

Extractive Distillation of Acetone – Methanol Mixture using 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate

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Acetone and methanol are organic solvents widely used in industry. Acetone with methanol forms a homogeneous minimum-boiling azeotrope which is not separable by conventional distillation processes. A common method for its separation is the extractive distillation in the presence of a selective solvent (such as water). In this paper, the use of an ionic liquid (1-ethyl-3-methylimidazolium trifluoro methanesulfonate [Emim][triflate]) for acetone–methanol separation by extractive distillation was designed. The aim of the design calculation was to obtain acetone with the purity of 99.5 mol % and methanol with the purity of above 99.0 mol %. Calculations were carried out in a proprietary program constructed in Matlab® by solving a set of material balances at individual theoretical stages of the distillation column combined with the vapor–liquid equilibrium (VLE) of the ternary system acetone–methanol–[Emim][triflate]. For the description of VLE of the above mentioned system, the NRTL equation was used. Several optimization cycles were done resulting in optimal parameters of the extractive distillation column (number of theoretical stages, solvent consumption, reflux ratio and position of the feed stage) in regard to the required purity of products (acetone and methanol). Regeneration of ionic liquid was provided by evaporation at the low pressure of 20 kPa. The heat and cooling consumption duties of the designed separation process were analyzed. Regeneration of the ionic liquid is energy-demanding compared to the separation of acetone–methanol in an extractive distillation column. The heat consumption is only 11 % of the heat used up by the whole separation process.

1. Introduction

Acetone and methanol are widely used as solvents or reagents in organic chemistry. Acetone is a good solvent for many plastics and some synthetic fibers. It is used as a solvent in the pharmaceutical industry and as a denaturant in denatured alcohol. Additionally, acetone is also present as an excipient in some pharmaceutical drugs. Methanol is a basic raw material for the synthesis of industrially important organic compounds, such as formaldehyde (and from there into products as diverse as plastics, plywood, paints, explosives, and permanent press textiles), acetic acid, methyl tert-butyl ether (fuel component and replacement for the very volatile diethyl ether), methyl esters in the production of bio-diesel.

Acetone cannot be completely removed from acetone–methanol mixtures by distillation because of the formation of a minimum boiling azeotrope. Acetone can be readily separated from methanol by extractive distillation in the presence of selective entrainers (solvents). Up to date, there are four kinds of solvents used in extractive distillation, i.e. liquid solvents, solid salts, a combination of liquid solvent and solid salt, and ionic liquids (Lei et al., 2003). Typical examples of effective classic liquid solvents are: glycerine, 1,5-pentanediol, dimethylsulfoxide, n-hexanol, dioctyl phthalate and *N,N*-dimethylacetamide (Patents US4584063), etc. It has been shown that water (Iglesias, 1999) and ethylene glycol (Lei et al., 2003) are also feasible entrainers used to displace the methanol–acetone azeotrope. The second group, solid salts, are inorganic salts (sodium iodide, calcium bromide, lithium nitrate, sodium thiocyanate, potassium thiocyanate, zinc chloride and lithium bromide); their effect resp. minimum values of mole fraction of entrainers needed to break the acetone–methanol azeotrope have been summarized by Orchillés et al. (2007). Arlt et al. (2001) were the first to suggest ionic liquids as selective compounds for the separation of azeotropic mixtures. They reported the effect of various ionic liquids

on different azeotropic systems: ethanol–water, water–acetic acid, tetrahydrofuran–water, cyclohexane–benzene, as well as the effect of 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF₄]) on vapor–liquid (V–L) equilibria of the acetone–methanol system (Seiler et al., 2002). Orchillés et al. (2007) studied 1-ethyl-3-methylimidazolium trifluorosulfonate ([Emim][triflate]) as a solvent for the acetone - methanol system azeotrope.

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The process of extractive distillation with ionic liquids is comparable to the process of extractive distillation with solid salts. Extractive distillation with an ionic liquid (IL) is suitable for the production of high-purity products. This process integrates the advantages of liquid solvent (easy operation) and solid salt (high separation ability). But compared to extractive distillation with the combination of a liquid solvent and solid salt, there is no problem of the solvent entrainment in the top product of the column. Compared to classic liquid entrainers, ionic liquids have two advantages: their ionic character resulting in stronger interactions with solvents and therefore greater separating effect, and their zero vapor pressure which allows their recovery and reuse free of a less-volatile component (Lei et al., 2003). The most interesting difference is the significantly higher energy consumption of the extractive distillation column employing a commercial liquid solvent compared to the column with an ionic liquid. Gutierrez et al. (2013) showed that energy savings in the process of extraction distillation depend on both non-volatility and selectivity of IL used as the solvent, although IL's selectivity is much more important. Non volatility of the IL can lead up to 6 % energy savings in a column for extraction distillation, while IL's selectivity accounts for 40 % of energy savings. The solvent recovery in a conventional extractive distillation process is mostly carried out using a second counter-current distillation column (Seiler, 2006). In contrast to this conventional process, the regeneration of a non-volatile IL allows using other less energy intensive unit operations as stripping column, appropriate thin-film evaporators, dryers,... (Seiler et al., 2002).

Some simulation studies of the extractive distillation process of the acetone–methanol mixture using water as the solvent have been reported. A comparison of simulation results was presented by Gil et al. (2009). Langston et al. (2005) investigated the effects of solvent conditions, solvent split stream, etc. on the separation; Pradhan et al. (2005) analyzed the process separation in a valve tray column; Luyben (2008) presented the economic optimum design, Botía et al. (2010) studied the effect of solvent to feed molar ratio combined with pressure reduction. The presented study is a continuation of our previous work (Graczoá et al., 2017a) dealing with the separation of a methyl acetate–methanol azeotropic mixture in the presence of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([Emim][Triflate]) as an entrainer and the work analyzing the energy aspects of regeneration of imidazolium ionic liquid used for the separation of *tert*-butanol–water (Graczoá et al., 2017b).

2. Selection of ionic liquid

At atmospheric pressure, acetone (Ac) and methanol (M) form an azeotrope with the mole composition of acetone about $x(\text{Ac}) = 0.78$ at the temperature of 55 °C. The aim of this study was to design the process for the acetone–methanol separation employing IL.

Seiler et al. (2002) describe the effect of 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF₄]) on the acetone–methanol VLE (at 55 °C). They show that, for the acetone–methanol system, only low concentrations of the IL are required (about 10 mol %) to surpass the azeotropic point. With the increasing amount of IL, the relative volatility of acetone increases; relative volatility of around 2 or higher can be achieved for 50 mol % of IL. Orchillés et al. (2007) proved that ionic liquid [Emim][triflate] is as effective as other inorganic salts in breaking the azeotrope of the Ac–M system. They found that the required amount of [Emim][triflate] is about 6.8 mol %. Relative volatility of acetone is around 1.5 even at 10 mol % of IL. Based on this information, [Emim][triflate] was applied to separate the Ac–M mixture.

3. Physical properties

Temperature dependence of the saturated vapor pressure of Ac and M is well known. Saturated vapor pressure of [Emim][triflate] is extremely low ($P^{\circ} \rightarrow 0$ Pa). Because of numerical problems in the V–L description of systems containing an IL (and then in simulation), this relationship was predicted. The method of $P_{iL}^{\circ} = f(T)$ prediction and evaluation of the parameters of the Antoine equation were described previously (Graczoá et al., 2017a). Coefficients of the Antoine equation for Ac and M were taken from Dykyj et al. (1984). The Antoine equation coefficients of all components are included in Table 1.

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

Table 1: Antoine equation coefficients, $\log P_i^s = A - B/(C + t)$, with P_i^s in kPa

Component	A	B	C
Ac	6.19052	1157.622	219.724
M	7.09498	1521.230	233.970
[Emim][triflate]	16.786	9,873.91	273.15

4. Phase equilibrium of the ternary system

Vapor–liquid equilibrium of the acetone–methanol–[Emim][triflate] ternary system was expressed by the extended Raoult’s law assuming ideal behavior of the vapor phase.

$$P y_i = \gamma_i x_i P_i^s \quad i = 1, 2, 3 \quad (1)$$

y_i and x_i are the mole fractions of component i in the vapor and liquid phase, respectively. P_i^s is the saturated vapor pressure of the i -th component expressed using the Antoine equation and γ_i are activity coefficients calculated based on the original NRTL model derived by Renon and Prausnitz (1968).

Binary interaction parameters Δg_{ij} of the original NRTL model for the ternary system acetone (Ac)–methanol (M)–[Emim][triflate] were evaluated from binary VLE data published by Orchillés et al. (2007) and are presented in Table 2.

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

Components	Δg_{ij} (J mol ⁻¹)	Δg_{ji} (J mol ⁻¹)	α_{ij}	d_x	d_t (°C)
Ac–M	485.23	1,423.75	0.45	0.0032	0.10
Ac–[Emim][triflate]	8,841.86	4,676.87	0.30	–	0.18
M–[Emim][triflate]	6,087.23	7,666.77	0.30	–	0.11

5. Design of the separation process

For the separation of the acetone–methanol azeotropic mixture, an extractive distillation column was designed. Based on the previous results (Graczová et al, 2017), a vacuum evaporator operating under reduced pressure was selected to regenerate IL. Conceptual design scheme of the separation of the system acetone–methanol in the presence of an IL is given in Figure 1. The extractive distillation column (I) was operated at atmospheric pressure, and vacuum evaporator (III) for the solvent recovery was operated at a reduced pressure, $P = 20$ kPa. The separated azeotropic mixture and IL-solvent were fed to the extractive distillation column (I), where acetone was obtained from the top of the column. The bottom product from column (I) containing mainly methanol and IL passed through a throttle valve into the separator (II), where the vapor phase produced by throttling was separated. The liquid phase was fed to the vacuum evaporator in which methanol was separated from the methanol–ionic liquid mixture and the ionic liquid was recycled to the extractive distillation column.

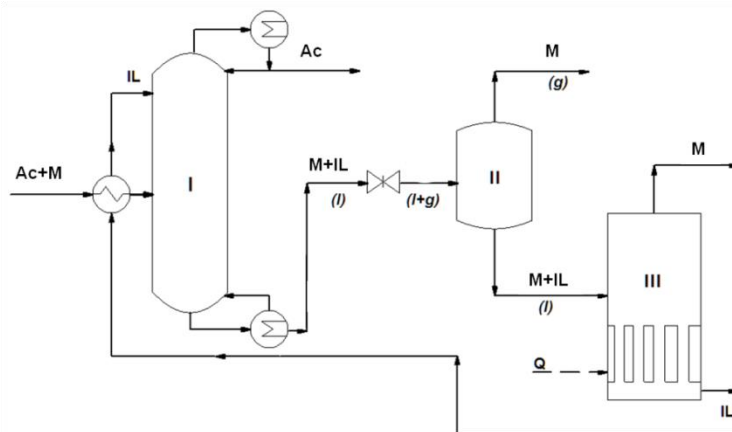


Figure 1: Conceptual scheme of extractive distillation of the acetone (Ac)–methanol (M) mixture in the presence of [Emim][triflate] (IL): I – extractive distillation column, II – separator, III – vacuum evaporator.

5.1 Design calculation of the extractive distillation column

The mixture to be separated consists of 78 mol % of acetone and 22 mol % of methanol. Molar flow of the feed (10 kmol h^{-1}) enters the column (I) as a boiling liquid at $58 \text{ }^\circ\text{C}$. The composition of the feed corresponds to the composition of the acetone–methanol azeotrope. IL solvent enters the top section of the column (I) as a subcooled liquid at $60 \text{ }^\circ\text{C}$. The entering IL-solvent is not pure, its composition corresponds to the regeneration conditions (IL contains 98 mol % of IL, 1.98 mol % of methanol and 0.02 mol % of acetone). The purity of the acetone product was set to 99.5 mol %.

The extractive distillation process for acetone–methanol separation was modeled and analyzed using a program constructed in Matlab. Parameters of the extractive distillation column: the number of theoretical stages (N), solvent to feed molar ratio (n_s/n_F), feed stage position (f_1), and reflux ratio (RR), were optimized in the computation steps described in a previous study (Gracsová and Steltenpohl, 2015). The solvent feed stage was set to be constant, $f_s = 3$, in all simulations. The first step of the simulation was to determine the optimal value of the solvent to feed molar ratio (n_s/n_F) considering the required purity of the Ac product. Sets of calculations were carried out for a column with different numbers of theoretical stages (N), and reflux ratios (RR) in the range of $n_s \in <4; 8> \text{ kmol h}^{-1}$. In the second step, for the calculated molar ratio n_s/n_F equal to 0.45, reflux ratio (RR), number of theoretical stages (N), and feed stage position (f_F) were optimized. Reflux ratio varied from 1.1 to 1.4 times the value of RR_{min} (2.4), the number of theoretical stages varied from 30 to 50, the position of the feed stage to the total number of theoretical stages f_F/N varied from 0.3 to 0.6. Results of the simulations are shown in Table 3. Optimum values of parameters RR , N , and f_F were selected with respect to the required purity of Ac.

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

N	RR	f_F	f_s	n_s/n_F
47	3.3	18	3	0.45

Finally, the temperature profile and concentration profiles of individual components in the liquid and vapor phases were calculated for the chosen column parameters. Information about the top and bottom products of the extractive distillation column are summarized in Table 4.

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

	Feed	Solvent	Distillate	Bottom product
Molar flow rate (kmol h^{-1})	10.00	4.50	7.800	6.70
Mole % Ac	78	0.02	99.74	0.32
Mole % M	22	1.98	0.26	33.86
Mole % IL	–	98	–	65.82
Temperature ($^\circ\text{C}$)	58.0	60	56.1	106.9

The resultant column parameters (Table 3) enable obtaining distillate at a concentration slightly higher than the required value ($> 99.5 \text{ mol \%}$ of Ac). The distillate also contains methanol, with the molar flow of $0.020 \text{ kmol h}^{-1}$ which corresponds to about 0.89 % of the original amount of the component in feed.

5.2 Design calculations of the regeneration process

Bottom product leaving the extractive distillation column (I) contains IL (65.82 mol %), methanol (33.86 mol %) and acetone. The molar ratio of acetone to methanol is 1:99. The design of the regeneration part considered also the same ratio as in all regeneration streams. The pressure reduction (to 20 kPa) was achieved by throttle valve setting. Calculated fraction of the evaporated liquid behind the throttle valve was 0.22 and temperature of the vapor–liquid mixture was $77.8 \text{ }^\circ\text{C}$. The temperature behind the throttle valve was calculated simultaneously by solving the enthalpy balance of the throttle valve and VLE data at reduced pressure. Vapor–liquid mixture then enters the phase separator (II) where the vapor phase ($1.474 \text{ kmol h}^{-1}$) is separated from the liquid phase. The liquid phase ($5.226 \text{ kmol h}^{-1}$) subsequently enters the vacuum evaporator. The required purity in IL-regeneration was specified as follows: 98 mol % for the IL and 99 mol % for M. The vacuum evaporator operates at the pressure of 20 kPa and at the temperature ($143.5 \text{ }^\circ\text{C}$) corresponding to the boiling point of binary mixture M–IL (98 mol % of IL and 2 mol % of M). Calculation of the boiling temperature of the mixture in the evaporator, no significant effect of acetone (0.02 mol %) on the boiling temperature of the ternary Ac–M–IL mixture is assumed. Results of the regeneration part simulation are illustrated in Table 5.

Table 5: Calculated data for the IL regeneration process at $P = 20$ kPa

	Throttle valve		Separator		Evaporator	
	In front of	Behind	Vapor	Liquid	Vapor	Liquid
Molar flow rate (kmol h^{-1})	6.70		1.47	5.23	0.73	4.50
Mole % Ac	0.32		0.93	0.14	0.93	0.02
Mole % M	33.86		99.07	15.47	99.07	1.98
Mole % IL	65.82		–	84.39	–	98.00
Pressure (kPa)	101.325	20	20	20	20	20
Temperature ($^{\circ}\text{C}$)	106.9	77.8	77.8	77.8	143.5	143.5

Simulation of the proposed regeneration process showed that methanol is not separated quantitatively. The molar flow of methanol in the regenerated IL is $0.089 \text{ kmol h}^{-1}$. The methanol vapor leaving the evaporator contains only a trace amount of acetone corresponding to 0.39 % of the original separation amount.

6. Energy consumption of the separation process

For the proposed separation process, the energy requirements were evaluated considering stream information and operating conditions presented in Tables 3, 4 and 5. Results of the heat exchangers duty calculations are given in Table 6.

Table 6: Calculated heat (Q_h) and cooling (Q_c) duty for extractive distillation (I), phase separator (II) and vacuum evaporator (III)

	Heat duty Q_h (kW)	Cooling duty Q_c (kW)
Heat exchanger for feed	12.67	-
Reboiler of column (I)	300.98	-
Condenser of column (I)	-	282.27
Condenser of phase separator (II)	-	16.44
Heat exchanger of evaporator (III)	37.18	-
Condenser of evaporator (III)		8.70

As it can be seen from Figure 1, the feed is preheated in the heat exchanger by the stream of recycled IL. The temperature of the IL-stream leaving the evaporator is $143.5 \text{ }^{\circ}\text{C}$. The recycled ionic liquid is capable of transferring 37.98 kW, which is more than the required value (12.67 kW). If the feed stream is fed as a saturated liquid, the IL stream has to be additionally cooled. On the other hand, the feed stream can be heated to produce a vapor-liquid mixture with the evaporated liquid fraction of 0.29.

7. Conclusions

The acetone-methanol separation process in the presence of an ionic liquid as the entrainer was designed. The aim of the separation was to obtain acetone of the purity of 99.5 mol %, the required purity of methanol was set to 99.0 mol %. As a separating column, an extractive distillation column operating at atmospheric pressure was proposed; for IL-regeneration, a vacuum evaporator combined with a phase evaporator both operating at reduced pressure (20 kPa) were suggested.

Design calculations of the extractive distillation column consisted of several steps resulting in the following column parameters: number of theoretical stages $N = 47$, reflux ratio $RR = 3.3$, position of the feed stage $f_F = 18$ and solvent consumption expressed in form of the solvent to feed molar ratio $n_S/n_F = 0.45$. The position of the solvent stage was set to 3. Acetone purity of 99.74 mol % was obtained at the top of the designed column. To achieve energy savings in the regeneration process, a phase separator was included between the throttle valve and the vacuum evaporator, in which the vapor phase (containing only volatile components methanol and acetone) was separated. In the liquid phase, ionic liquid was concentrated to 84.39 mol % and then in the evaporator to 98 mol %. Also, only volatile components - acetone and methanol - were evaporated in the vacuum evaporator. The purity of methanol in the vapor leaving the evaporator was 99.07 mol %.

The distillation is an energy-intensive process. Heat consumption of the reboiler was 301 kW and that of the condenser was 282 kW, which is relatively high in both cases, since the molar flow of vapor in both parts of the column was about 33.5 kmol h^{-1} . In the vacuum evaporator, the heat consumption was low corresponding to only 11 % of the heat demand needed for the whole separation process. Heat consumption in the reboiler of the

distillation column can be partially reduced using the complete heat flow of the regenerated ionic liquid for feed stream preheating.

On basis of the results obtained, it can be concluded that [Emim][triflate] has a potential to be used as a selective solvent for the acetone–methanol mixture separation.

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