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IONIC LIQUIDS FOR THE EXTRACTION
OF \textit{n}-BUTANOL FROM AQUEOUS SOLUTIONS

Abstract: The article describes the extraction of \textit{n}-butanol from four-component aqueous solutions, also containing acetone and ethanol. All of these three chemicals are the main constituents of the so-called fermentation broth – a product of ABE (Acetone-Butanol-Ethanol) fermentation process. Nowadays, ABE fermentation, which is one of the oldest butanol production technologies, seems to be a viable alternative to petrochemical methods that have so far dominated the industry. Such considerations are driven by the steady depletion of fossil fuels, and thus, worldwide tendencies to use renewable resources instead, but also by the popularization of clean production and green chemistry principles. The physicochemical properties of biobutanol are very similar to that of gasoline and diesel fuel. Therefore, there exists a real potential for its widespread use as a fuel additive, if not a direct application in internal combustion engines. For that reason, the effective separation of biochemically derived butanol may have a great impact on fuel production technology, which is by far crude oil oriented. The main challenges of applying traditional solvents in liquid-liquid extraction are their toxicity and usually high volatility that prevents an economically justified partitioning of the extract components. Hence, there arises a growing interest in non-volatile, thermally stable and water immiscible ionic liquids. Properties of these new ‘designer solvents’ have not been fully recognized yet, but the full range of their possible applications may appear as unlimited. In this study, phase separation research has been made in five-component systems of water, acetone, butanol, ethanol and ionic liquid. Two different ionic liquids have been used: 1-hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF\textsubscript{6}] and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [Bmim][Tf\textsubscript{2}N]. Experimental results confirm the efficient recovery of \textit{n}-butanol from aqueous solutions when volumes of both liquid phases are approximately equal.

Keywords: liquid-liquid extraction, ionic liquids, biobutanol, renewable resources

Introduction

Butanol is a chemical capable of numerous industrial and non-industrial applications, but, first and foremost, it should be considered as a viable alternative to gasoline. It

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displays favourable combustion characteristics and, as a fuel additive, it is superior to widely used ethanol in many aspects (e.g., lower volatility, higher energy content, better miscibility with diesel fuel and gasoline). From a technical standpoint, appropriate modifications in the existing combustion engines are also possible [1]. Comparison of butanol with other fuels is shown in Table 1 [2, 3].

Table 1

<table>
<thead>
<tr>
<th>Property</th>
<th>Butanol</th>
<th>Gasoline</th>
<th>Diesel fuel</th>
<th>Ethanol</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy density [MJ/dm³]</td>
<td>29.2</td>
<td>32.0</td>
<td>35.9</td>
<td>19.6</td>
<td>16.0</td>
</tr>
<tr>
<td>Air-fuel ratio (AFR)</td>
<td>11.2</td>
<td>14.7</td>
<td>14.6</td>
<td>9.0</td>
<td>6.5</td>
</tr>
<tr>
<td>Heat of vaporization [MJ/kg]</td>
<td>0.43</td>
<td>0.36</td>
<td>0.23</td>
<td>0.92</td>
<td>1.20</td>
</tr>
<tr>
<td>Research Octane Number (RON)</td>
<td>96</td>
<td>91–99</td>
<td></td>
<td>129</td>
<td>136</td>
</tr>
<tr>
<td>Motor Octane Number (MON)</td>
<td>78</td>
<td>81–89</td>
<td></td>
<td>102</td>
<td>104</td>
</tr>
</tbody>
</table>

Since the 1950s butanol has been produced almost solely from fossil fuels. However, one of the oldest industrial biochemical techniques of butanol production, which has been superseded by crude oil processing, is the ABE fermentation exploiting certain types of anaerobic Clostridium bacteria. In view of the steady depletion of non-renewable resources and recent proecological regulations this method is certainly worth looking into again.

Of all the applicable bacterial species, the genetically modified strain Clostridium beijerinckii is the most butanol selective – the total concentration of products (i.e., acetone, butanol and ethanol) obtained in the fermentation broth ranges between 15–26 g/dm³ depending on the substrates, with butanol yield approaching 19–20 g/dm³ [4].

Separation of biobutanol from the fermentation broth poses a complex technical problem. First of all, it must be carried out in a continuous manner, because an excessive concentration of products inhibits the bacteria [5, 6]. Secondly, the applied technique should not be demanding in terms of energy and costs. Finally, classical extraction solvents might be of practical use, but they are mostly toxic and volatile, in other words, not environmentally friendly.

A variety of methods have been proposed for the stated purpose, such as gas stripping, adsorption, liquid-liquid extraction (LLE), pervaporation and membrane solvent extraction. However, liquid-liquid extraction, along with pervaporation, appear to be the most suitable techniques [7]. Therefore, ionic liquids, which recently gained some notable recognition in science and industry, may turn out to be highly appropriate for the recovery of biobutanol.

Ionic liquids (ILs) are liquid substances composed solely of ions (in a general sense, molten salts). However, most salts melt in high temperatures. Therefore, contemporary ionic liquids are molten salts with a melting point below 100 °C [8]. There are also salts melting in temperatures lower than 20 °C and they are called room-temperature ionic liquids (RTILs). Ionic liquids are often described as designer solvents. Because of
practically unlimited number of combinations between anions and cations, their properties may be “adjusted” to suit certain process requirements [9, 10].

The main attributes of ionic liquids making them useful in separation of mixtures are very low volatility and wide liquid range (often exceeding 200 °C) [11, 12], which may allow their relatively easy regeneration (via low pressure distillation) and recirculation. A lack of toxic fumes is the additional benefit.

It is of fundamental significance that the ionic liquid employed as the extracting solvent should be hydrophobic, *i.e.*, immiscible with the aqueous phase. It has been noted that some of the ILs are water-miscible while others are not, even if their chemical structures are not much different [13]. Nevertheless, hydrophobicity is the main quality determining the choice of ILs for this study.

**Materials and methods**

The study of phase equilibrium was conducted in five-component two-phase systems of water, acetone, butanol, ethanol and ionic liquid, corresponding to the fermentation broth composition. Acetone, butanol and ethanol used in the experiments were of at least 99% purity (CHEMPUR, Poland). Two hydrophobic ionic liquids, 1-hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF₆] and 1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide [Bmim][Tf₂N] (IoLiTec, Germany), whose chemical structures are shown in Figs. 1 and 2, were applied as extractants.

![Fig. 1. Structural formula of 1-hexyl-3-methylimidazolium hexafluorophosphate](image1)

![Fig. 2. Structural formula of 1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide](image2)

The experiments were carried out with four-component feed solutions containing water, acetone, *n*-butanol and ethanol. Mass fractions of acetone, butanol and ethanol varied between 0 and 6%. Volumes of solutions ranged from 0.5 to 2.0 cm³. Approximately 1.0 cm³ of ionic liquid was added to each feed solution. Then the mixtures were placed in a thermostated water bath and shaken for about 1.5–2.0 hrs. At the end of that period they were centrifuged to expedite phase separation (Fig. 3).

The extraction was conducted at temperatures of 10, 30 and 50 °C.
Concentrations of acetone, butanol and ethanol in the raffinate (water-rich phase) were measured with a gas chromatograph (TraceGC ThermoFinnigan with Quadrex Corp. column) using internal standard (methanol).

Water content in the extract (IL-rich phase) was determined by Karl-Fischer titration (Mettler Toledo T70 Titrator).

Measurements showed that the presence of solvents, especially butanol and acetone, as well as temperature augmented solubility of water in both ionic liquids. Likewise, solubility of ionic liquids in water was enhanced by the same factors.

ILs content in the raffinate was calculated based on a separate set of experiments, in which all mixture components, but ionic liquid, were evaporated.

Preliminary tests revealed that both ionic liquids were practically non-volatile at the boiling point of the highest boiling component of the mixture, in this case butanol.
(BP = 116–118 °C). Therefore, ionic liquid was the only component that did not evaporate from the solution of known mass and content.

Complete compositions of both phases were calculated on the basis of the above mentioned measurements.

**Results**

Phase equilibrium of five-component systems has been described by distribution coefficients, extraction efficiency and selectivity defined as follows:

– Extraction efficiency

\[
\eta = \left(1 - \frac{C_W}{C_F}\right) \times 100
\]

where:  
- \(C_F\) – concentration of a component in the feed solution (aqueous phase) [g/g],  
- \(C_W\) – concentration of a component in the raffinate (water-rich phase) after separation [g/g].

– Distribution coefficient

\[
\alpha = \frac{C_{IL}}{C_W}
\]

where:  
- \(C_{IL}\) – concentration of a component (also water) in the IL-rich phase after separation [g/g],  
- \(C_W\) – concentration of a component (also water) in the water-rich phase after separation [g/g].

– Selectivity

\[
\beta = \frac{\alpha}{\alpha_W}
\]

where:  
- \(\alpha\) – distribution coefficient of a component,  
- \(\alpha_W\) – distribution coefficient of water.

Calculated distribution coefficients and selectivities are given in Tables 2 and 3, where \(m_{IL}/m_W\) is a mean ionic liquid and water mass ratio for a given set of experiments. This ratio’s value results from the differences between densities of ILs and water. Assuming approximately equal volumes of both phases, the IL-rich phase is heavier. The experiments have been done with ca 0.5, 1.0 and 2.0 cm³ volumes of aqueous solutions.
Table 2
Distribution coefficients and selectivity of [Hmim][PF$_6$]

<table>
<thead>
<tr>
<th>Temperature [$^\circ$C]</th>
<th>$m_{IL}/m_W$</th>
<th>$\alpha_A$</th>
<th>$\alpha_B$</th>
<th>$\alpha_E$</th>
<th>$\alpha_W$</th>
<th>$\beta_A$</th>
<th>$\beta_B$</th>
<th>$\beta_E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>0.609</td>
<td>1.043</td>
<td>1.089</td>
<td>0.181</td>
<td>0.024</td>
<td>45.77</td>
<td>47.44</td>
<td>7.32</td>
</tr>
<tr>
<td>10.0</td>
<td>1.201</td>
<td>0.917</td>
<td>0.889</td>
<td>0.124</td>
<td>0.022</td>
<td>41.32</td>
<td>39.85</td>
<td>5.48</td>
</tr>
<tr>
<td>10.0</td>
<td>2.575</td>
<td>0.999</td>
<td>0.912</td>
<td>0.111</td>
<td>0.021</td>
<td>47.38</td>
<td>43.70</td>
<td>5.20</td>
</tr>
<tr>
<td>30.0</td>
<td>0.625</td>
<td>1.122</td>
<td>1.371</td>
<td>0.200</td>
<td>0.029</td>
<td>39.43</td>
<td>43.92</td>
<td>7.01</td>
</tr>
<tr>
<td>30.0</td>
<td>1.219</td>
<td>1.110</td>
<td>1.242</td>
<td>0.162</td>
<td>0.027</td>
<td>41.14</td>
<td>47.23</td>
<td>6.03</td>
</tr>
<tr>
<td>30.0</td>
<td>2.478</td>
<td>1.081</td>
<td>1.178</td>
<td>0.169</td>
<td>0.025</td>
<td>43.84</td>
<td>46.16</td>
<td>6.91</td>
</tr>
<tr>
<td>50.0</td>
<td>0.601</td>
<td>1.269</td>
<td>1.808</td>
<td>0.237</td>
<td>0.033</td>
<td>39.73</td>
<td>56.31</td>
<td>7.19</td>
</tr>
<tr>
<td>50.0</td>
<td>1.206</td>
<td>1.176</td>
<td>1.546</td>
<td>0.214</td>
<td>0.031</td>
<td>38.85</td>
<td>50.63</td>
<td>6.99</td>
</tr>
<tr>
<td>50.0</td>
<td>2.475</td>
<td>1.205</td>
<td>1.492</td>
<td>0.190</td>
<td>0.027</td>
<td>45.68</td>
<td>56.67</td>
<td>7.15</td>
</tr>
</tbody>
</table>

Table 3
Distribution coefficients and selectivity of [Bmim][Tf$_2$N]

<table>
<thead>
<tr>
<th>Temperature [$^\circ$C]</th>
<th>$m_{IL}/m_W$</th>
<th>$\alpha_A$</th>
<th>$\alpha_B$</th>
<th>$\alpha_E$</th>
<th>$\alpha_W$</th>
<th>$\beta_A$</th>
<th>$\beta_B$</th>
<th>$\beta_E$</th>
</tr>
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<tr>
<td>10.0</td>
<td>0.789</td>
<td>0.907</td>
<td>1.153</td>
<td>0.145</td>
<td>0.023</td>
<td>40.62</td>
<td>51.04</td>
<td>6.28</td>
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<tr>
<td>10.0</td>
<td>1.574</td>
<td>1.065</td>
<td>1.330</td>
<td>0.154</td>
<td>0.022</td>
<td>48.45</td>
<td>60.54</td>
<td>7.02</td>
</tr>
<tr>
<td>10.0</td>
<td>3.140</td>
<td>0.935</td>
<td>1.247</td>
<td>0.124</td>
<td>0.021</td>
<td>45.02</td>
<td>60.31</td>
<td>5.96</td>
</tr>
<tr>
<td>30.0</td>
<td>0.787</td>
<td>1.124</td>
<td>1.695</td>
<td>0.215</td>
<td>0.028</td>
<td>39.50</td>
<td>59.05</td>
<td>7.57</td>
</tr>
<tr>
<td>30.0</td>
<td>1.570</td>
<td>1.037</td>
<td>1.516</td>
<td>0.192</td>
<td>0.027</td>
<td>39.00</td>
<td>56.37</td>
<td>7.25</td>
</tr>
<tr>
<td>30.0</td>
<td>3.154</td>
<td>1.040</td>
<td>1.464</td>
<td>0.169</td>
<td>0.024</td>
<td>43.76</td>
<td>61.56</td>
<td>7.06</td>
</tr>
<tr>
<td>50.0</td>
<td>0.789</td>
<td>1.167</td>
<td>2.053</td>
<td>0.257</td>
<td>0.034</td>
<td>35.77</td>
<td>62.61</td>
<td>7.73</td>
</tr>
<tr>
<td>50.0</td>
<td>1.578</td>
<td>1.097</td>
<td>1.869</td>
<td>0.228</td>
<td>0.031</td>
<td>36.03</td>
<td>61.12</td>
<td>7.44</td>
</tr>
<tr>
<td>50.0</td>
<td>3.165</td>
<td>1.249</td>
<td>1.970</td>
<td>0.239</td>
<td>0.027</td>
<td>46.87</td>
<td>74.31</td>
<td>8.96</td>
</tr>
</tbody>
</table>

Distribution coefficients of butanol are presented below in form of diagrams, where $m_{IL}/m_W$ on the horizontal axis are overall mean ionic liquid and water mass ratios corresponding to each of the three different volumes of feed solutions (as noted above).

In general, rise in temperature causes the increase of distribution coefficients, and thus extraction efficiency, which is illustrated with the example of butanol in Figs. 4 and 5. At the same time, at constant temperatures distribution coefficients tend to diminish, or at least remain within quite a narrow range, when $m_{IL}/m_W$ ratios are higher. Similar tendencies may be observed for acetone and ethanol. It is important to mention that both the accuracy and number of experiments that have been performed may be insufficient to draw unequivocal conclusions about the nature of these changes. Of course, very low distribution coefficients of water reflect its bad miscibility with ionic liquids used as extracting agents, in other words both ILs are strongly hydrophobic.
Selectivities, which are dependent on distribution coefficients, also show erratic behaviour. For butanol and perhaps ethanol they seem to grow with increasing temperature, but this relation is not visible in case of acetone. Both ionic liquids provide comparable selectivities for acetone (in the range of 35.0–50.0) and ethanol (in the range of 5.5–8.5), but [Bmim][Tf₂N] seems to be more butanol-selective than [Hmim][PF₆], especially at higher temperatures.

Comparisons of the extraction efficiencies are presented in Figs. 6–11.

As can be seen from the diagrams, [Bmim][Tf₂N], compared with [Hmim][PF₆], provides slightly better separation of all the three substances from aqueous solutions, but still the efficiency for ethanol is quite low. Under economically reasonable conditions, that is at room temperature and with volumes of ILs equal to the volumes of feed solutions, it does not exceed about 20 %. Under the same conditions separation efficiencies for acetone and butanol are much higher reaching up to ca. 55 % and 58 %, respectively after extraction by [Hmim][PF₆] and ca 60 % and 69 % after extraction by [Bmim][Tf₂N]. The highest efficiencies for all components have been obtained with
Fig. 6. Efficiency of acetone separation by [Hmim][PF₆]}

Fig. 7. Efficiency of butanol separation by [Hmim][PF₆]

Fig. 8. Efficiency of ethanol separation by [Hmim][PF₆]
Fig. 9. Efficiency of acetone separation by [Bmim][Tf$_2$N]

Fig. 10. Efficiency of butanol separation by [Bmim][Tf$_2$N]

Fig. 11. Efficiency of ethanol separation by [Bmim][Tf$_2$N]
maximum relative volumes of ILs at 50 °C, the lowest efficiencies – with minimum relative volumes of ILs at 10 °C. Both of these factors, namely the amount of IL and temperature, influence the extraction process in the most significant way. However, the separation of butanol as well as ethanol seems to be more temperature-dependent than the separation of acetone.

**Conclusions**

From the results presented it is evident that there are two main factors having a decisive influence on the extraction efficiency, namely temperature and the amount of extractant. The highest efficiencies of butanol separation for both ILs studied, ca 77 % and 85 %, respectively, were reached at 50 °C with volumes of ILs approximately two-fold greater than volumes of feed solutions. Distribution coefficients for all substances essentially grow as temperature rises, but their variations resulting from different $m_{IL}/m_{W}$ ratios at constant temperatures cannot be explained at this stage of the study. Also, an increase in temperature appears to favour separation of butanol over acetone and ethanol, which is reflected by growing selectivity (not so obvious for the other two substances). The extraction of butanol and ethanol seems to be more temperature-sensitive than the extraction of acetone, for which the efficiency relies mostly on the amount of extracting agent.

Generally speaking, both ionic liquids, when used in quantities comparable with the amount of feed solution, ensure about 50–65 % efficiency of extraction at room temperature for both acetone and butanol, which is of some significance from an energy consumption standpoint. At the same time, ethanol gets separated rather poorly. It is necessary to note that butanol, besides being the key product of ABE fermentation, has the strongest inhibitory effect on bacterial metabolism and, as such, needs to be removed from the fermentation broth in the first place. However, an excessive accumulation of by-products should also be prevented. Hence, further studies will be conducted to find ionic liquids most suitable for ABE extraction.

**References**

CIECZE JONOWE W EKSTRAKCJI N-BUTANOLU Z ROZTWORÓW WODNYCH

Katedra Termodynamiki Procesowej, Wydział Inżynierii Procesowej i Ochrony Środowiska
Politechnika Łódzka

**Abstrakt:** Przedmiotem artykułu jest proces ekstrakcji \textit{n}-butanolu z czteroskładnikowych roztworów wodnych zawierających ponadto aceton i etanol. Wymienione substancje są głównymi składnikami tzw. brzeczki fermentacyjnej stanowiącej produkt fermentacji ABE (acetonowo-butanolowo-etanolowej). Fermentacja ABE, jako jedna z najstarszych metod uzyskiwania biobutanolu stosowanych na skalę przemysłową, jest obecnie rozważana jako alternatywa dla dominujących w przemyśle procesów petrochemicznych. Znacząco przyczynia się ku temu perspektywa wyczerpania dostępnego zapasów paliw kopalnych, jak również podejmowane na szeroką skalę próby wdrażania zasad czystej produkcji i korzystania z odnawialnych źródeł energii. Z uwagi na bardzo korzystne właściwości fizykochemiczne istnieją realne możliwości bezpośredniego zastosowania biobutanolu w silnikach spalinowych, bądź wykorzystania go jako dodatku do oleju napędowego i benzyny. Skuteczna separacja biobutanolu pozyskiwanego przy pomocy metod biochemicznych może mieć zatem ogromny wpływ na rozwój technologii produkcji paliw półnych. Problemem przy stosowaniu klasycznych rozpuszczalników w ekstrakcji ciecz-ciecz jest często ich toksyczność, jak również wysoka lotność uniemożliwiająca opłacalny ekonomicznie rozdział ekstraktu. Dlatego też w kręgu zainteresowań pojawiają się niskolotne i stabilne termicznie ciecz ciecz升温. Wyniki badań w pokładach zawierających wodę, aceton, butanol, etanol i ciecz jonową. Wykorzystano w tym celu dwie ciecz升温: heksafluorofosforan 1-heksylo-3-metyloimidazolu oraz bis(trifuorometylosulfonylo)imid 1-butylo-3-metyloimidazolu. Wyniki eksperymentów potwierdzają wysoką skuteczność procesu ekstrakcji \textit{n}-butanolu przy zbliżonych objętościach roztworu surowego i ekstrahenta.

**Słowa kluczowe:** ekstrakcja ciecz-ciecz, ciecz升温, biobutanol, odnawialne źródła energii