Acetone-Methanol Mixture Separation by Extractive Distillation Using 1-Allyl-3-Methylimidazolium Chloride

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Acetone with methanol form a minimum boiling point azeotrope. To separate the mixture components, extractive distillation in the presence of new ionic liquid, 1-allyl-3-methylimidazolium chloride ([Amim]Cl), was assumed. The aim of the present study was the design of an extractive distillation column (number of theoretical stages, position of input stages, reflux ratio) in which acetone with the purity of 99.5 mole % is obtained at the minimum heat duty of the column reboiler. Higher acetone–methanol separation efficiency of [Amim]Cl in comparison with e.g. 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [Emim][triflate] IL was reflected in the resulting parameters of the optimised extractive distillation column: for solvent to feed ratio of 0.42, the number of theoretical stages of the extractive distillation column was 13 and the reflux ratio was 0.1. Heat demand in the reboiler of the extractive distillation column was about four times lower than that in the extractive distillation column employing [Emim][triflate] solvent. Based on the obtained results, [Amim]Cl seems to be a very good solvent for the acetone–methanol azeotropic mixture separation.

1. Introduction

Acetone and methanol are compounds frequently used in the chemical industry but also in the household. In industry, acetone is used as a solvent for various plastic materials and synthetic fibers. Methanol is a raw material in the production of several chemicals and it is also considered as an alternative fuel. Mixtures of acetone and methanol appear in the chemical industry quite frequently, e.g. as side products in biochemical processes, pharmaceutical industry or in the Fisher–Tropsch synthesis.

Taking into account the utility of individual components, separation of acetone–methanol mixtures is meaningful. In general, one of the processes used for azeotropes breaking is extractive distillation applying a convenient extraction solvent. Considering large expenses connected with distillation processes, it is advisable to find a solvent that allows minimising capital and operation expenditures of this separation process. As an interesting alternative to traditional solvents, ionic liquids (ILs) were suggested (Gutierrez et al., 2013). In recent decades, ILs became very popular solvents in chemical industry. Not considering other beneficial properties of ILs, solely their negligible volatility makes them a very attractive solution of several challenges in chemical technology, e.g. in the development of fuel cells (Earle et al., 2006).

Ionic liquids composed of complex cations and anions possess interesting physical-chemical properties. Especially, the large variability of ILs components and fine tuning of their properties are very attractive for chemical industry in terms of process efficiency optimisation and minimisation of the respective expenditures (Pereiro et al., 2012). Ionic liquids are non-volatile, non-flammable, chemically and thermally stable salts and are classified as practically non-toxic. Low toxicity of ILs makes them interesting also in environmental applications as ecologic alternatives in various processes. In comparison with inorganic salts, ILs are less corrosive.

In chemical industry, ionic liquids are employed as alternative solvents due to their ability to increase separability of components with close boiling points, i.e. those forming mixtures with low relative volatility or azeotropes. Thanks to their practical non-volatility, ILs can be readily regenerated (Lei et al., 2003).

Although ionic liquids are more expensive than traditional solvents, they have higher separation efficiency, which allows reducing annual costs of the extractive distillation column operation and, thanks to their almost

zero saturated vapour pressure, also to reduce the costs of solvent recovery and the expenditures of the entire separation process.

Extraction solvent, IL, regeneration is a vital part of the separation process. Negligible volatility of ILs in comparison with traditional (organic) solvents is manifested in their simpler regeneration. Different procedures of ILs regeneration, simple distillation, distillation coupled with stripping with cold or hot nitrogen as well as with supercritical CO_2, were studied by Meindersma et al. (2016). Experimental testing of imidazolium-based ionic liquids regeneration was carried out in a laboratory vacuum film evaporator (Graczová et al., 2020).

The presented study is a continuation of a previous work (Graczová et al., 2017a) dealing with the separation of methyl acetate–methanol azeotropic mixture and acetone–methanol mixture (Graczová and Vavrušová, 2018) in the presence of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([Emim][triflate]) as an entrainer. In the present study, design calculations of an extractive distillation column for acetone–methanol mixture separation in the presence of 1-allyl-3-methylimidazolium chloride [Amim]Cl are presented. Simulation results are compared to those obtained using [Emim][triflate] IL and presented in the study by Graczová et al. (2018). Purity of extraction solvent in the extractive distillation column affects the column operation and, also the optimum operation conditions. The present study is focused also on the regenerated solvent composition effect on product purity.

2. Selection of ionic liquid

Between 2007 and 2018, several imidazolium-based ionic liquids were tested to separate the acetone–methanol mixture (Graczová et al., 2018). Review of ILs recently tested in the acetone–methanol mixture separation is given in Table 1.

Table 1: Overview of ionic liquids used in acetone–methanol separation by extractive distillation; x_3 – mole fraction of IL in ternary mixture, at which the acetone–methanol azeotrope disappeared

Abbreviation of IL	Systematic name of IL	x_3	Reference
[Emim][triflate]	1-ethyl-3-methylimidazolium trifluoromethanesulfonate	0.078	Orchillés et al. (2007)
[Emim][Ac]	1-ethyl-3-methylimidazolium acetate	0.100	Orchillés et al. (2012)
[Emim] [Br]	1-ethyl-3-methylimidazolium bromide	0.050	Orchillés et al. (2012)
[Emim][DCA]	1-ethyl-3-methylimidazolium dicyanoamide	0.050	Seiler et al. (2002)
[Emim][BF$_4$]	1-ethyl-3-methylimidazolium tetraboroflorate	0.100	Chen et al. (2015)
[Emim][DEP]	1-ethyl-3-methylimidazolium diethylphosphate	0.050	Li et al. (2014)
[Amim][Br]	1-allyl-3-methylimidazolium bromide	0.020	Li et al. (2018)
[Amim][Cl]	1-allyl-3-methylimidazolium chloride	0.020	Li et al. (2018)
[Pmim][Br]	1-propyl-3-methylimidazolium bromide	0.020	Li et al. (2018)
[Hmea][Cl]	monoethanolamine chloride	0.100	Orchilles et al. (2011)
[Hmea][Ac]	monoethanolamine acetate	0.100	Kurzin et al. (2007)
[Bmim][Br]	1-butyl-3-methylimidazolium bromide	0.060	Orchillés et al. (2012)
[Bmim][triflate]	1-butyl-3-methylimidazolium trifluoromethanesulfonate	0.055	Orchillés et al. (2012)
[bpy][PF$_6$]	*n*-butylpyridinium hexafluorophosphate	0.100	Kurzin et al. (2007)
[Mim][Ac]	1-methylimidazolium acetate	0.060	Li et al. (2017)
[Mim][HPr]	1-methylimidazolium 2-hydroxypropionate	0.060	Li et al. (2017)
[Mmi][Pr]	1-methylimidazolium propionate	0.060	Li et al. (2017)

Recently, Li et al. (2018) recommended 1-allyl-3-methylimidazolium chloride, [Amim]Cl, as an excellent extraction solvent for the acetone–methanol mixture separation. It was found that [Emim][triflate] is capable of splitting the acetone–methanol azeotrope at concentrations as low as 7.8 mole % of IL in its ternary mixture with the above azeotrope. In case of [Amim]Cl, even lower IL content, 2 mole %, enables acetone–methanol azeotrope breaking. Selectivity of [Amim]Cl towards the acetone–methanol mixture is by approximately 50 % higher in comparison with that of [Emim][triflate]. [Amim]Cl efficiency in separation of the mixture of interest is expected to be high.

3. Separation process in the presence of [Amim]Cl

Principal goal of the design calculations was to suggest construction and operation parameters of an extractive distillation column for acetone–methanol mixture separation while obtaining practically pure acetone (purity of 99.5 mole % and higher). Design calculations and optimisation of the extractive distillation column operation for acetone–methanol mixture separation in the presence of [Amim]Cl were carried out according to the procedure introduced by Graczová et al. (2018). Vapour–liquid equilibrium of the acetone–methanol–[Amim]Cl ternary system was expressed in terms of the extended Raoult´s law assuming ideal behavior of the

vapour phase. Activity coefficients of the mixture components in the liquid phase were computed using the original NRTL equation (Renon and Prausnitz, 1968) with the parameters taken from the paper by Li et al. (2018).

3.1 Design calculation of the extractive distillation column

Parameters of feed and solvent entering the modelled distillation column are summarised in Table 2. Basis of calculations is the molar flow of feed, $\dot{n}_F$ = 10 kmol h^{-1}. Composition of feed, x_{Fi}, was similar to that of the acetone (A)–methanol (M) azeotropic mixture and its temperature, t_F, to that of the azeotrope boiling point. In the initial simulation, the use of pure extraction solvent, x_S = 1, was assumed. Temperature of solvent entering distillation column, t_S, was the same as that at the solvent input stage. Molar flow of extraction solvent was defined in terms of specific extraction solvent demand, $\dot{n}_S/\dot{n}_F$.

Table 2: Initial input data used for simulation and optimisation of the extractive distillation column operation

$\dot{n}_F$ (kmol h^{-1})	x_{FA}	x_{FM}	$t_F/°C$	$\dot{n}_S/\dot{n}_F$	x_S	$t_S/°C$
10	0.78	0.22	57.97	0.42	1.00	60

Optimisation procedure was carried out in several inosculating cycles that yielded optimum values of the following parameters: N – the number of column theoretical stages, R – reflux ratio, f_F – feed input stage position and $\dot{n}_S$ – extraction solvent demand. The same optimisation method has been applied previously (Graczová and Vavrušová, 2018) and its detailed description is given in the paper by Graczová and Steltenpohl (2015).

The first optimisation step was carried out to estimate the number of theoretical (equilibrium) stages and the value of the optimum reflux ratio. The optimisation constraint applied was the purity of acetone in distillate from the extractive distillation column, x_D = 0.995. Minimum reflux ratio was low, and optimum reflux ratio varied between 0.3 and 0.7 for the column with 18 theoretical stages.

Sensitivity analysis was carried out to assess variation of the distillate (acetone) purity with the number of column theoretical stages and the reflux ratio for the preset specific extraction solvent demand of $\dot{n}_S/\dot{n}_F$ = 0.42 (Figure 1a). In continuation, the effect of specific extraction solvent demand on the distillate purity was investigated assuming different reflux ratio values for the preset number of column theoretical stages N = 18 (Figure 1b).
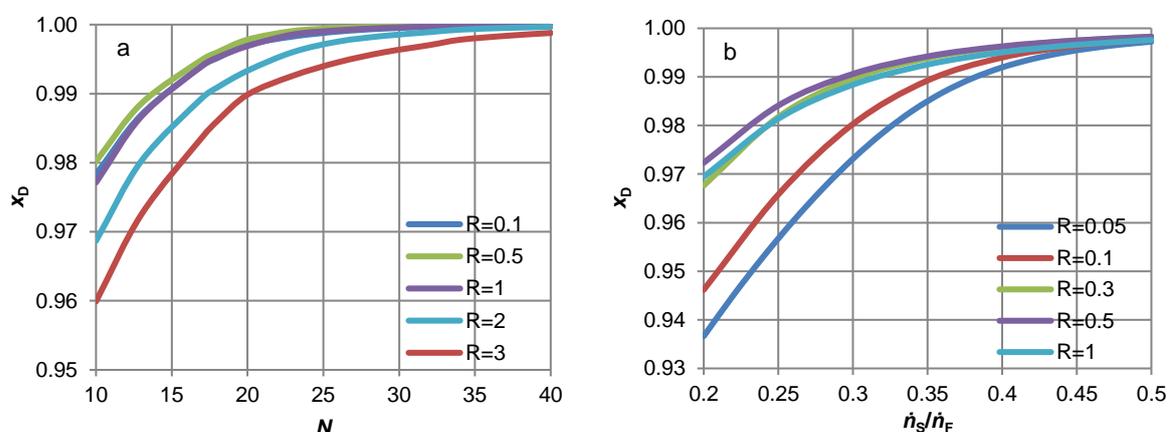

Figure 1: Effect of simulation conditions on the distillate purity at different values of reflux ratio: effect of the number of theoretical stages (a) and specific extraction solvent demand (b)

During the reflux ratio optimisation, the number of theoretical stages and specific extraction solvent demand as well as reboiler heat duty, Q_W, were considered (Figure 2a). It was observed that the value of reboiler heat duty in the extractive distillation column is primarily affected by the position of the feed input stage, f_F. Sensitivity analysis regarding the effect of feed input stage on the reboiler heat duty was also carried out (Figure 2b).

Analyzing Figure 2b, the relative position of feed input stage in the extractive distillation column, f_F/N, from the interval of 0.55–0.75, showed the lowest reboiler heat duty. Consequently, optimum f_F/N value of 0.67 was used in further simulations. In comparison with the simulations with [Emim][triflate] IL as the extraction solvent,

the position of feed input stage for [Amim]Cl was shifted to higher f_F/N values, i.e. feed input stage for simulations with [Amim]Cl as extraction solvent is situated closer to the column bottom.
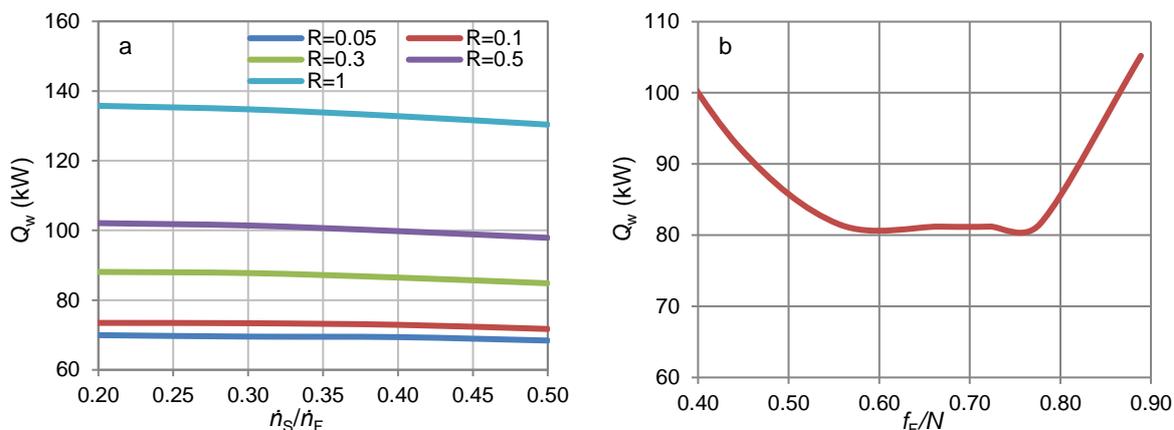

Figure 2: Effect of simulation conditions on the reboiler heat demand: effect of specific extraction solvent demand at different values of reflux ratio (a) and feed input stage position in extractive distillation column (b)

Considering the value of the reboiler heat demand, reflux ratio and the number of theoretical stages of the extractive distillation column can be effectively lowered. Repeated optimisation of the column construction and operation parameters allowed decreasing the reflux ratio from 0.3 to 0.1 and the number of column theoretical stages from 18 to 13. Feed input stage position was $f_F = 8$. At these conditions, the calculated value of the reboiler heat demand dropped from 94 kW to 67 kW.

3.2 Comparison of [Emim][triflate] and [Amim]Cl

Table 3 summarises optimum (see chapter 3.1) parameters of extractive distillation columns for acetone–methanol azeotrope separation in the presence of two ionic liquids, [Emim][triflate] (Graczová and Vavrušová, 2018) and [Amim]Cl (present study). Comparison of these parameters showed several advantages of the latter extraction solvent use in acetone–methanol mixture separation. In case when [Amim]Cl is used as the extraction solvent, smaller column (lower number of theoretical stages) and lower reflux ratio are required compared to the situation when [Emim][triflate] is employed to break the acetone–methanol azeotrope. Based on these observations, separation of the chosen mixture in the presence of [Amim]Cl can be assumed to be associated with lower investment as well as operation costs in comparison with those computed for the less efficient extraction solvent, [Emim][triflate].

Table 3: Comparison of selected construction and operation parameters of extractive distillation column for acetone–methanol mixture separation in the presence of two ionic liquids at atmospheric pressure

Parameter	Extraction solvent used in separation	
	[Emim][triflate]	[Amim]Cl
$\dot{n}_F$ (kmol h^{-1})	10	
x_{FA}	0.78	
x_{FM}	0.22	
t_F (°C)	57.97	
t_F/N	0.38	0.67
$\dot{n}_S/\dot{n}_F$	0.45	0.42
x_S	1.00	
t_S (°C)	60	
f_S	3	2
N	43	13
R	3.3	0.1
Q_W (kW)	301	67

3.3 Use of regenerated IL in extractive distillation

Considering ecological burden minimisation and efficient utilisation of all components of the original feed and extraction solvent, methanol should be separated from the extractive distillation bottom product and regenerated IL reused in extractive distillation. Complete recovery of methanol from its mixture with IL is economically inconvenient. Regenerated IL will contain a small amount of methanol. The effect of impurities content on the extractive distillation column performance is given in Figure 3. In these simulations, variation of the distillate (acetone) purity with the methanol content in regenerated IL was investigated at different reflux ratios. All other simulation conditions were kept constant (see Table 3).
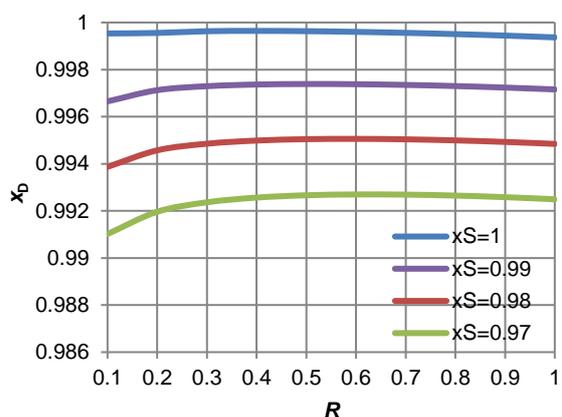

Figure 3: Effect of solvent purity on the composition of distillate from extractive distillation column at different reflux ratio values. Column parameters and operation conditions: $N = 18$, $f_S = 3$, $f_F/N = 0.67$ and $\dot{n}_S/\dot{n}_F = 0.42$

From Figure 3 it is clear that purity of the extraction solvent plays an important role in the acetone–methanol azeotrope breaking. While increasing the content of impurities (methanol) in the regenerated ionic liquid, a column with higher number of theoretical stages and higher reflux ratio is required to reach the preset separation goal at a constant solvent-to-feed mole ratio. If pure IL was used for the acetone–methanol mixture separation, the required purity of methanol was reached in column with $N = 13$ operated at $R = 0.1$. With the IL containing 1 mole % of methanol, the number of theoretical stages and the reflux ratio increased to 14 and 0.2. These values further increased to 18 and 0.5 for IL containing 2 mole % of impurities. If the content of impurities exceeds 2 mole %, the preset purity of acetone in distillate cannot be reached for the given solvent-to-feed mole ratio.

4. Conclusions

An alternative to [Emim][triflate] in the acetone-methanol nearly azeotropic mixture separation by extractive distillation, [Amim]Cl IL, was tested. This new extraction solvent shows better separation efficiency in acetone–methanol azeotrope breaking and makes the chosen separation process less economically demanding and more viable.

Seeing that [Emim][triflate] is not the most appropriate extraction solvent for the acetone–methanol azeotrope separation (extractive distillation column with relatively large number of theoretical stages, $N = 43$, and reflux ratio, $R = 3.3$, is required), new solvent, [Amim]Cl, was tested for its separation ability in this process.

The new extraction solvent, [Amim]Cl, is a promising candidate for the acetone–methanol azeotrope separation. While simulating the extraction column operation, the optimum number of theoretical stages, $N = 13$, and optimum reflux ratio, $R = 0.1$, were obtained. Compared to the column operated using [Emim][triflate] as the extraction solvent, capital expenditures for [Amim]Cl-based extractive distillation column are much lower. Also, costs associated with column operation are only a part of those of acetone–methanol mixture separation using [Emim][triflate], e.g. reboiler heat duty for [Amim]Cl (67 kW) was approximately four-times lower than that for the former extraction solvent (301 kW).

Acknowledgements

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