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RATE-BASED MASS TRANSFER PERFORMANCE ANALYSIS OF [EMIM][EtSO4] AND ETHYLENE GLYCOL IN THE EXTRACTIVE DISTILLATION OF WATER-ETHANOL MIXTURES

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Abstract

The mass transfer efficiency of an extractive distillation column was compared for the ionic liquid 1-Ethyl-3-methylimidazolium ethyl sulfate and ethylene glycol as solvents for the separation of water-ethanol. A rate based model was established in ASPEN Plus. Tray efficiency profiles along the column showed a reduction in mass transfer performance when the ionic liquid was used due to its relatively high viscosity. Indeed, this reduction was more pronounced when the liquid phase viscosity was increased by means of a higher solvent-to-feed ratio. Finally, a sharp decline in efficiency was observed at high liquid phase viscosities, approaching the flooding point.

Keywords: Rate-based model, Extractive distillation, Ionic liquids, mass transfer efficiency, water-ethanol separation

1. Introduction

Extractive distillation enables the efficient separation of azeotropic or close boiling mixtures by adding a solvent that improves the relative volatility. Figure 1 shows a typical extractive distillation column where the solvent is added at the top. Numerous solvents are available for this purpose, most of them being organic[1] even though several applications have used solid salts[2]. However, organic fluids present several drawbacks such as the often high amount of solvent fed to obtain a desired product concentration, leading to high energy consumption. Ionic liquids arise to replace those volatile solvents because of their high selectivity in separation processes, extremely low vapor pressures, wide liquid range and potential to be reused or recycled. Several experimental studies have demonstrated their potential use in extractive distillation and their ability to improve relative volatilities of mixtures[3-5]. However, despite of their merits, ionic liquids show high viscosities (up to 100 mPa.s) compared to common organic solvents (1 – 10 mPa.s).

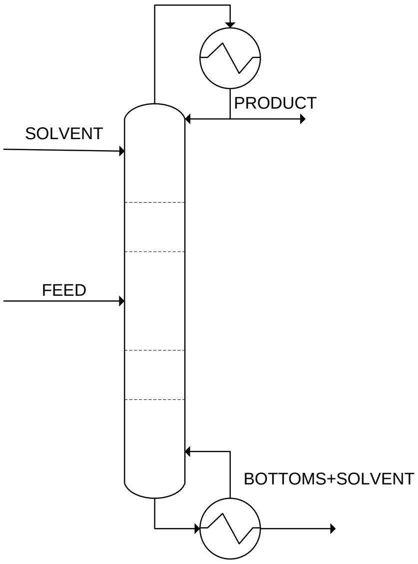


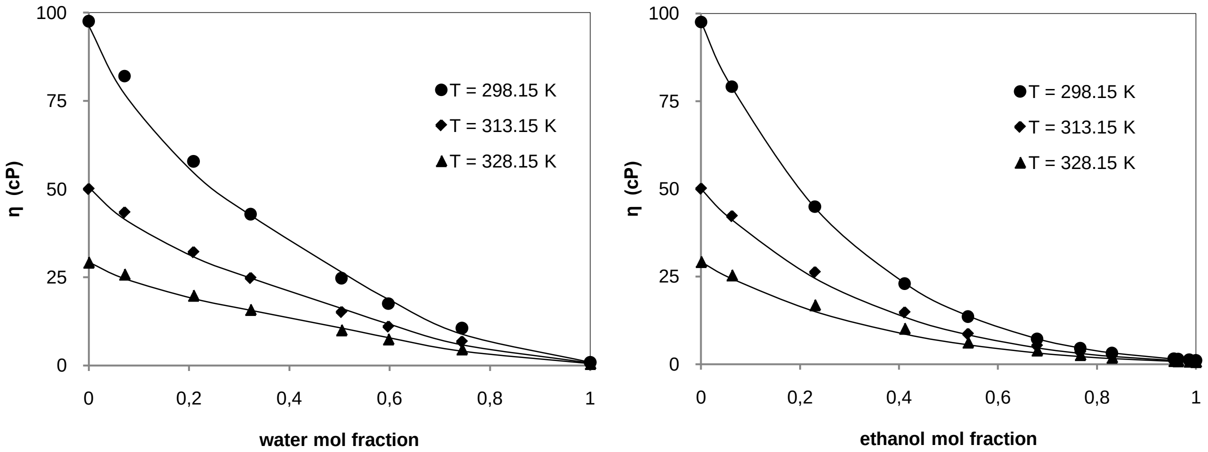
Figure 1. Extractive distillation column

The aim of this work is to compare the effect of solvent properties of the ionic liquid 1-Ethyl-3-methylimidazolium ethyl sulfate, [EMIM][EtSO4], and a commonly used organic fluid, ethylene glycol, EG, in the extractive distillation process for water-ethanol mixtures on the mass transfer performance. Given the disadvantages of ionic liquids, this work concentrates on the effect of solvent viscosity on mass transfer efficiency. Weiss and Arlt[6] found experimentally a decrease in efficiency, for valve and bubble caps trays, related to the solvent concentration in the column, resulting from an increase in viscosity. Since the evidence about this phenomena in extractive distillation is scarce, it is particularly important to quantify to what extent the ionic liquid viscosity can affect the mass transfer efficiency. Rate-based or non-equilibrium modeling[7] allows to predict these mass transfer efficiencies in multi-component distillation processes, which it is not possible using equilibrium stage models.

2. Case study

Extractive distillation is a multi-component separation process. Therefore, in order to obtain mass transfer efficiency results, reliable ternary-VLE data have to be collected. However, when the rated-based model is used, physical and transport properties must be provided additionally. Many thermodynamic works are available lately, but transport property data are still poor and even more critical when mixture transport properties are needed.

Several ionic liquids have been proposed[3,8] for water-ethanol separation according to their VLE performance, but only [EMIM][EtSO4] has been widely studied, hence it is possible to obtain both ternary VLE[9] and physical/transport properties[10-14]. ASPEN plus (Rate-based) is used to perform extractive distillation simulations and it provides alternatives to include new chemical components through correlation of experimental data. Figure 2 shows the regression results of experimental data[14] with the ASPEN model for liquid viscosity in binary mixtures.



(a) (b)

Figure 2. ASPEN data regression for liquid viscosity in binary mixtures with [EMIM][EtSO4].

Average errors of the regression are 5.08% for the water-[EMIM][EtSO4] mixture (Figure 2.a) and 2.72% for the ethanol-[EMIM][EtSO4] mixture (Figure 2.b). Additionally, a quadratic mixing rule was used to correlate the liquid density in mixtures, giving errors less than 0.2%. Mixing rules were used in absence of some experimental data. For surface tension and thermal conductivity, the modified Mc-Leod Sudgen and Li relations were used respectively. These relations give errors between 5 and 10%. Liquid phase diffusion coefficients were estimated by using the Wilke-Chang method. The predictions of these mixing rules give satisfactory results in a wide range of temperatures and concentrations. The Ternary liquid phase non-ideality is correctly represented by NRTL model[3,9].

Additionally, column internals have to be defined. Specifications of a typical column simulation are given in Table 1. Finally, mass transfer, heat transfer and interfacial area are given by Chan and Fair (Sieve trays)[15], Chilton-Colburn analogy and Zuideweg[16] respectively.

Table 1. Column specification

Specification	Column parameters
Column Internals	Sieve trays
Tray spacing (m)	0.61
Weir height (mm)	50
Deck thickness	10 gauge
Hole area to active area	0.12
Hole diameter (mm)	2.85
Number of passes	1
Vapor flow type	Vapor plug
System foaming factor	No foam
Flooding calculation	80%

3. Results

3.1 Column design

Table 2 compares the most important features of both solvents. Although [EMIM][EtSO4] enhances the relative volatility (α) better than ethylene glycol, whose values were calculated just in the azeotropic point of water-ethanol, it has higher viscosity (η), even at higher temperatures.

Table 2. Some features of the solvents

Solvent	α_{12}^{*}	η (cP) T=25 C	η (cP) T=80 C
Ethylene Glycol	1.87	16.75	3.23
[EMIM][EtSO4]	2.33	97.58	14.66

*Calculated when solvent mol fraction is $x_{solvent}$ = 0.2, where Σx_i=1, at the water-ethanol azeotropic composition.

Before comparing efficiencies for both solvents, column design calculations have been done. These involve the determination of the number of stages, reflux ratio, solvent-to-feed ratio and column diameter. For this purpose there are shortcut methods[17,18], based on non-equilibrium stage[19] and repeated performance simulations by using the rigorous model. Aspen Plus provides a powerful tool to solve the complete rate based model and performs design calculations even though it is more intensive and, therefore, the last method was chosen. Table 3 shows the design results for both columns:

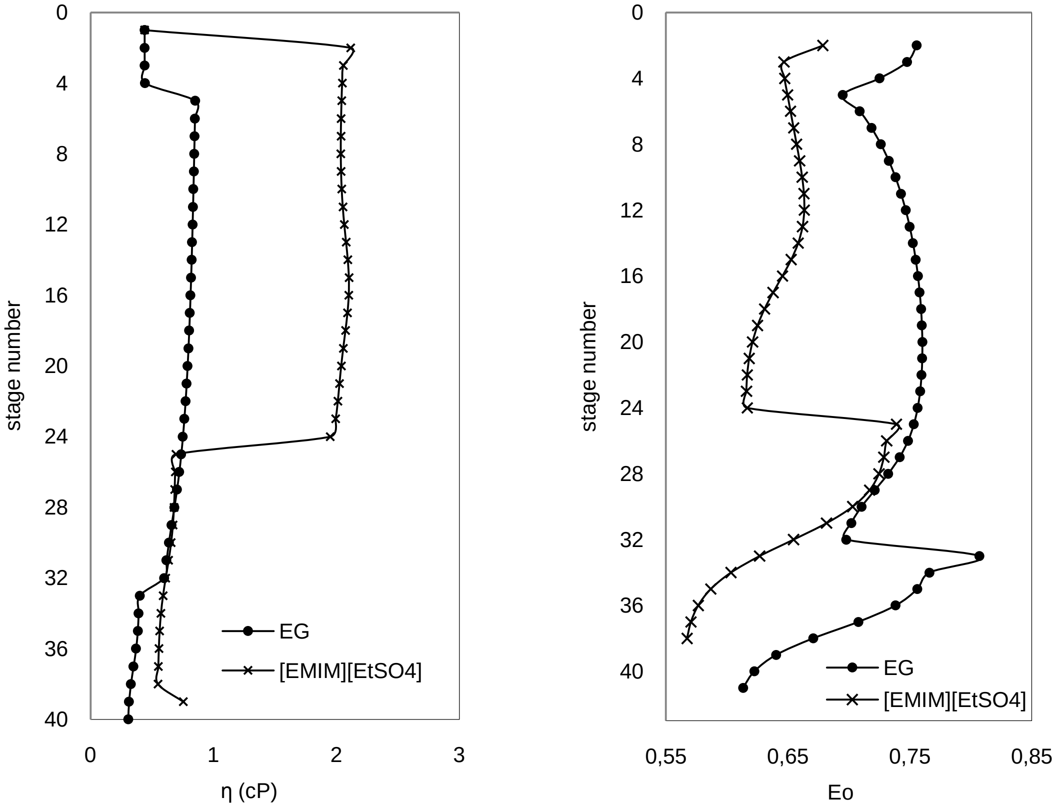
Table 3. Column design results

Parameter	EG	[EMIM][EtSO4]
Number of actual stages	42	39
Reflux ratio	1.07	1.11
Solvent-to-feed ratio (S/F)	0.12	0.12
Feed stage	33	25
Solvent stage	5	2
Column diameter (m)	0.157	0.155
Reboiler duty (kW)	61.36	59.32

The base calculations were performed for 10 kmol/hr of feed, containing 80% water and 20% ethanol (mol) at 50ºC. The distillate-to-feed ratio was set at 0.2 to obtain 99.8% (mol) of ethanol at the top of the column. The results in Table 3 show that when the ionic liquid is used as solvent, less real stages are needed at the same solvent-to-feed ratio to achieve the ethanol purity, because [EMIM][EtSO4] has a stronger effect on the relative volatility. However, the differences of those parameters are not significant. On the other hands, reflux ratio if slightly higher when the ionic liquid was used as solvent. It is because higher liquid flow was observed in this extractive distillation column. Feed stages have been chosen considering the minimum energy consumption at the reboiler, where minimum differences in energy consumption can be seen. Moreover, similar column diameters were obtained for both solvents at 80% flooding.

3.2 Mass transfer performance

To compare both solvent performances, the tray efficiency concept was adopted where the number of transfer units was used for its calculations[7]. Figure 3 shows (a) liquid phase viscosity and (b) tray efficiency (Eo) profiles along the extractive distillation columns. The stage numbering starts at the top of the column.



(a) (b)

Figure 3. (a) Liquid phase viscosity and (b) tray efficiency profiles in both extractive distillation column for S/F = 0.12

Figure 3.a illustrates the effect of ionic liquid viscosity on the liquid phase viscosity profiles in the column. This behavior is clearer in the extractive section. Here the ionic liquid concentration is higher than in the stripping section where it is diluted by the feed flow. As consequence of the high viscosities, the tray efficiency decreases along the extractive distillation column (Figure 3.b). Since the viscosity of [EMIM][EtSO4] is 5 – 6 times higher than the viscosity of EG, the average tray efficiency has decreased approximately 11%. However, this reduction can be even stronger at higher solvent-to-feed ratios.

Figure 4 shows the average tray efficiency at different solvent-to-feed ratios. When the amount of solvent increases the average tray efficiency decreases in both extractive distillation columns. However, this effect is more pronounced when [EMIM][EtSO4] is used as the solvent. Moreover, the efficiency line for the ionic liquid is shorter. This is explained in Figure 5.a where a strong decline in tray efficiency as function of viscosity is observed.

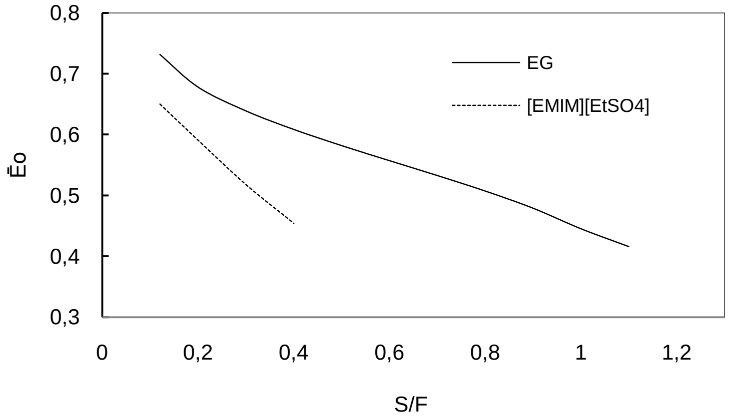
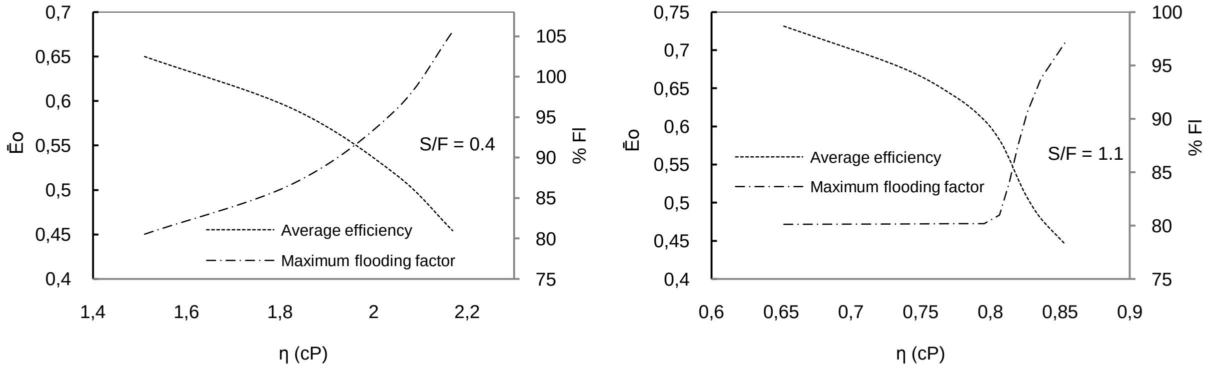


Figure 4. Average tray efficiency as function of the solvent-to-feed ratio for both extractive distillation columns

An increment in the solvent-to-feed ratio increases the liquid phase viscosity because the ionic liquid concentration is higher in the column. Additionally, more liquid is present in the column raising the vapor velocity and reaching the maximum column capacity. Although the same situation occurs when ethylene glycol is used as solvent (Figure 5.b), where lower viscosities can be seen, the flooding point is reached at a lower solvent-to-feed ratio when the more viscous ionic liquid is used.



(a) (b)

Figure 5. Average tray efficiency and flooding as function of viscosity for (a) [EMIM][EtSO4] as solvent and (b) Ethylene glycol.

4. Conclusions

In conclusion, the mass transfer performance of the ionic liquid 1-Ethyl-3-methylimidazolium ethyl sulfate has been compared with the common solvent ethylene glycol in the extractive distillation of water-ethanol mixtures by using rate based modeling. The ionic liquid used here is one of the most studied for water-ethanol separation, but it shows a relatively low increase in relative volatilities with regard to ethylene glycol. Even so, the high liquid phase viscosities caused by this ionic liquid in the column produced a decrease in mass transfer performance of roughly 11%. Moreover, high ionic liquid concentrations can lead to a marked reduction in tray efficiency and capacity of the extractive distillation column.

Acknowledgements

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References

1. Z. Lei, Ch. Li and B. Chen, *Separation and Purification reviews,* 32(2003) 121-213
2. M. Llano-Restrepo and J. Aguilar-Arias, *Computers and Chemical Engineering,* 27(2003) 527-549
3. Y. Ge, L. Zhang, X. Yuan, W. Geng and J. Ji, *J. Chem. Thermodynamics*, 40(2008) 1248-1252
4. L. Zhang, J. Han, D. Deng and J. Ji, *Fluid Phase Equilibria*, 255(2007) 179-185
5. L. Zhang, B. Qiao, Y. Ge, D. Deng and J. Ji, *J. Chem. Thermodynamics*, 41(2009) 138-143
6. S. Weiss and R. Arlt, *Chem. Eng. Process.*, 21(1987) 107-113
7. R. Taylor and R. Krishna, *Multicomponent Mass Transfer*, John Wiley & Sons, Inc. (1993) 371-434
8. J. Wang, Ch. Li, Z. Wang, Z. Li and Y. Jiang, *Fluid Phase Equilibria*, 255(2007) 186-192
9. N. Calvar, B. González, E. Gómez and Á. Domínguez, *J. Chem. Eng. Data,* 53(2008) 820-825
10. R. Ge, C. Hardacre, P. Nancarrow and D. Rooney, *J. Chem. Eng. Data*, 52(2007) 1819-1823
11. R. Gardas and J. Coutinho, *AiChE J.*, 55(2009) 1274-1290
12. Z. Zhang, Z. Tan, L. Sun, Y. Jia-Zhen, X. Lv and Q. Shi, *Thermochimica Acta*, 447(2006) 141-146
13. J. Valderrama, W. Sanga and Lazzús, *Ind. Eng. Chem. Res.*, 47(2008) 1318-1330
14. E. Gómez, B. González, N. Calvar, E. Tojo and Á. Domínguez, *J. Chem. Eng. Data*, 51(2006) 2096-2102
15. H. Kooijman and R. Taylor, *The Chemical Engineering Journal*, 57(1995) 177-188
16. F. Zuiderweg, *Chemical engineering Science*, 37(1982) 1441-1464
17. S. Levy and F. Doherty, *Ind. Eng. Chem. Fundam.*, 25(1986) 269-279
18. P. Tiverios and V. Van Brunt, *Ind. Eng. Chem. Res.*, 39(2000) 1614-1623
19. S. Agarwal and R. Taylor, *Ind. Eng. Chem. Res.*, 33(1994) 2631-2636