

# Separation of Methyl Acetate–Methanol Azeotropic Mixture Using 1-Ethyl-3-Methylimidazolium Trifluoromethanesulfonate

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In this work, potential use of ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([Emim][triflate]) in the extractive distillation of a methyl acetate–methanol mixture forming an azeotrope was studied. The primary objective was to design the separation process for the production of highly concentrated methyl acetate. The process is proposed to be run in two distillation columns, an extractive distillation column and a regeneration column for the ionic liquid (IL) solvent recovery.

Within the design calculation of the extractive distillation column, column parameters such as the number of theoretical plates, position of the feed input plate, solvent consumption, and reflux ratio for the required content of methyl acetate (MA) in the distillate (99.5 mole % of MA) were optimized. The objective of the IL regeneration was to obtain highly concentrated IL (more than 99 mole % of IL). For IL regeneration, a distillation column was proposed. Operating conditions of the regeneration column such as pressure and thermal conditions of feed (temperature and vapor-to-liquid mole ratio) were optimized. For the regeneration column, the number of theoretical plates, reflux ratio, and position of the feed input plate were determined. To represent the vapor–liquid equilibrium (VLE) of the ternary system at the atmospheric pressure and binary VLE at reduced pressures, the original NRTL model was used; its parameters were evaluated from the VLE data of the corresponding binaries taken from literature.

Based on the results of columns simulation, heat consumption required in the extractive and regeneration column reboilers and condensers was evaluated. In conclusion, energy-saving alternatives are proposed.

## 1. Introduction

During acetic acid production by methanol carbonylation on industrial scale, a secondary product, methyl acetate, is formed. It is used as volatile non-toxic solvent for adhesives, dyes, and nail varnish removers. On the other hand, methanol is a primarily crude material for the synthesis of several organic compounds and it is also used as fuel for internal combustion engines. In laboratory, it is used as a denaturation agent and as a solvent in spectroscopy due to its low cut-off of ultraviolet radiation.

The methyl acetate–methanol system forms a minimum boiling point azeotrope at atmospheric pressure; which is why its components cannot be separated by ordinary distillation processes. Extractive distillation seems to be more efficient for the separation of this mixture. Anyhow, separation of the methyl acetate–methanol mixture requires the use of an appropriate solvent allowing the azeotrope breaking (Berg and Yeh, 1984). Organic solvents, inorganic salt, and also hyperbranched polymers are the most commonly used solvents for this purpose. Unfortunately, there are several drawbacks connected with the use of these solvents, namely their high cost, lower separation efficiency and problems with pollution. As an alternative to these solvents, ionic liquids (ILs) have been proposed recently (Domańska, 2012). Extractive distillation with ionic liquids (Schuur, 2015) used as the separation agent integrates the advantages of a liquid solvent (easy operation) and solid salt (high separation ability). The remarkable azeotrope breaking capacity of ILs, their almost null volatility at room temperature and the simplicity of their recycling, have granted them recognition as possible sustainable alternatives to conventional solvents (Pereiro, 2012). Thanks to the properties of ILs (mainly their negligible vapor pressure at ambient temperature), the chance of their loss to the atmosphere is

minimum, which reduces environmental issues, increases the ILs' recyclability and reusability thereby minimizing their costs.

As a continuation of our previous work (Graczová and Steltenpohl, 2015) and further work presented in this issue (Graczová et al., 2017), this study is focused on the separation of a methyl acetate–methanol azeotropic mixture in the presence of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([Emim][triflate]) as the entrainer. Together with the base separation column, a regeneration column was also proposed and the working conditions of the columns were optimized.

## 2. Selection of ionic liquid

The aim of this study was to design a distillation column for extractive distillation of an originally binary azeotropic mixture methyl acetate (MA)–methanol (M). MA and M form an azeotrope with the mole composition of  $x(\text{MA}) = 0.67$  at atmospheric pressure. Orchillés et al. (2007) proved that [Emim][triflate] has an obvious effect on VLE of the MA–M system and it can eliminate azeotropes in the whole concentration range (at the IL concentration of about 30 mole %). Based on this information, [Emim][triflate] IL was applied in MA–M separation.

## 3. Physical properties

Saturated vapor pressure variation with temperature for methyl acetate and methanol are well known. For [Emim][triflate], this relation is not known and it had to be predicted. For the prediction of ILs' saturated vapor pressure, the Antoine equation was used, the parameters of which were obtained using the information on the [Emim][triflate] boiling temperature at atmospheric pressure ( $T_b = 662$  K, (Valderrama and Rojas, 2009)) and on the saturated vapor pressure of similar ILs at temperatures from 441 K to 484 K (Zaitsau et al., 2006). Model parameters A, B, and C (see Table 1) were evaluated based on non-linear regression. Coefficients of the Antoine equation for methyl acetate and methanol (valid for a broad temperature range from 5 °C to 224 °C) were taken from Dykyj et al. (1984) and are included in Table 1.

Table 1: Parameters of Antoine equation,  $P_i^\circ$  /kPa

Component	A	B	C
MA	6.19052	1,157.622	219.724
M	7.6278	1,905.90	273.15
[Emim][triflate]	16.786	9,873.91	273.15

Molar heat capacity of [Emim][triflate] was predicted using the contribution method of Chueh and Swanson (Reid et al., 1988),  $c_P = 386.4$  J mol<sup>-1</sup> K<sup>-1</sup> at 20 °C. Temperature variation of heat capacity values for methyl acetate and methanol is readily available in literature (Reid et al., 1988).

## 4. Phase equilibrium of the ternary system

Vapor–liquid equilibrium (VLE) was expressed by the extended Rault's law assuming ideal behavior of vapor and real behavior of liquid phases. For constant temperature and pressure values, the VLE condition is given by the equation:

$$Py_i = \gamma_i x_i P_i^\circ \quad i = 1, 2, 3 \quad (1)$$

$y_i$  and  $x_i$  are the mole fractions of component  $i$  in the vapor and liquid phase, respectively.  $P_i^\circ$  is the saturated vapor pressure of the  $i$ -th component expressed using the Antoine equation Eq(2):

$$\log P_i^\circ = A_i - \frac{B_i}{C_i + t} \quad (2)$$

Activity coefficients,  $\gamma_i$ , were calculated based on the NRTL model equation derived by Renon and Prausnitz (1968):

$$\ln \gamma_i = \frac{\sum_j^n x_j \tau_{ji} G_{ji}}{\sum_j^n x_j G_{ji}} + \sum_k^n \frac{x_k G_{ik}}{\sum_j^n x_j G_{jk}} \left( \tau_{ik} - \frac{\sum_j^n x_j \tau_{jk} G_{jk}}{\sum_j^n x_j G_{jk}} \right) \quad (3)$$

Binary parameters  $\tau_{ij}$  and terms  $G_{ij}$  are defined by as follows:

$$\tau_{ij} = \frac{\Delta g_{ij}}{RT} \quad G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad i, j = 1, 2, 3 \quad i \neq j \quad (4)$$

where  $\tau_{ij} \neq \tau_{ji}$ ,  $\tau_{ii} = \tau_{jj} = 0$ ,  $G_{ii} = G_{jj} = 1$ ,  $R$  is the universal gas constant,  $\Delta g_{ij}$  are binary interaction parameters, and  $\alpha_{ij}$  is the non-randomness parameter of the NRTL model equation.

The binary interaction parameters  $\Delta g_{ij}$  of the original NRTL equation for the ternary system methyl acetate (MA)–methanol (M)–[Emim][triflate] were evaluated from binary VLE data published by Orchillés et al. (2007) and are presented in Table 2.

Table 2: Parameters of the NRTL equation and mean deviation of temperature and mole fraction in the liquid phase

Components	$\Delta g_{ij}/\text{J mol}^{-1}$	$\Delta g_{ji}/\text{J mol}^{-1}$	$\alpha_{ij}$	$d_x$	$d_t/^\circ\text{C}$
MA–M	1,498.47	1,550.07	0.300	0.0016	0.03
MA–[Emim][triflate]	11,551.37	–3,496.56	0.300	–	0.21
M–[Emim][triflate]	–3,527.02	1,017.57	0.300	–	0.11

## 5. Design of the separation process

The azeotropic mixture to be separated consists of 67 mole % of MA and 33 mole % of methanol. As the extraction solvent, ionic liquid ([Emim][triflate]) was used with purity of 99.5 mole %. The desired purity of methyl acetate was 99.5 mole % and that of methanol in the regeneration column of 99.5 mole %.

Conceptual design scheme of the separation of the system methyl acetate–methanol in the presence of an IL is given in Figure 1. The separation process was designated for two distillation columns: basic extractive distillation column (I) operated at atmospheric pressure, and distillation column (II) for the solvent recovery operated at a reduced pressure,  $P = 20$  kPa.

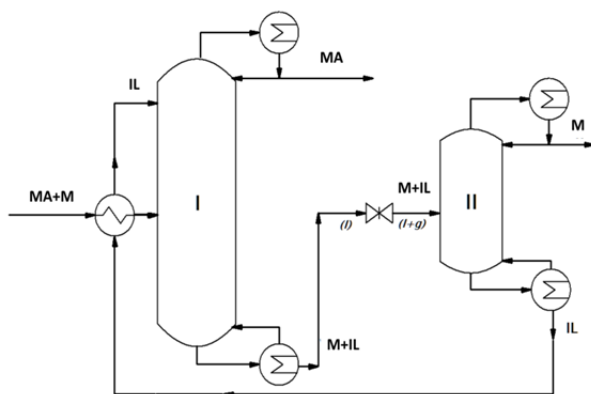


Figure 1: Conceptual scheme of extractive distillation of the methyl acetate (MA)–methanol (M) mixture in the presence of [Emim][triflate] (IL): I – extractive distillation column, II – regeneration column.

The feed and IL-solvent streams enter the extractive distillation column (I). Methyl acetate product is obtained at the column (I) head. The bottom product from column (I), which is a binary mixture of methanol and IL passes through a throttle valve into the recovery column (II). In the recovery column, as head and bottom products methanol and IL are obtained, respectively. IL from the recovery column (II) is returned to the extractive distillation column (I). Optimization criterion for the column operation was set as the purity of the top product obtained in the basic distillation column (MA purity higher than 99.5 mole %).

The aim of the design calculation of extractive distillation column (I) was to optimize the column parameters such as the number of theoretical plates ( $N$ ), solvent consumption ( $n_s$ ), position of the feed input plate ( $f_1$ ), and reflux ratio ( $RR$ ); for column II, to determine the type of the column, the number of theoretical plates ( $N$ ), reflux ratio ( $RR$ ), and position of the feed input plate ( $f$ ). The calculations were carried out in a proprietary program constructed in Matlab® capable of solving a set of material balance equations together with a vapor–liquid equilibrium relation of the ternary system. Parameters of the distillation columns were optimized in some computation steps described in a previous study (Graczořová and Steltenpohl, 2015).

### 5.1 Design calculation of the extractive distillation column

The basic extractive distillation column operates at atmospheric pressure. Molar flow of the feed ( $10 \text{ kmol h}^{-1}$ , containing 67 mole % of MA and 33 mole % of methanol) entered column (I) as a boiling liquid at  $53.2 \text{ }^\circ\text{C}$  (it corresponds to the thermal condition of the feed  $q_1 = 1$ ). IL solvent is fed to column (I) as subcooled liquid at  $64.0 \text{ }^\circ\text{C}$ . The solvent feed stage position was set to be constant,  $f_2 = 2$ , in all calculations.

The solvent to feed mole ratio ( $n_S/n_F$ ) directly influences the purity of the distillate. In the first step of the simulation, the optimal value of this parameter had to be determined taking into account the required purity of the MA product. Sets of calculations were carried out for a column with different number of theoretical plates ( $N$ ), and reflux ratios ( $RR$ ), the solvent consumption varied from  $5 \text{ kmol h}^{-1}$  to  $10 \text{ kmol h}^{-1}$ . In the second step, for the calculated  $n_S/n_F$  ratio equal to 1.1, the values of reflux ratio ( $RR$ ), number of theoretical plates ( $N$ ), and feed stage position ( $f_1$ ) were optimized. Results of the simulations are shown in Table 3. Optimum values of parameters  $RR$ ,  $N$ , and  $f_1$  were selected with respect to the required purity of MA.

Table 3: Calculated parameters of extractive distillation column (I)

$N$	$RR$	$f_1$	$f_2$	$n_S/n_F$
20	1.3	10	2	1.1

In the third step, the temperature profile and concentration profiles of individual components in liquid and vapor phases were calculated for the optimum column parameters. Information about the head and bottom products of the extractive distillation column are summarized in Table 4.

Table 4: Calculated data for the separation of the MA–M–[Emim][triflate] mixture in extractive distillation column (I) at  $P = 101.3 \text{ kPa}$

	Feed	Solvent	Distillate	Bottom product
Molar flow rate / $\text{kmol h}^{-1}$	10.0	11.06	6.70	14.36
Mole % MA	67	–	99.81	0.09
Mole % M	33	0.5	0.19	23.29
Mole % IL	–	99.5	–	76.62
Temperature / $^\circ\text{C}$	53.2	64.0	56.5	127.8

At the head of extractive distillation column (I), the required purity of MA in the vapor phase ( $y_{1MA} = 0.9981$ ,  $y_{1M} = 0.0019$ ,  $t_D = 56.9 \text{ }^\circ\text{C}$ ) was obtained. No IL was present in the vapor phase. Bottom product was obtained at the temperature of  $127.8 \text{ }^\circ\text{C}$ , and it contained methanol, ionic liquid, and a small amount of MA ( $x_{WMA} = 0.0009$ ).

### 5.2 Design calculations of the regeneration process

Bottom product from the column (I) (Table 4) was used as feed for the regeneration column (II). Despite of the negligible MA content in the bottom product from the column (I), separation of the ternary mixture MA–M–[Emim][triflate] in the column (II) was considered.

Since the boiling point of [Emim][triflate] at atmospheric pressure is  $387.8 \text{ }^\circ\text{C}$ , the solvent regeneration in the distillation column at a reduced pressure was assumed. Therefore, a throttle valve was included between the extractive distillation and the regeneration columns (Figure 1). Throttling of fluids to reduce their pressure is considered to be an isoenthalpy process during which partial evaporation of the originally liquid mixture occurs. Taking into account VLE of the mixture to be separated, vapor phase after throttling is practically pure methanol, while IL prevails in the liquid phase. Fraction of thus obtained vapor phase ( $X$ ) and temperature of the two phase system ( $t$ ) are unknown. The relation between  $X$  and  $t$  can be found by simultaneous solution of material and energy balance equations of the throttle valve together with the VLE relation of the methanol–[Emim][triflate] system at the pressure of the two phase system after throttling.

VLE data of the binary system methanol–[Emim][triflate] were measured at atmospheric pressure only (Orchillés et al., 2007). Equilibrium data of this system at the reduced pressure had to be predicted by extrapolation of the data obtained at  $P_{atm}$  to the reduced pressure ( $P$ ).

Calculation of the values of  $X$  and  $t$  is shown in Table 5 for the pressure of  $10 \text{ kPa}$ . For the chosen values of temperature, the vapor fraction was computed either from the enthalpy balance ( $X(EB)$ ) or from the binary VLE ( $X(VLE)$ ). Intercept of these two dependences (Table 5) gives the two phase system temperature of  $t = 112 \text{ }^\circ\text{C}$  and the respective vapor fraction of  $X = 0.18$  for the equilibrium pressure of  $10 \text{ kPa}$  after throttling of the bottom product from the column (I). Similarly, the values obtained for pressures of  $50 \text{ kPa}$ ,  $40 \text{ kPa}$ ,  $30 \text{ kPa}$ , and  $20 \text{ kPa}$  are given in Table 6.

Extrapolation of the data in Table 6 provides parameters for a simple distillation process. By lowering the pressure to 6.85 kPa, the computed value of the vapor fraction ( $X = 0.23$ ) corresponds to the amount of methanol originally present in the feed to the throttling valve. However, for the chosen values of pressure and temperature ( $P = 6.85$  kPa,  $t = 108.2$  °C), the results based on the predicted VLE of the binary system methanol–[Emim][triflate] show that a relatively large portion of methanol (4.51 mole %) still remains in the liquid phase and the IL should be further purified prior to its reuse in the extractive distillation column.

Table 5: Fraction of vapors and temperature of two phase mixture at  $P = 10$  kPa

$t/^\circ\text{C}$	120	110	100	90	80	70
$X(\text{EB})$	0.09	0.21	0.32	0.42	0.52	0.61
$X(\text{VLE})$	0.19	0.18	0.17	0.14	0.11	0.06

Table 6: Calculated vapor fractions and temperatures of two phase mixture at different pressures

$P/\text{kPa}$	101.3	50	30	20	10	6.85*
$t/^\circ\text{C}$	127.8	122.0	117.0	115.4	112.0	108.2
$X$	0.00	0.07	0.12	0.15	0.18	0.23

\*extrapolated data

For the IL regeneration, a distillation column operated at the pressure of 20 kPa was proposed. The vapor–liquid mixture enters the regeneration column at the temperature of 115.4 °C; thermal condition of feed ( $q = 1 - X$ ) is 0.85. For the regeneration column, optimization of the number of theoretical plates ( $N$ ), reflux ratio ( $RR$ ), and position of the feed input plate ( $f$ ) was done. Optimal design and operation parameters of the regeneration column (II) are presented in Table 7, including also information on distillate and bottom product molar flows.

Table 7: Input and calculated operation parameters of the regeneration column (II)

$P/\text{kPa}$	$N$	$R$	$f$	$n_F/\text{kmol h}^{-1}$	$n_D/\text{kmol h}^{-1}$	$n_W/\text{kmol h}^{-1}$
20	3	1.6	2	14.36	3.30	11.06

At the head of regeneration column (II), the required purity of M in the vapor phase ( $y_{1\text{MA}} = 0.9961$ ,  $y_{1\text{MA}} = 0.0039$ ) was obtained at  $t_D = 27.7$  °C. No IL was present in the vapor phase. Bottom product contained concentrated ionic liquid ( $x_{\text{WIL}} = 0.9950$ ) and a small amount of M ( $x_{\text{WM}} = 0.0050$ ). Calculated temperature at the bottom of the regeneration column was 244.0 °C. Very small amount of IL was present here in the vapor phase, saturated vapor pressure of IL at this temperature is about 5 Pa. IL from the regeneration column can be returned to the column (I) and reused in the process (Figure 1).

## 6. Analysis of energy consumption of the separation process

Simplified energetic balance of the proposed separation scheme was carried out with the aim to assess energy consumption of the separation process (Figure 1). For this purpose, enthalpy balances of heat exchangers (reboilers and condensers) of the columns (I) and (II) were considered. Calculations were based on the results of the columns simulation. Computed heat demand of extractive distillation (I) and regeneration (II) columns reboilers were 131.4 kW and 39.3 kW. The cooling demand of condensers at the respective columns' heads was determined assuming the distillate composition in columns (I) and (II) and the corresponding temperatures. Calculated cooling demand of extractive distillation (I) and regeneration (II) columns' condensers were 130.3 kW and 91.5 kW.

## 7. Conclusions

Design calculations of a unit for methyl acetate–methanol separation in the presence of [Emim][triflate] IL were carried out. For original mixture components and the chosen IL, relevant physical properties were found or predicted. For [Emim][triflate], parameters of the Antoine equation and the value of molar heat capacity were obtained. From dependences of the saturated vapor pressure on temperature, heat of vaporization of [Emim][triflate] and MA were predicted. For calculation of the components' activity coefficients, the original NRTL model was used. Parameters of this model were evaluated from the binary VLE data published by Orchillés et al. (2007).

Design calculations of the extractive distillation and regeneration columns were carried out using proprietary computing programs. As design specifications, purity of the products was set to 99.5 mole % of methyl acetate in the distillate from the extractive distillation column and 99.5 mole % of [Emim][triflate] in the bottom product

from the regeneration column. Based on the [Emim][triflate] selectivity in the MA–M mixture separation, its amount in the column (mole ratio  $n_S/n_F = 1.1$ ) was selected. Then, optimal number of theoretical plates ( $N = 20$ ), reflux ratio ( $RR = 1.3$ ), and the position of input plates for feed and extractive solvent ( $f_1 = 10$ ,  $f_2 = 2$ ) were obtained. In the distillate from the extractive distillation column (I), the required content of MA was achieved at the given conditions, while the presence of IL was not noted. Bottom product (methanol and IL) contained only a small amount of MA (0.09 mole %).

Regeneration of the solvent from its mixture with methanol using simple distillation was considered. It was found that this procedure yields IL with relatively high methanol content. Therefore, distillation column for the IL regeneration was proposed and its operation parameters were optimized. Simulations were carried out at the reduced pressure due to the high normal boiling point of pure IL. Pressure reduction was carried out by throttling the bottom product from the extractive distillation column to pressure 20 kPa and the corresponding temperature of 115.4 °C. These conditions were obtained by simultaneous solution of the enthalpy balance equation and VLE. The proposed regeneration column ( $N = 3$ ,  $RR = 1.6$ ,  $f = 2$ ) allowed practically quantitative separation of methanol and [Emim][triflate] IL.

Heating demand in the reboilers amounted to 131.4 kW and 39.3 kW for extractive distillation and regeneration columns, respectively. The calculated cooling duty in condensers was 130.3 kW and 91.5 kW for the two columns considered. Based on these calculations the heat and cooling usage per kg of the produced MA is 1239.4 kJ and 1607.6 kJ, respectively. Enthalpy of the bottom product from the regeneration column has the potential to pre-heat the feed of the extractive distillation column. Moreover, lower operational costs can be achieved when using the bottom product from the regeneration column as an auxiliary heating medium for the extraction distillation column and to pre-heat the feed to this column.

It can be concluded that [Emim][triflate] is a suitable extraction solvent for the methyl acetate–methanol mixture separation, as purity specifications of both methyl acetate and methanol were achieved.

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