

Application of Ionic Liquids in the Separation of Butanol from Aqueous Solutions

Artur Kubiczek, M.Sc. Eng.

Supervisor: Prof. Władysław Kamiński, Ph.D., D.Sc.

Abstract

The article treats of the extraction of butanol from aqueous solutions that also contain ethanol and acetone. These three chemicals are the main components of the so called fermentation broth – the product of ABE (Acetone-Butanol-Ethanol) fermentation process. Effective separation of biobutanol may have great impact on fuel production technology, which is by far crude oil oriented. ABE fermentation, which was given up after World War II due to petroleum processing, uses renewable energy sources. Ionic liquids, on the other hand, gain more and more interest in the scientific community. Low volatility and thermal stability make them highly applicable for extraction and distillation.

The research shows that 1-hexyl-3-methylimidazolium hexafluorophosphate ionic liquid enables over 50% efficiency of the room temperature extraction process with more or less equal volumes of both liquid phases. Therefore, further experiments are well-justified.

Keywords

Liquid-liquid extraction, phase equilibrium, ionic liquid, butanol, biofuel, ABE fermentation

1. Introduction

1.1 Butanol production

Butanol is a chemical capable of numerous industrial and non-industrial applications. Since the 1950s, when previously used fermentation techniques were superseded by crude oil processing, it has been produced almost solely from fossil fuels. In recent years, however, due to proecological trends and popularization of principles of so-called “green chemistry”, biochemical methods of butanol production have been taken into account again.

One of the oldest industrial techniques of butanol production, considered as an alternative for petrochemical processes, is the ABE fermentation. The main products – acetone, butanol and ethanol – are obtained thanks to anaerobic *Clostridium* bacteria. The improvement of fermentation efficiency through the employment of genetically modified species is a crucial part of the research. Use of cheap, renewable resources as well as high efficiency of the product separation are also very important.

The most popular and chiefly used bacterial species is *Clostridium acetobutylicum* giving the total concentration of products (i.e., acetone, butanol and ethanol) of ca. 20 g/L with their approximate mass ratio of 1:6:3. *Clostridium beijerinckii* is more butanol selective – the concentration of products in the fermentation broth amounts to 33 g/L with their mass ratio of 1:16:3. There are also other species applicable: *Clostridium aurantibutyricum* (producing acetone, butanol and isopropanol) or *Clostridium tetanomorphum* (producing even amounts of ethanol and butanol).

1.2 Properties of butanol

Most promisingly, butanol could be utilized directly in internal combustion engines because of sufficiently similar characteristics to that of gasoline. As a fuel additive it is superior to ethanol in many aspects, e.g., lower volatility, higher energy content, better miscibility with diesel fuel and gasoline.

From a technical point of view, it is speculated that increased production of butanol together with appropriate modifications in the combustion process might make the automotive industry independent from fossil fuels [1].

Table 1 shows the comparison of butanol with other fuels [2].

Table 1. – Properties of fuels

	Butanol	Gasoline	Diesel fuel	Ethanol	Methanol
Energy density [MJ/L]	29,2	32,0	35,9	19,6	16,0
Air-fuel ratio (AFR)	11,2	14,7	14,6	9,0	6,5
Heat of vaporization [MJ/kg]	0,43	0,36	0,23	0,92	1,20
Research Octane Number (RON)	96	91 – 99	–	129	136
Motor Octane Number (MON)	78	81 – 89	–	102	104

1.3 Application of ionic liquids in liquid-liquid extraction

Separation of biobutanol from the fermentation broth poses a complex technical problem. A variety of methods have been proposed such as gas stripping, adsorption, liquid-liquid extraction (LLE), pervaporation and membrane solvent extraction. However, liquid-liquid extraction and pervaporation appear to be the most suitable techniques [3]. Separation of fermentation products must be carried out in a continuous manner, because their excessive concentration inhibits the bacteria [4]. Energy demand and costs of potential technical solutions are another important criteria. Classical solvent extraction may be of practical use, but then volatility and toxicity of solvents come into conflict with the above-mentioned principles of green chemistry.

Therefore, ionic liquids, which gain more and more recognition in science and industry, may come along as highly appropriate for the recovery of biobutanol.

Ionic liquids have been investigated by many authors (Welton, Holbrey, Seddon). The first room-temperature ionic liquid – ethyl ammonium nitrate [EtNH₃][NO₃] (melting point: 12°C) – was discovered in 1914 [5].

Ionic liquid (IL) is a liquid substance composed solely of ions, in a general sense, a molten salt. However, most salts melt in high temperatures (e.g., melting point of sodium chloride is 800 °C). Therefore, contemporary ionic liquids are salts whose melting point is lower than 100 °C. There are also salts melting in temperatures lower than 20 °C and they are called *room-temperature ionic liquids (RTILs)*.

A room-temperature ionic liquid usually consists of a big, asymmetric cation (e.g., 1-alkyl-3-methylimidazolium, 1-alkylpyridinium, N-methyl-N-pyrrolidinium) and one of the broad variety of anions. While simple halide anions (e.g., chlorine) increase the melting point, anions comprised of many fluorine atoms (BF₄⁻, PF₆⁻) or complex organic anions decrease it. For instance, the melting point of 1-butyl-3-methylimidazolium tetrafluoroborate is -80 °C.

Ionic liquids are often described as *designer solvents*. Thus, their properties may be “adjusted” to suit certain process requirements [6].

The main attributes of ionic liquids making them useful in separation of mixtures are very low volatility and a wide liquid range (often exceeding 200 °C) [7,8]. It allows their relatively easy regeneration (via 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.

The relation between types of ions and mutual solubilities of ionic liquids and water has not been clearly defined yet, however, some observations have been made. A few authors point that the influence of anions on the hydrophobicity of ionic liquids is greater than the influence of cations. Interactions of water with ions can be observed thanks to IR spectroscopic methods. It was found that those interactions are stronger with anions. Consequently, anions such as halides, nitrates and methylsulphonates strongly enhance the solubility of ILs in water, while anions such as hexafluorophosphate or bis(trifluoromethylsulfonyl)imide usually prevent it. Cations also affect the miscibility of ILs with water, but to a significantly lesser degree. Properties depend on the length of alkyl chains (longer alkyl chains are less water-soluble) and the type of cationic central groups (for instance, pyridinium and pyrrolidinium cations are less water-soluble than imidazolium cations, whereas piperidinium cations are least water-soluble) [9].

2. Extraction experiments

2.1 Research objectives

The primary aim of research is to ascertain and describe the extraction equilibria (in particular, activity coefficients of each substance in raffinate and extract) in the five-component two-phase system of water, acetone, butanol, ethanol and ionic liquid. This system corresponds to the fermentation broth composition.

2.2 Reagents and materials

The experiments are conducted with acetone, n-butanol and ethanol of at least 99 % purity (*CHEMPUR, Poland*). 1-hexyl-3-methylimidazolium hexafluorophosphate [*Hmim*][*PF₆*] (*Io•Li•Tec, Germany*) of chemical structure shown in Figure 1 is used as the extracting solvent. It is intended that 1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide [*Bmim*][*Tf₂N*] specifically as well as other ionic liquids will be used in the next stages of research depending on the results. The choice of ionic liquids is determined primarily by their low miscibility with water and market availability.

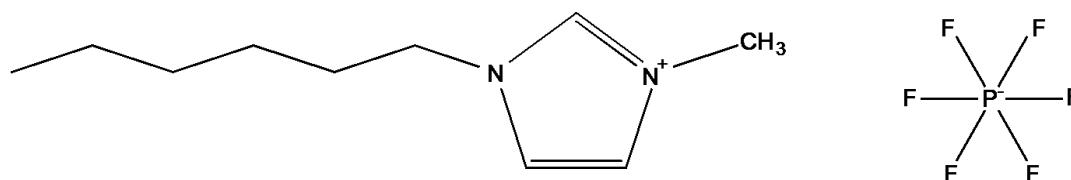


Fig. 1. Structural formula of 1-hexyl-3-methylimidazolium hexafluorophosphate

2.3 Methods

The experiments are carried out with four-component feed solutions containing water, acetone, n-butanol and ethanol. Mass fractions of acetone, butanol and ethanol vary between 1 and 5 %. Volumes of solutions range from 1 to 2 mL. Approximately 1 mL of ionic liquid is added to each feed solution. Then the mixtures are placed in a water bath for about 1.5-2.0 hrs and shaken for a few minutes in the meantime. At the end of that period they are centrifuged to expedite phase separation (Figures 2 & 3).

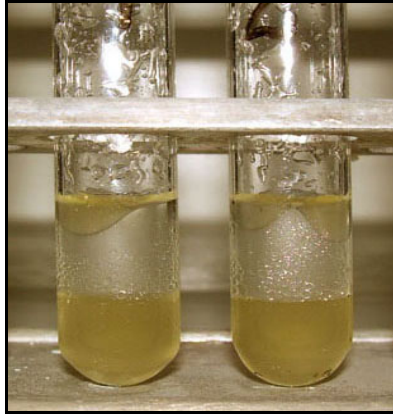


Fig. 2. Mixtures before centrifugation

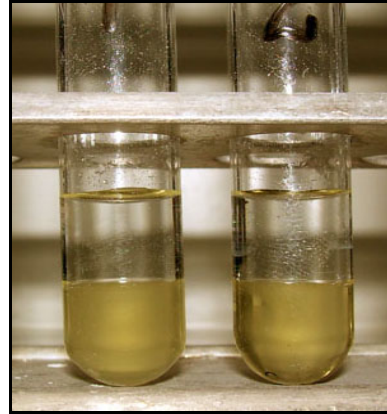


Fig. 3. Mixtures after centrifugation

The extraction is conducted at temperatures of 20, 30 and 40 °C. Mass of each component is determined with ± 0.0001 g accuracy.

Concentrations of acetone, butanol and ethanol in the raffinate (water-rich phase) are measured with a gas chromatograph (*TraceGC ThermoFinnigan* with *Quadrex Corp.* column) using internal standard (methanol).

2.4 Results

At the current point of research the phase equilibrium has been described by distribution coefficients, extraction efficiency and selectivity defined as follows:

- Extraction efficiency

$$\eta = \left(1 - \frac{C_W}{C_F}\right) \cdot 100 \quad (1)$$

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

$$\alpha = \frac{C_{IL}}{C_W} \quad (2)$$

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

$$\beta = \frac{\alpha}{\alpha_W} \quad (3)$$

where:

- α – distribution coefficient of a component,
- α_W – distribution coefficient of water.

The results are shown in Tables 3 and 4, where m_{IL}/m_W is a mean ionic liquid and water mass ratio for a given set of experiments¹. For the purpose of calculating the specified quantities mutual miscibilities of [Hmim][PF₆] and water have been taken from available literature data (Table 2). They will be investigated further on in time².

Table 2. – Mutual solubilities of [Hmim][PF₆] and water (in wt%) (according to [3])

[Hmim][PF ₆] in H ₂ O			H ₂ O in [Hmim][PF ₆]		
T = 20°C	T = 30°C	T = 40°C	T = 20°C	T = 30°C	T = 40°C
0,480	0,720	0,960	2,248	2,252	2,256

Table 3. – Distribution coefficients of acetone, butanol, ethanol and water after extraction by [Hmim][PF₆]

Temperature, °C	m_{IL}/m_W	α_A	α_B	α_E	α_W
20,0	0,621	0,9831	1,1145	0,1960	0,0231
20,0	1,239	0,9488	1,0618	0,1461	0,0232
30,0	0,824	1,2418	1,2954	0,2038	0,0229
40,0	0,636	1,1512	1,4338	0,2085	0,0230
40,0	1,267	1,2027	1,5869	0,2066	0,0230

Table 4. – Selectivity and efficiency of extraction (in %) of acetone, butanol and ethanol by [Hmim][PF₆]

Temperature, °C	m_{IL}/m_W	β_A	β_B	β_E	η_A	η_B	η_E
20,0	0,621	42,553	48,237	8,488	35,38	38,48	7,35
20,0	1,239	40,980	45,887	6,300	51,39	54,21	9,88
30,0	0,824	54,259	56,606	8,901	48,44	49,55	10,42
40,0	0,636	50,004	62,320	9,048	39,84	45,37	8,15
40,0	1,267	52,251	68,873	8,961	57,97	64,87	15,45

¹ Density of ionic liquid is greater than density of water. Therefore, assuming approximately equal volumes of both phases, the IL-rich phase is heavier. The experiments have been done with ca. 1.0, 1.5 and 2.0 mL volumes of the feed solution.

² Preliminary measurements of the IL-rich phase by Karl Fischer titration show that the presence of solvents (especially butanol and acetone) augments solubility of water in [Hmim][PF₆]. However, when the feed solution contains about 5 wt% of acetone, butanol and ethanol respectively, increase in the concentration of water in the IL-rich phase remains within less than 1.5 wt%. Therefore, it does not change the calculated results in a significant manner. Likewise, it is expected that the presence of solvents in the water-rich phase will enhance the solubility of ionic liquid in it, but to a relatively smaller degree. A few experiments have been made that support this assumption.

3. Conclusions

Comparing the results shown in Tables 3 and 4 one may easily notice that the temperature and the amount of extractant are factors decisive of extraction efficiency. However, the latter of the two seems of greater importance. A volume of [Hmim][PF₆] more or less equal to a volume of the feed solution allows approximately 65 % efficiency of separation at 40 °C. In addition, an increase in temperature appears to favor separation of butanol over acetone to a certain degree. At first glance, the above-mentioned dependencies suggest that experiments should be conducted at higher temperatures and with greater volumes of ionic liquid used. Nevertheless, the energy consumption is another notable question. Therefore, physical conditions applied during the separation should be a result of a compromise between its costs and efficiency. One should also consider that a rise in temperature causes increased volatility of solvents and may accelerate their evaporation.

The experiments reveal that, practically speaking, [Hmim][PF₆] is not applicable for the separation of ethanol. The highest efficiency obtained for this component equals around 15 %. The results may be deemed encouraging further research with the use of other extractants. The two key questions need to be answered: which of ionic liquids investigated exhibits the highest selectivity for butanol and what the most favourable conditions of the extraction process are.

References

- [1] Kamiński W., Tomczak E., Górak A., *Biobutanol – production and purification methods*, Ecological Chemistry and Engineering S, .Vol. 18, No. 1, 31-37, 2011.
- [2] Sang Yup Lee et al., *Fermentative butanol production by Clostridia*, Biotechnology and Bioengineering, Vol. 101, No. 2, October 1, 2008.
- [3] Ha SH et al., *Butanol recovery from aqueous solution into ionic liquids by liquid-liquid extraction*, Process Biochemistry, 2010.
- [4] Simoni L.D., Chapeaux A., Brennecke J.F., Stadtherr M.A., *Extraction of biofuels and biofeedstocks from aqueous solutions using ionic liquids*, Computers and Chemical Engineering, Vol. 34, 1406-1412, 2010.
- [5] Earle M.J., Seddon K.R., *Ionic Liquids. Green solvents for the future*, Pure and Applied Chemistry, Vol. 72, No. 7, 1391-1398, 2000.
- [6] *Electrochemical aspects of ionic liquids*, Edited by Hiroyuki Ohno, John Wiley & Sons, Inc., 2005.
- [7] Fredlake C.P., Crosthwaite J.M., Hert D.G., Aki S.N.V.K., Brennecke J.F., *Thermophysical properties of imidazolium-based ionic liquids*, Journal of Chemical & Engineering Data, 2004, 49, 954-964.
- [8] Johnson K.E., *What's an ionic liquid?* The Electrochemical Society Interface, Spring 2007.
- [9] Klähn M., Stüber C., Seduraman A., Wu P., *What determines the miscibility of ionic liquids with water? Identification of the underlying factors to enable a straightforward prediction*, The Journal of Physical Chemistry, B 2010, 114, 2856-2868.