

Energetic Aspects of Imidazolium-Based Ionic Liquid Regeneration from Aqueous Solutions

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Separation processes are common in chemical industry. Higher prices of energies and environmental threats led to increased interest in the design of new and the optimization of real technologies. As an example, the effort to replace conventional solvents in extractive distillation and liquid extraction can be used. In the last years, ionic liquids have emerged as suitable alternative solvents.

The presented work deals with the separation of a tert-butyl alcohol–water mixture by extractive distillation using a methylimidazolium-based ionic liquid (1-ethyl-3-methylimidazolium bromide, [EMim]Br). For the ionic liquid regeneration from its aqueous solution (bottom product from the extractive distillation column working at atmospheric pressure), an alternative separation method, evaporation at reduced pressure, was assumed. Two case studies of ionic liquid (IL) regeneration were evaluated. In the first case, pressure of the liquid bottom stream was reduced by passing through a throttle valve and the created vapor–liquid stream entered an evaporator in which the extraction solvent is pre-concentrated to be re-used in the extractive distillation column. In the second case, after the pressure reduction in the throttle valve, the vapor phase (pure water steam) was separated in a phase separator, and the stream entering the evaporator was the concentrated liquid mixture of [EMim]Br with water. Both regeneration procedures were analyzed for the heat and cooling consumption duty and compared to that corresponding to IL regeneration by distillation.

1. Introduction

Tert-butyl alcohol (TBA) is widely used in chemical and pharmaceutical industries as a solvent, ethanol denaturant, paint remover component, and gasoline octane number booster. It is a chemical intermediate used to produce methyl tert-butyl ether and ethyl tert-butyl ether (gasoline additives, used to increase the octane number), and tert-butyl hydroperoxide (an organic peroxide widely used in a variety of oxidation processes) (Billing, 2000).

Depending on the source, alcohol mixtures have different content of water and the requirements on the separation and recovery processes are different. Purification or pre-concentration of alcohols from their aqueous solutions is a difficult task as they form azeotropic mixtures with water. Conventional distillation is inefficient in providing high purity alcohols. In practice, this problem is solved by extractive (or azeotropic) distillation using a suitable solvent added to the aqueous alcohol mixture to promote the effect of separation. Nature and properties of the chosen solvent have crucial effect on the separation process economy, environment, and on the product quality. Traditional organic solvents and metal salts used for organic phase salting-out from its aqueous solution show several disadvantages as high cost, lower efficiency, and enhanced pollution problems (Lek-utaiwan et al., 2011).

In recent years, new types of solvents for separation technology have attracted interest. Ionic liquids, known as green solvents, offer the possibility of azeotropic mixture separation process modification and its efficiency increase. Because of their outstanding physicochemical properties, low saturated vapor pressure, low melting point, and high stability, as well as their environmental-friendliness, ionic liquids (ILs) are under intensive investigation focused on their potential as substitute solvents for extractive distillation (Schoor, 2015).

In industrial scale, the potential of ionic liquids as extraction solvents is still underestimated despite their extraordinary properties (compared to the commercially used solvents). Solvent regeneration is one of the key

tasks in the design of separation processes. Quantitative regeneration of conventional solvents is a complicated and energy-consuming process. Regeneration of ionic liquids is expected to be much easier and less energy-consuming as that of conventional solvents.

In this study, the evaporation process was examined as a solvent recovery method. Energy consumption of the evaporation process carried out by two different procedures was analyzed and compared with the results obtained by the distillation process.

2. Design of separation process

The presented work is a continuation of the work (Graczová and Šulgan, 2016) dealing with separation of a tert-butyl alcohol (TBA)–water (W) azeotrope mixture using a methylimidazolium-based ionic liquid (1-ethyl-3-methylimidazolium bromide, [EMim]Br). Previously, the separation process was designed for two distillation columns (presented in Figure 1): an extractive distillation column (I) operated at the atmospheric pressure, and a distillation column (II) for the solvent recovery operated at a reduced pressure, $P = 10$ kPa. The mixture to be separated consists of TBA (10 mole %) and water (90 mole %) at 20 °C. As the extraction solvent, pure [EMim]Br IL was used. Optimization criterion was set as the purity of the top product obtained in the basic extractive distillation column (TBA purity higher than 99.95 mole %). The objective of the IL regeneration was to obtain extraction solvent quantitatively.

Optimum operation parameters of both distillation columns were evaluated for the pre-set optimization criteria. Calculations were carried out in a proprietary program constructed in Matlab® capable of solving a set of material balances written for the column and its equilibrium plates considering the vapor–liquid equilibrium of the ternary systems TBA–water–IL (Zhang et al., 2016). Parameters of the distillation columns were optimized in computation steps described in previous studies (Graczová and Steltenpohl, 2015). Calculated optimum parameters for the extractive distillation column (I) operation were as follows: the number of theoretical plates ($N = 11$), feed and extractive solvent positions in the column ($f_2 = 7$ and $f_1 = 2$), reflux ratio ($R = 1.3$) and ionic liquid consumption (mole ratio $n_S/n_F = 0.12$). The feed was fed as a liquid stream at its boiling point (thermal condition of the feed, $q_1 = 1$) while the IL stream was assumed to be cold liquid with the temperature under its boiling point ($q_2 = 1.7$). Calculated optimum parameters for the regeneration distillation column (II) operation were as follows: the number of theoretical plates ($N = 4$), reflux ratio ($R = 0.10$). The bottom product was fed into the regeneration column as a vapor–liquid mixture at 10 kPa ($q = 0.877$); positions in the column $f = 2$. Information about the head and bottom products from the extractive distillation and regeneration columns are summarized in Tables 1 and 2, respectively. It was also found that simple distillation cannot be used to quantitatively separate the components of the above mixture. For complete separation of the [EMim]Br IL from its mixture with water, repeated distillation in the distillation column is necessary.

According to the results presented by Graczová and Šulgan (2016), extractive distillation is an effective procedure for TBA separation from its aqueous mixture affording practically pure product (water content in the distillate was lower than 4×10^{-3} mole %). Moreover, [EMim]Br regeneration was also quantitatively achieved in the second distillation column (water content in the bottom product was also lower than 4×10^{-3} mole %).

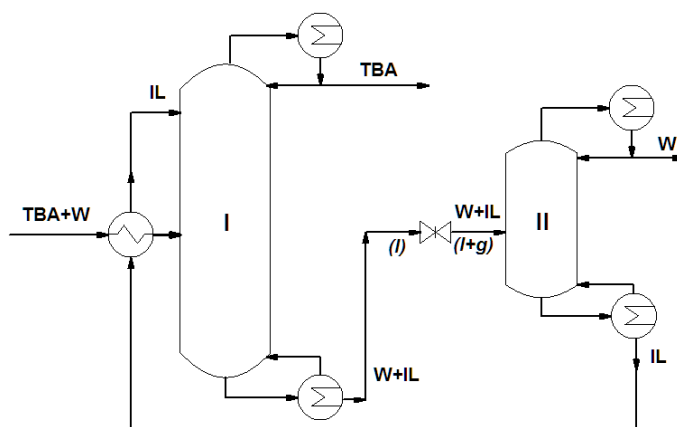


Figure 1: Conceptual scheme of extractive distillation of the system tert-butyl alcohol (TBA)–water (W) in the presence of [EMim]Br (IL); I – extractive distillation column, II – regeneration column.

Table 1: Calculated data for the separation of the system TBA–water–[Emim]Br in the extractive distillation column (I) at $P = 101.3 \text{ kPa}$

	Feed	Solvent	Distillate	Bottom product
Molar flow rate (kmol h^{-1})	30.0	3.5	3.0	30.5
Mole % TBA	10	–	100	4×10^{-4}
Mole % W	90	–	4×10^{-3}	88.53
Mole % IL	–	100	–	11.47
Temperature ($^{\circ}\text{C}$)	83.7	83.0	82.4	103.8
State of feed	$q_1 = 1$	$q_2 = 1.7$		

Table 2: Calculated data for the separation of the system water–[Emim]Br in the regeneration column (II) at $P = 10 \text{ kPa}$

	Feed	Distillate	Bottom product
Molar flow rate (kmol h^{-1})	30.5	27.0	3.5
Mole % W	88.53	100	4×10^{-3}
Mole % IL	11.47	–	100
Temperature ($^{\circ}\text{C}$)	48.5	45.8	235.4
State of feed	$q = 0.877$		

3. Physical properties

There is a lack of information on IL's characteristics; especially on the dependence of IL saturated vapor pressure on temperature, dependence of heat capacity on temperature as well as heat of vaporization at the required temperatures and heat of mixing. For the purpose of separation equipment design and energy consumption calculations, properties of the [EMim]Br IL were predicted. Normal boiling point of the IL ($t_b = 267.8 \text{ }^{\circ}\text{C}$) and its critical parameters ($t_c = 523.1 \text{ }^{\circ}\text{C}$ and $P_c = 27,630.0 \text{ torr}$) (Valderrama, 2008) were used to predict the IL vaporization heat and the variation of the IL's saturated vapor pressure with temperature ($P_i^s = f(t)$) in form of the Antoine equation (Gracsová and Šulgan, 2016). Parameters of the Antoine equation are summarized in Table 3; data for the other components, TBA and water, were taken from literature (Zhang et al., 2016).

Table 3: Parameters of the Antoine equation, P_i^s/torr

Component	A	B	C
[EMim]Br	18.6719	8,543.02	273.15
TBA	7.3199	1,154.48	177.66
W	8.0713	1,730.63	233.43

Heat capacity of [EMim]Br at the temperature of $20 \text{ }^{\circ}\text{C}$, $C_p = 258.0 \text{ J mol}^{-1} \text{ K}^{-1}$, was obtained using the contribution method introduced by Chueh and Swanson (Reid et al., 1988). Temperature variation of heat capacity values for TBA and water are available in literature (Reid et al., 1988).

4. Analysis of energy consumption of separation processes

4.1 Heat and cooling demand of distillation columns

Simplified energetic balance of the proposed separation scheme (Figure 1) was done with the aim to assess energy consumption of the separation. For this purpose, enthalpy balances of heat exchangers used to pre-heat the feed to extractive distillation column (I) as well as reboilers and condensers of columns (I) and (II) were considered. First, heat consumption in the feed pre-heater was determined. Initial feed temperature was set to $20 \text{ }^{\circ}\text{C}$ and its final value corresponded to the feed boiling temperature ($q_1 = 1$). The corresponding heat demand was 48.90 kW . Calculation of the heat demand of columns I and II reboilers, Table 4, was done using enthalpy balances of the respective column based on the results of the columns material balances simulation presented in Tables 1 and 2. Cooling demand of condensers at the respective column head was determined assuming the distillate composition (pure TBA for column (I), pure water for column (II)) and the corresponding temperature (boiling temperature of TBA at the atmospheric pressure, $82.35 \text{ }^{\circ}\text{C}$; boiling temperature of water at the pressure of 10 kPa , $45.83 \text{ }^{\circ}\text{C}$). The heat loss was omitted. Results of the heat exchangers duty calculations are given in Table 4.

Table 4: Calculated heat (Q_h) and cooling (Q_c) demand of extractive distillation (I) and regeneration (II) columns' reboilers and condensers

Column	Heat duty Q_h/kW	Cooling duty Q_c/kW
I	77.59	76.28
II	356.02	355.60

4.2 Alternatives of the IL regeneration

As shown in Table 4, the use of distillation for IL regeneration is a highly energy-demanding process. Heat consumption in the regeneration column was 4.6 times higher than that in the base extractive distillation process. For that reason, it is interesting to find an alternative to this process. This alternative should afford sufficiently high purity of the regenerated IL at reasonably low regeneration costs. High purity of the regenerated IL is a prerequisite of efficient TBA separation in the extractive distillation column.

The main aim of this study was to analyze the replacing of the distillation process by the evaporation process as an alternative for the regeneration of ILs from their aqueous mixtures (Schoor, 2015). It is important to decide the minimum required purity of regenerated IL. At very low water content in the concentrated IL mixture, also ionic liquid can be found in the vapor phase. In this study, a mixture containing 2 mole % of water was considered as sufficiently pure [EMim]Br assuming that the vapor phase from the evaporator is pure water. Considering this mixture as a solvent used in the extractive distillation column (Figure 1), the performance of this column was not affected and the distillate composition was maintained. Simulation results presented in Table 1 (composition and amount of distillate and bottom products) were used as the basis for further calculations.

4.2.1 [EMim]Br regeneration in a single-effect vacuum evaporator

First alternative considered was the [EMim]Br regeneration from its mixture with water in a vacuum evaporator (Figure 2).

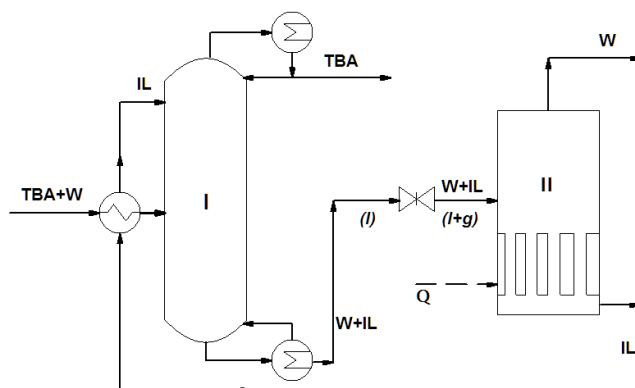


Figure 2: Conceptual scheme of extractive distillation of the system TBA–water in the presence of IL; I – extractive distillation column; II – single-effect vacuum evaporator.

As a feed of evaporator (II), the vapor–liquid stream obtained by throttling the bottom product from extractive distillation column (I) was used. By lowering the pressure to 10 kPa at adiabatic conditions (constant enthalpy), the temperature was decreased to 48.5 °C. At the same time, partial evaporation of the originally liquid stream occurred. The computed vapor-to-liquid mole ratio in the feed entering the evaporator was 12.3 : 87.7 (Graczová et al., 2017). In evaporator, the content of [EMim]Br in the liquid phase was increased to 98 mole %. Boiling temperature of 228.0 °C was determined for this mixture (providing that the saturated vapor pressure of the ionic liquid at the operating temperature of the evaporator was close to 0 Pa). Results of the evaporator design calculations are given in Table 5.

In the active heat duty calculation, heat loss from the heat exchangers to the ambient was omitted. Computed active heat and cooling duties connected with the evaporator operation were 376.88 kW and 378.00 kW, respectively. Compared to the IL regeneration by distillation, heat consumption in the single-effect vacuum evaporator was by 5.9 % higher. Also, cooling consumption was higher by almost 6.3 %.

Table 5: Calculated data for the separation of the system water–[Emim]Br in evaporator (II) at $P = 10$ kPa

	Feed	Vapor	Liquid
Molar flow rate (kmol h^{-1})	30.57	27	3.57
Mole % W	88.55	100	2.00
Mole % IL	11.45	–	98.00
Temperature ($^{\circ}\text{C}$)	48.5	228.0	228.0

4.2.2 [EMim]Br regeneration using a phase separator and single-effect vacuum evaporator

Some savings of operational costs were achieved when introducing a phase separator (II) between the throttle valve and evaporator (III) as shown in Figure 3. In the phase separator, vapor phase formed by water vapor is bypassing the evaporator. Then, the IL content in the liquid phase is increased to 13.05 mole % compared to the bottom product from the extractive distillation column (11.45 mole %). Liquid phase from the phase separator (II) enters vacuum evaporator (III) where further concentration of the IL up to 98 mole % occurs. Results of the design calculations are listed in Table 6.

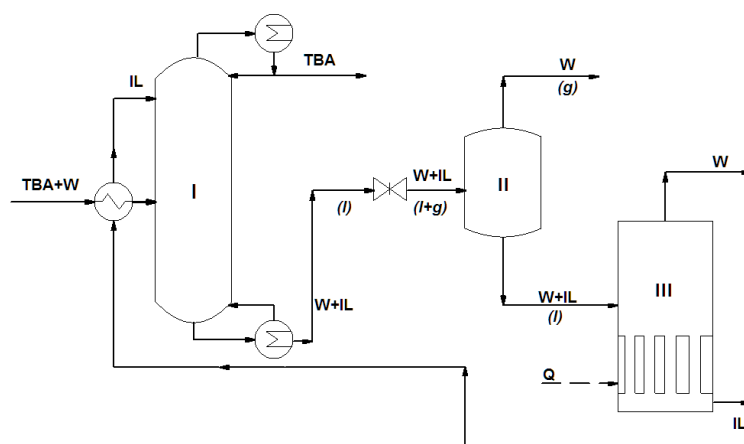


Figure 3: Conceptual scheme of extractive distillation of the system TBA–water in the presence of IL; I – extractive distillation column; II – separator, III - vacuum evaporator.

Table 6: Calculated data for the separation of the system water–[Emim]Br in separator (II) and evaporator (III) at $P = 10$ kPa

	Feed	Phase separator		Evaporator	
		Vapor	Liquid	Vapor	Liquid
Molar flow rate (kmol h^{-1})	30.57	3.76	26.81	23.24	3.57
Mole % W	88.55	100	86.95	100	0.02
Mole % IL	11.45	–	13.05	–	0.98
Temperature ($^{\circ}\text{C}$)	48.5	48.5	48.5	228.0	228.0

Active heat duty of a vacuum evaporator (III) with an upstream phase separator (II), 369.38 kW, is 2.0 % lower compared to the values computed for the previous alternatives of IL regeneration. The calculated cooling demand of separator and evaporator condensers are 325.37 kW and 45.12 kW, respectively. Overall cooling duty of the procedure is 370.49 kW, which is slightly lower (also by 2.0 %) than the cooling duty computed for IL regeneration in a stand-alone evaporator.

4.2.3 Summary of [EMim]Br regeneration calculations

Results of active heat and cooling duties in individual studied alternative procedures proposed for [Emim]Br ionic liquid regeneration are summarized in Table 7. From the economy point of view, IL regeneration in a single-effect vacuum evaporator with an upstream phase separator is recognized as the less energy-demanding from the two chosen alternatives. Taking into account the results of material balance calculations presented in Table 6, about 13.9 % of water from the bottom product of the extractive distillation column was removed already in the phase separator (Figure 3). The amount of water vapor removed in the phase separator was 3.76 kmol h^{-1} and its temperature was 48.5°C . It is a substantially lower temperature compared to that of the water vapor leaving the evaporator (228.0°C). It proves that active heat duty of the

evaporator with the upstream phase separator is lower than that computed for the IL regeneration in a stand-alone vacuum evaporator. Use of the phase separator allows lowering the evaporator heat demand by 7.51 kW. Comparing this procedure to the IL regeneration by distillation, cost savings connected with heat duty have not been achieved, the costs are comparable or even higher (by 3.8 %). Moreover, the operational costs connected with cooling duty are slightly higher, by approximately 4.2 %.

Table 7: Comparison of calculated heat (Q_h) and cooling (Q_c) demands for IL regeneration processes

Regeneration process	Q_h /kW	Q_c /kW
Distillation column	356.02	355.60
Evaporator	376.88	378.00
Evaporator with Separator	369.38	370.49

5. Conclusions

In the work, the possibility to replace distillation with the alternative evaporation process for ILs regeneration from their aqueous mixtures was studied. Replacing distillation with evaporation is limited due to the quantitative water removal. Evaporation cannot be used to reach the 100 % purity of the regenerated ionic liquid (with respect to the vapor–liquid phase equilibrium of the ionic liquid–water solution). For this reason, regeneration is designed to reach the 98 mole % purity of ionic liquid (otherwise the vapor phase could contain also some amount of ionic liquid). On the other hand, in the distillation regeneration column it is possible to achieve practically pure IL even at the boiling point temperature of the bottom product in the reboiler, while in the distillation column vapors, ionic liquid can be found.

Both evaporation procedures were analyzed and the results were compared to that corresponding to IL regeneration by distillation. The results obtained have shown that heat and cooling consumption for IL regeneration in water mixture provided by the evaporation are comparable or slightly higher with those of the distillation process. Introducing the phase separator before the vacuum evaporator led to only minimal energy savings (2.0 %) despite the fact that 13.6 % of water was separated from the total water content.

Acknowledgments

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