of Physical Chemistry. B. 2013;**117**:10271-10283. DOI: 10.1021/jp405913b

[31] Nanda R, Rai G, Kumar A. Interesting viscosity changes in the aqueous urea-ionic liquid system: Effect of alkyl chain length attached to the cationic ring of an ionic liquid. Journal of Solution Chemistry. 2015;**44**:742-753. DOI: 10.1007/s10953-015-0320-6

[32] Gomez E, Gonzalez B, Dominguez A, Tojo E, Tojo J. Dynamic viscosities of a series of 1-alkyl-3-methylimidazolium chloride ionic liquids and their binary mixtures with water at several temperatures. Journal of Chemical & Engineering Data. 2006;**51**:696-701. DOI: 10.1021/je050460d

[33] AlTuwaim MS, Alkhaldi KHAE, Al-Jimaz ALS, Mohammad AA. Temperature dependence of physicochemical properties of imidazolium-, pyroldinium-, and phosphonium-based ionic liquids. Journal of Chemical & Engineering Data. 2014;**59**:1955-1963. DOI: 10.1021/je500093z

[34] Taylor R, Krishna R. Multicomponent Mass Transfer. Toronto: Wiley; 1993. ISBN: 9780471574170

[35] Quijada-Maldonado E, Meindersma GW, de Haan AB. Ionic liquid effects on mass transfer efficiency in extractive distillation of water-ethanol mixtures. Computers & Chemical Engineering. 2014;**71**:210-219. DOI: 10.1016/j.compchemeng.2014.08.002

[36] Fendt S, Padmanabhan S, Blanch HW, Prausnitz JM. Viscosities of acetate or chloride-based ionic liquids and some of their mixtures with water or other common solvents. Journal of Chemical & Engineering Data. 2011;**56**:31-34. DOI: 10.1021/je1007235

[37] Quijada-Maldonado E, Meindersma GW, de Haan AB. Viscosity and density data for the ternary system water(1)-ethanol(2)-ethylene glycol(3) between 298.15K and 328.15K. The Journal of Chemical Thermodynamics. 2013;**57**:500-505. DOI: 10.1016/j.jct.2012.08.024

[38] Quijada-Maldonado E, Meindersma GW, de Haan AB. Pilot plant study on the extractive distillation of toluene-methylcyclohexane mixtures using NMP and the ionic liquid [hmim][TCB] as solvents. Separation and Purification Technology. 2016;**166**:196-204. DOI: 10.1016/j.seppur.2016.04.041

[39] Kister H. Distillation Design. New York: McGraw-Hill Education; 1992. ISBN: 9780070349094

[40] Lockett MJ. Distillation Tray Fundamentals. New York: Cambridge University Press; 1986. ISBN: 9780521321068

[41] AIChE. Bubble-Tray Design Manual: Prediction of Fractional Efficiency. New York: American Institute of Chemical Engineers; 1958

[42] Wilke CR, Chang P. Correlation of diffusion coefficients in dilute solutions. AICHE Journal. 1955;**1**:264-270. DOI: 10.1002/aic.690010222

[43] Rocha JA, Bravo JL, Fair JR. Distillation columns containing structured packings: A comprehensive model for their performance. 2. Mass-transfer model. Industrial and Engineering Chemistry Research. 1996;**35**:1660-1667. DOI: 10.1021/ie940406i

[44] Quijada-Maldonado E, Aelmans TAM, Meindersma GW, de Haan AB. Pilot plant validation of a rate-based extractive distillation model for water-ethanol separation with the ionic liquid [emim][DCA] as solvent. Chemical Engineering Journal. 2013;**223**:287-297. DOI: 10.1016/j.cej.2013.02.111

[45] Uerdingen M, Treber C, Balser M, Schmitt G, Werner C. Corrosion behaviour of ionic liquids. Green Chemistry. 2005;**7**:321-325. DOI: 10.1039/B419320M

[46] Dong K, Wang Q, Lu X, Zhou Q, Zhang S. Structure, interaction and hydrogen bond. In: Zhang S, Wang J, Lu X, Zhou Q, editors. Structures and Interactions of Ionic Liquids. Berlin, Heidelberg: Springer; 2014. pp. 1-38. DOI: 10.1007/978-3-642-38619-0_1