Computers and Chemical Engineering 71 (2014) 210–219

Contents lists available at ScienceDirect

Computers and Chemical Engineering

journal homepage: www.elsevier.com/locate/compchemeng

Ionic liquid effects on mass transfer efficiency in extractive distillation of water–ethanol mixtures

E. Quijada-Maldonado[a,*], G. Wytze Meindersma[b], André B. de Haan[c]

[a] University of Santiago de Chile, Department of Chemical Engineering, Av. Lib. Bdo. O'Higgins 3363, Estación Central, Santiago, Chile
[b] Eindhoven University of Technology, Department of Chemistry and Chemical Engineering, Eindhoven, The Netherlands
[c] Delft University of Technology, Faculty of Applied Sciences, Department of Chemical Engineering, Delft, The Netherlands

ARTICLE INFO

Article history:
Received 13 September 2013
Received in revised form 30 July 2014
Accepted 2 August 2014
Available online 11 August 2014

Keywords:
Rate-based model
Extractive distillation
Ionic liquids
Mass transfer efficiency
Water–ethanol separation
ASPEN® simulations

ABSTRACT

The relatively high viscosities of ionic liquids could reduce the mass transfer efficiency of the extractive distillation process. The rate-based model was adopted to analyze this phenomenon since it predicted the performance of an extractive distillation pilot plant using ionic liquids as solvent. For the water–ethanol separation, three ionic liquids: 1-ethyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium acetate and 1-ethyl-3-methylimidazolium dicyanamide and the organic solvent ethylene glycol were used for the analysis. Simulations were conducted for sieve trays and Mellapak® 250Y. The results indicate that relatively high viscosities affect the mass transfer efficiency. However, the improvements in relative volatilities obtained from the ionic liquids help to overcome this effect. However, with high solvent viscosities (>65 mPa s at $T = 353.15$ K) it was not possible to overcome the reductions. Additionally, at higher distillate rates high relative volatilities yielded negative effects on mass transfer efficiency because of a decrease in vapor velocity.

1. Introduction

Extractive distillation (ED) is an energy efficient technology that allows the separation of complex mixtures by the addition of a solvent at the top of the column that modifies the activity coefficients at the liquid phase to increase the relative volatilities. Fig. 1 depicts a scheme of a conventional ED process including solvent recovery step.

Most of the solvents used in the ED process are volatile organic fluids. Ionic liquids have lately become a real alternative as solvent in extractive distillation because efforts have already been made to successfully bring fundamental vapor–liquid equilibrium experiments to pilot plant scale experiments (Meindersma et al., 2012). This has become possible due to their properties such as high selectivity in ED process and negligible vapor pressure resulting in high recyclability and no solvent loss (Verma and Banerjee, 2010; Lei et al., 2003; Pereiro et al., 2012; Roughton et al., 2012). The higher selectivity requires less reflux ratio and therefore less boil up making the ionic liquids more energy efficient solvents than the common solvents (Meindersma et al., 2012; Quijada-Maldonado et al., 2013a). Furthermore, the high selectivity allows decreasing the number of separation stages due to the increased relative volatilities. This advantage brings reductions of capital costs and reductions in ionic liquid usage to achieve a desired purity. Despite the above mentioned advantages, ionic liquids show high liquid viscosity and this could bring mass transfer limitations to the separation process.

It is recognized that increased viscosity of a solvent in ED lowers the mass transfer efficiency of the process. This is a very important parameter in the design of a ED column because a lower efficiency leads to columns with more trays or higher packing to achieve a required separation. This problem becomes more important when applying ionic liquids as solvents in ED because their viscosities can be up to 20 times higher compared to the commonly used organic solvents. Other properties such us density, surface tension and thermal conductivities are similar to the common organic solvents (Quijada-Maldonado et al., 2012, 2013a,b). So then, there will not be mass transfer efficiency differences between ionic liquids and common solvents produced by these properties. Several studies have pointed out the high viscosity of ionic liquids as a reason to discard promising ionic liquids in spite of their excellent vapor–liquid equilibrium performance (Ge et al., 2008). There are three phenomena

---

* Corresponding author. Tel.: +56 227181801.
E-mail address: esteban.quijada@usach.cl (E. Quijada-Maldonado).

http://dx.doi.org/10.1016/j.compchemeng.2014.08.002

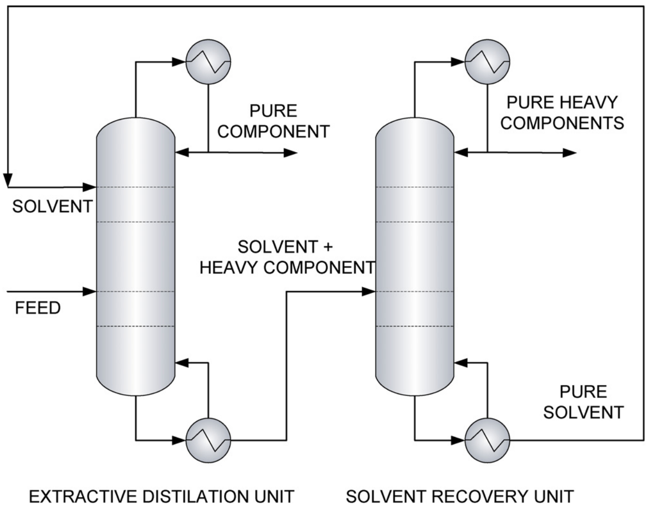

Fig. 1. Scheme of a conventional extractive distillation unit and the solvent recovery step.

that could help to reduce this "fear" for reduced mass transfer efficiency:

1. The solvent is dissolved in the mixture to be separated, which strongly decreases the solvent viscosity (Quijada-Maldonado et al., 2012; Gomez et al., 2006a,b).
2. The high temperatures inside the ED column considerably reduce the viscosity of ionic liquids (Quijada-Maldonado et al., 2012).
3. The improvements in relative volatility over conventional solvents help to reduce the number of separation stages which could compensate for the negative effect of viscosity (Quijada-Maldonado et al., 2013a).

However, the knowledge about the effect of solvent viscosity on mass transfer efficiency in distillation is fairly limited. Only one study experimentally showed this effect (Weiss and Arlt, 1987). In classical distillation operations, only a few studies have related the effect of viscosity to mass transfer efficiency (O'Connell, 1946; Bocker and Ronge, 2005). Furthermore, the effect of the solvent viscosity on mass transfer efficiency is not studied yet for extractive distillation with ionic liquids.

Therefore, the objective of this paper is to study the effect of the solvent viscosity on the mass transfer efficiency in the ED process for the water–ethanol mixture using several ionic liquids and the commonly used organic solvent ethylene glycol (EG) by means of a rigorous rate-based mass transfer model. In our previous work (Quijada-Maldonado et al., 2013a) it was demonstrated that the developed rated-based model to describe this separation using 1-ethyl-3-methylimidazolium dicyanamide, [emim][DCA], was able to predict the performance of an extractive distillation pilot plant while only knowing the physical, transport and vapor–liquid equilibrium (VLE) properties of the system. Therefore, this model allows the analysis of a possible decrease in mass transfer efficiency with solvent viscosity. On the other hand, the use of various ionic liquids allows the study of a wide range of solvent viscosities and relative volatilities. Therefore, the combined effect of viscosity and relative volatility on mass transfer efficiency is studied. Additionally, the mass transfer efficiency of sieve trays and Mellapak® 250Y structured packing are compared and two solvent-to-feed ratios evaluated to increase the liquid phase viscosities inside the ED column as this is the most important operating variable when higher purities are desired. Finally, the recovery of the ionic liquids (see Fig. 1) has been studied elsewhere (Meindersma et al., 2012; Jongmans et al., 2012). Hence, it is not studied in this work.

Table 1
Relative volatilities, α, at different S/F ratios (mass basis) for different solvents calculated at the water–ethanol azeotropic point and pure solvent viscosities, η, at $T = 298.15$ and 353.15 K.

Solvent	α			η [mPa s]		
	S/F = 1	S/F = 2	Ref.	$T = 298.15$ K	$T = 353.15$ K	Ref.
[emim][Cl]	2.62	3.98	[b]	2597.69[a]	65.18	[c]
[emim][OAc]	2.24	2.92	[b]	132.91	13.60	[d]
[emim][DCA]	1.89	2.58	[b]	14.90	4.66	[d]
EG	1.83	2.41	ASPEN®	16.61	3.14	[e]

[a] Extrapolated viscosity from three experimental data points.
[b] Ge et al. (2008).
[c] Fendt et al. (2010).
[d] Quijada-Maldonado et al. (2012).
[e] Quijada-Maldonado et al. (2013b).

2. Case study

The separation of water–ethanol mixtures by means of ED has been an important research topic for years due to applicability of ethanol as biofuel (Garcia-Herreros et al., 2011; Lee and Pahl, 1985; Ravagnani et al., 2010; Ligero and Ravagnani, 2003; Li and Bai, 2012; Huang et al., 2008; Kumar et al., 2010; Gil et al., 2012; Maciel and Brito, 2011). Table 1 shows the change in relative volatility of the water–ethanol mixture at two different solvent-to-feed ratios (S/F) calculated at the azeotropic point using the NRTL model. From this table it is observed that at both S/F ratios the order is [emim][Cl] > [emim][OAc] > [emim][DCA] > [EG]. Eventually, the best candidate to be chosen as a solvent would be [emim][Cl] due to the highest achieved relative volatilities followed by [emim][OAc]. This means that, an ED column operating with [emim][Cl] as solvent would require less stages to achieve a required ethanol purity at the top. Table 1 also lists the viscosities of the solvents at $T = 298.15$ and 353.15 K. Especially for [emim][Cl] relatively high values are observed that could limit the mass transport. Here on the contrary, a column operating with this solvent would need more separation stages to obtain a certain ethanol top purity. However, at higher temperatures a drastic viscosity decrease is observed. Besides that, the solvent concentration is reduced in the mixture. For these conditions the actual decrease in mass transfer efficiency needs to be analyzed.

The study of mass transfer efficiency comprises the analysis of the overall number of transfer units for trays and the overall height of transfer units for packing:

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

$$HETP = H_{OV}\frac{\ln(\Lambda)}{\Lambda - 1} \tag{2}$$

$$\frac{1}{N_{OV}} = \frac{1}{N_V} + \frac{\Lambda}{N'_L} \tag{3}$$

$$H_{OV} = H_V + \Lambda H_L \tag{4}$$

where *HETP* is the height equivalent to a theoretical plate that represents the mass transfer efficiency of a packed column; H_{OV}, H_L and H_V are the overall, liquid side and vapor side height of transfer units; N_{OV}, N_L and N_V are the overall, liquid side and vapor side number of transfer units and Λ is the stripping factor. Eqs. (1)–(4) describe the change in efficiency with physical properties, vapor–liquid equilibrium and the column internals for both trays and packing. 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 present in Eqs.