Application of Ionic Liquids in Extractive Distillation of Ethanol – Water System

Elena Graczová*, Pavol Steltenpohl

Institute of Chemical and Environmental Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia
elena.graczova@stuba.sk

Extractive distillation is one of the most common processes used to separate components of azeotropic mixtures. Its most distinct constrains are the tremendous energy costs required to achieve a fluid phase system. In the given process, solvent interacting with the components of the original mixture and changing their relative volatility is used. Extractive distillation with conventional solvents provides products of poor quality and the solvents occur at the top of the column. Therefore, additional separation steps are required to separate the solvent from both the distillate and the bottom products. The use of ionic liquids (ILs) as the extractive solvents provides a cost-effective solution. Due to the negligibly low vapor pressure of ILs, the distillate obtained by extractive distillation does not contain solvent and IL can be separated from the bottom product relatively easily in a secondary regeneration column. Thus, appreciable investment and also operational costs reduction can be achieved by simple substitution of common extractive solvents with ILs. The present study focuses on the separation of the azeotropic system ethanol – water using extractive distillation. As the extractive solvents, two ionic liquids were compared: 1-butyl-3-methylimidazolium methylsulfate and 1-ethyl-3-methylimidazolium ethylsulfate. The separation was carried out in two distillation columns, extraction and recovery ones. Purity of the final products (ethanol and recovered IL) was prescribed. For the extraction and regeneration columns, various parameters were optimized, such as the reflux ratio, number of theoretical stages, quality of feed, position of the feed stage, solvent consumption, etc. Qualitative comparison of the operational costs for ethanol – water mixture separation using the two extraction solvents is discussed.

1. Introduction

In view of the pollution prevention and minimization of the human activity impact on the environment, substitution of traditional fuels (gasoline) with renewable ones (e.g. ethanol) is a promising alternative. Ethanol is a high quality fuel used as alternative to gasoline in internal combustion engines. Its advantages are environmental friendliness and anti-detonation properties. A disadvantage of ethanol as a fuel is its affinity to water, the presence of which may cause increased corrosion of the car engine.

At atmospheric pressure, ethanol forms an azeotropic mixture with water containing 95.57 mol\% of ethanol. This solution cannot be separated by conventional distillation. For this purpose, extractive distillation is used. Azeotropic mixture separation is achieved in the presence of an extractive solvent that changes the relative volatility of components of the original mixture. As extractive solvents, different conventional liquids can be employed. Nowadays, extensive attention is dedicated to the use of novel alternative solvents, ionic liquids (ILs). ILs represent a class of ionic salts that are liquid at common temperatures (Pereiro, 2012). Thanks to their unique properties, high extraction selectivity and capacity, non-volatility, thermal stability, electric conductivity, non-flammability, etc., ILs have found a broad application in chemical industry (Johnson, 2007). Principal disadvantage of ILs is their elevated price, although these investment costs are single shot. Moreover, the extraction properties of ILs, especially their capacity and selectivity, can be tailor-maid to cope with goal of the separation procedure by finding out the right combination of anionic and cationic part of the IL (Domanska, 2009). Recently, simulation of ILs use in azeotropic mixture separation was carried out assuming aromatics separation from a model
hydrocarbons blend by extraction. Influence of the ILs use on the equipment design parameters (Graczová et al., 2014) as well as selected economical parameters (Steltenpohl and Graczová, 2014) were discussed.

In this paper, the effect of ILs formed by homologous cations and also anions is compared in ethanol separation from its aqueous mixture by extractive distillation.

2. Theoretical

In calculation of the vapor–liquid equilibrium (VLE) of a multi-component system, ideal behavior of vapor and real behavior of liquid phases is assumed. For VLE of a more component system at constant temperature and pressure, \( T \) and \( P \), the equilibrium criterion for each component of the mixture is written as:

\[
P_{yi}^{*} = P_{i}^{*} x_{i} \quad i = A, B, C \quad [T, P]
\]

where \( P_{yi}^{*} \) is the \( i \)-th component's saturated vapor pressure; \( y_{i} \) and \( x_{i} \) are the mole fractions of component \( i \) in the vapor and liquid phase, respectively. Activity coefficients, \( \gamma_{i} \), were calculated using the NRTL equation (Renon and Prausnitz, 1968):

\[
\ln Y_{i} = \frac{\sum t_{ij} G_{ij} x_{j}}{\sum G_{ix_{i}}} + \frac{x_{i} G_{ij}}{\sum G_{ix_{i}}} \left( t_{ij} - \frac{\sum t_{jk} G_{jk} x_{k}}{\sum G_{jk}} \right) \quad i, j, k, l = A, B, C
\]

Binary parameters \( t_{ij} \) and \( G_{ij} \) are defined by the following expressions:

\[
t_{ij} = \frac{g_{ij} - g_{ji}}{RT} \quad G_{ij} = \exp \left(-\alpha_{ij} t_{ij}\right) \quad i, j = A, B, C \quad i \neq j
\]

where \( t_{ij} \neq t_{ji} \), \( t_{ii} = t_{jj} = 0 \), \( R \) is the universal gas constant, \( (g_{ij} - g_{ji}) \) represent the extent of interactions between molecules \( i \) and \( j \); and \( \alpha_{ij} \) is the non-randomness parameter of the NRTL equation.

3. Experimental

Simulation of an ethanol – water mixture containing 20 mol% of ethanol was carried out assuming a column for extractive distillation followed by extractive solvent regeneration in a second distillation column. As the extractive solvent, two ionic liquids, namely 1-butyl-3-methylimidazolium methylsulfate, \([\text{BMim}]\text{[MSO}_{4}])\), and 1-ethyl-3-methylimidazolium ethylsulfate, \([\text{EMim}]\text{[ESO}_{4}])\), were applied (Figure 1).

![Figure 1: Structure of the ILs considered](image)

Figure 2 shows flow-chart of the aqueous ethanol mixture separation in the presence of IL. In the first column, extractive distillation is carried out. Feed (ethanol – water mixture) and extractive solvent (IL) enter the column as independent streams. The pre-set purity of distillate is 99.5 mol% of ethanol and the maximum content of this component in the bottom product is lower than 0.5 mol%. The bottom product from the first column is fed to the second, regeneration column. Here, water is separated from IL. The required purity of IL in the bottom product from the regeneration column is 99.9 mol% and its maximum content in the distillate from this column is lower than 0.1 mol%. As a result, practically pure ethanol, water, and IL are obtained; the later one can be recycled back to the first column.
Basic operation parameters of an extractive distillation column such as the number of theoretical stages, \( N \), reflux ratio, \( RR \), position of the solvent, \( f_1 \), and feed, \( f_2 \), input stages, as well as the solvent-to-feed mole ratio, \( \tilde{n}_S/\tilde{n}_F \), were investigated and optimized. A proprietary model of the distillation column was prepared in the Matlab® simulation program suitable for simultaneous solution of material balances at individual equilibrium stages. VLE calculations correspond to Eq(1); computation of the components activity coefficients was based on the NRTL equation - Eq(2) and Eq(3). Experimental VLE data and the original binary NRTL parameters for the respective ternary systems were taken from literature (Calvar et al., 2008) and in (Calvar et al., 2009) and are summarized in Table 1. For both ternary systems, the NRTL binary parameters were obtained by direct fitting of the ternary VLE data.

### Table 1: Parameters of the NRTL equation for VLE calculation of the ternary system ethanol (A) – water (B) – IL (C) at \( P = 101.3 \text{ kPa} \)

<table>
<thead>
<tr>
<th>Binary</th>
<th>( g_i - g_j )</th>
<th>( g_j - g_i )</th>
<th>( \alpha_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol – Water</td>
<td>1,045.21</td>
<td>4,454.85</td>
<td>0.57</td>
</tr>
<tr>
<td>Ethanol – [BMim][MSO_4]</td>
<td>-3,995.68</td>
<td>263.88</td>
<td>-0.05</td>
</tr>
<tr>
<td>Water – [BMim][MSO_4]</td>
<td>-14,038.66</td>
<td>40,030.36</td>
<td>0.04</td>
</tr>
<tr>
<td>Ethanol – Water</td>
<td>4,459.63</td>
<td>-3,099.34</td>
<td>-0.404</td>
</tr>
<tr>
<td>Ethanol – [EMim][ESO_4]</td>
<td>-4,647.33</td>
<td>73,1067</td>
<td>0.3018</td>
</tr>
<tr>
<td>Water – [EMim][ESO_4]</td>
<td>-1,749.17</td>
<td>-4,045.64</td>
<td>0.996</td>
</tr>
</tbody>
</table>

### 4. Results and Discussion

Parameters of an extractive distillation column were obtained assuming the two chosen extractive solvents, [BMim][MSO_4] and [EMim][ESO_4] ILs, and atmospheric pressure. Due to the large number of optimized parameters, \( N, RR, f_1, f_2, \tilde{n}_S/\tilde{n}_F \), calculations were done in three consecutive steps. Further, optimization of the distillation column for the extractive solvent regeneration was carried out.

#### 4.1 Extractive distillation of the ethanol – water – [BMim][MSO_4] system, design calculations

In the first calculation step, a guess of the basic column parameters, \( RR = 1.2–2, N = 10, f_1 = 2 \), as well as of the actual state of the solvent and feed input streams \( q_f = 1.5 \) and \( q_g = 1 \), respectively, was used to optimize the solvent-to-feed mole ratio, \( \tilde{n}_S/\tilde{n}_F \). A series of computations using different sets of values of the column design parameters showed that the estimated number of theoretical stages \( N = 10 \) is satisfactory for this separation. Based on the prescribed composition of the distillate and bottom product, the solvent-to-feed mole ratio of \( \tilde{n}_S/\tilde{n}_F = 2/7 \) was chosen as the optimum one at which the highest ethanol purity in the distillate (> 99.5 mol%) was achieved. Moreover, the amount of the extractive solvent was kept at the lowest value possible in order to minimize the operational cost.

In the second calculation step, for the chosen \( \tilde{n}_S/\tilde{n}_F \) values of the reflux ratio, the number of theoretical stages, and the position of the feed input stage were optimized. The reflux ratio was varied between 1 and 2.2, the number of theoretical stages from 5 to 15, and the position of the feed input stage depending on...
the number of theoretical stages. Optimization carried out on the variation of the distillate and bottom product composition with the reflux ratio and the number of theoretical stages. As the optimum, the following values were obtained: $RR = 1.5$, $N = 10$, $f_1 = 2$, and $f_2 = 8$. At the given conditions, the ethanol content in the distillate and bottom product was 99.59 mol% and 0.08 mol%.

In the last computation step, the column mass balance was solved for the optimum design parameters obtained in the previous step. Calculation results are presented in Figure 3 in form of composition (Figures 3a and 3b) and temperature (Figure 3c) profiles within the distillation column.

![Graph](image-url)

*Figure 3: Calculated concentration profiles in the vapour (a) and liquid (b) phases and temperature profile (c) at individual stages of the distillation column: ethanol (diamonds), water (squares), and [BMim][MSO₄] (triangles)*
4.2 Extractive distillation of the ethanol – water – [EMim][ESO₄] system, design calculations
A similar procedure was used to obtain the optimum design parameters for the column for extractive distillation of the ethanol – water – [EMim][ESO₄] mixture separation at $P = 101.3$ kPa. The optimum values of the column design parameters obtained by this procedure were as follows: $\frac{n_s}{n_F} = 4/7$, $RR = 1.6$, $N = 15$, $f_1 = 2$, and $f_2 = 12$. Concentration and temperature profiles for these optimum values and for the actual state of the input streams $q_1 = 2$ and $q_2 = 1$ are shown in Figure 4. Calculated content of ethanol in the distillate was 99.5 mol% while that in the bottom product was 0.07 mol%.

![Figure 4: Calculated concentration profiles in the vapour (a) and liquid (b) phases and temperature profile (c) at individual stages of distillation column: ethanol (diamonds), water (squares), and [EMim][ESO₄] (triangles)](image-url)
4.3 [BMim][MSO₄] and [EMim][ESO₄] extractive solvent regeneration, design calculations

In the regeneration column, bottom product from the first (extractive) distillation column is separated at atmospheric pressure. These mixtures can be considered as binary water – IL systems due to their negligibly low content of ethanol. The optimization procedure was carried out with the aim to assess the column design parameters, namely the reflux ratio, the number of theoretical stages, and the position of the feed input stage. For both considered ILs, the same separation efficiency was prescribed, i.e. the maximum content of IL in the distillate of 0.1 mol% and its content in the bottom product not lower than 99.9 mol%.

Results of the computations show that the required distillate and bottom product purity was achieved using the column with three theoretical stages and at the reflux ratio of 0.5. This observation is valid for regeneration of both, [BMim][MSO₄] as well as [EMim][ESO₄]. ILs. Due to the high purity of the regenerated ILs at atmospheric pressure, the bottom product temperature corresponded with the boiling points of the respective imidazolium salts (bp > 400 ºC). When lowering the total pressure in the regeneration column, e.g. to the value of P = 10 kPa, the temperature of the bottom product was still very high (> 300 ºC).

5. Conclusions

In this study, simulation calculations of columns for extractive distillation and solvent regeneration were used to compute the column optimum design parameters assuming diluted ethanol – water mixture separation in the presence of [BMim][MSO₄] or [EMim][ESO₄] ILs. In case of the first extractive solvent, [BMim][MSO₄], the pre-set distillate and bottom product composition was achieved in a column with lower number of theoretical stages (10) compared to that required for [EMim][ESO₄] (N = 15). From the economical point of view, even more important is the twice lower consumption of [BMim][MSO₄] in comparison with that of [EMim][ESO₄] needed to reach the prescribed separation efficiency. This fact affects both investment and operational costs connected with the distillation column operation. The same is valid when looking on the regeneration column design. Although the number of theoretical stages required to reach the desired product purity is 3 for both ILs assumed, the mass of the feed to be processed differs considerably.

On the other hand, unacceptably high temperature of the bottom product was observed at the given conditions (P = 101.3 kPa). In order to prevent thermal damage of the extraction solvent, a vacuum column should be used for the solvent regeneration or, preferentially, a column for stripping of water from the solvent into a gas should substitute the distillation equipment.

The use of ILs in separation of azeotropic mixtures seems to be beneficial, therefore, from the economical point of view it is interesting to investigate another (new) ILs for their separation efficiency in this process.

Acknowledgement

The authors acknowledge the Research and Development Assistance Agency (APVV-0858-12).

References


Graczyk E, Thomas L., Steltenpohl P., 2014, Aromatics extraction. 1. Extraction characteristics of ILs for the toluene/heptane separation and equipment design aspects, Chemical Engineering Transactions, 39, 1333-1338.


