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IONIC LIQUIDS FOR THE EXTRACTION OF *n*-BUTANOL FROM AQUEOUS SOLUTIONS

CIECZE JONOWE W EKSTRAKCJI *n*-BUTANOLU Z ROZTWORÓW WODNYCH

Abstract: The article describes the extraction of *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 techniques, 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 or even for 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. 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_6] and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [Bmim][Tf_2N]. Experimental results confirm highly efficient separation of *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 displays favourable combustion characteristics and, as a fuel additive, it is superior to widely used ethanol in many aspects (*eg*, 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 (according to [2, 3]) is shown in Table 1.

Table 1

Properties of fuels

	Butanol	Gasoline	Diesel fuel	Ethanol	Methanol
Energy density [MJ/dm^3]	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

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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 anaerobic *Clostridium* bacteria. In view of the steady depletion of hydrocarbon deposits 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 (*ie* acetone, butanol and ethanol) obtained in the fermentation broth ranges between 15-26 g/dm^3 depending on the substrates, with butanol yield approaching 19-20 g/dm^3 [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]. 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, appears to be the most suitable techniques [6]. 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 salts whose melting point is lower than 100ºC. There are also salts melting in temperatures lower than 20ºC 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 [7, 8].

The main attributes of ionic liquids making them useful in separation of mixtures are very low volatility and wide liquid range (often exceeding 200ºC) [9, 10], 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, *ie*, 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 [11]. 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][PF_6] and 1-butyl-3-methylimidazolium

bis(trifluoromethylsulphonyl)imide [Bmim][Tf_2N] (*Io•Li•Tec, Germany*), whose chemical structures are shown in Figures 1 and 2, were applied as extractants.

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 cm^3. Approximately 1.0 cm^3 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 50ºC.

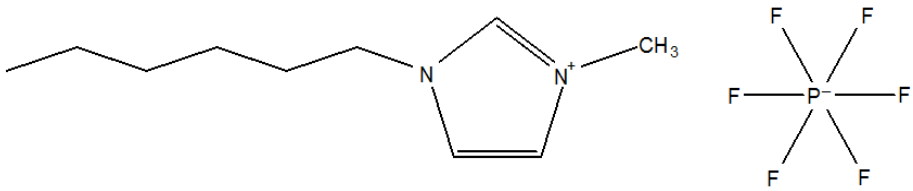


Fig. 1. Structural formula of 1-hexyl-3-methylimidazolium hexafluorophosphate

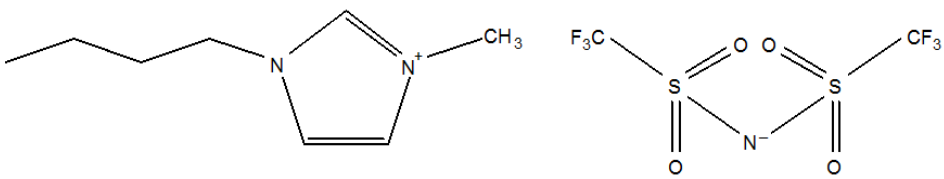


Fig. 2. Structural formula of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

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).

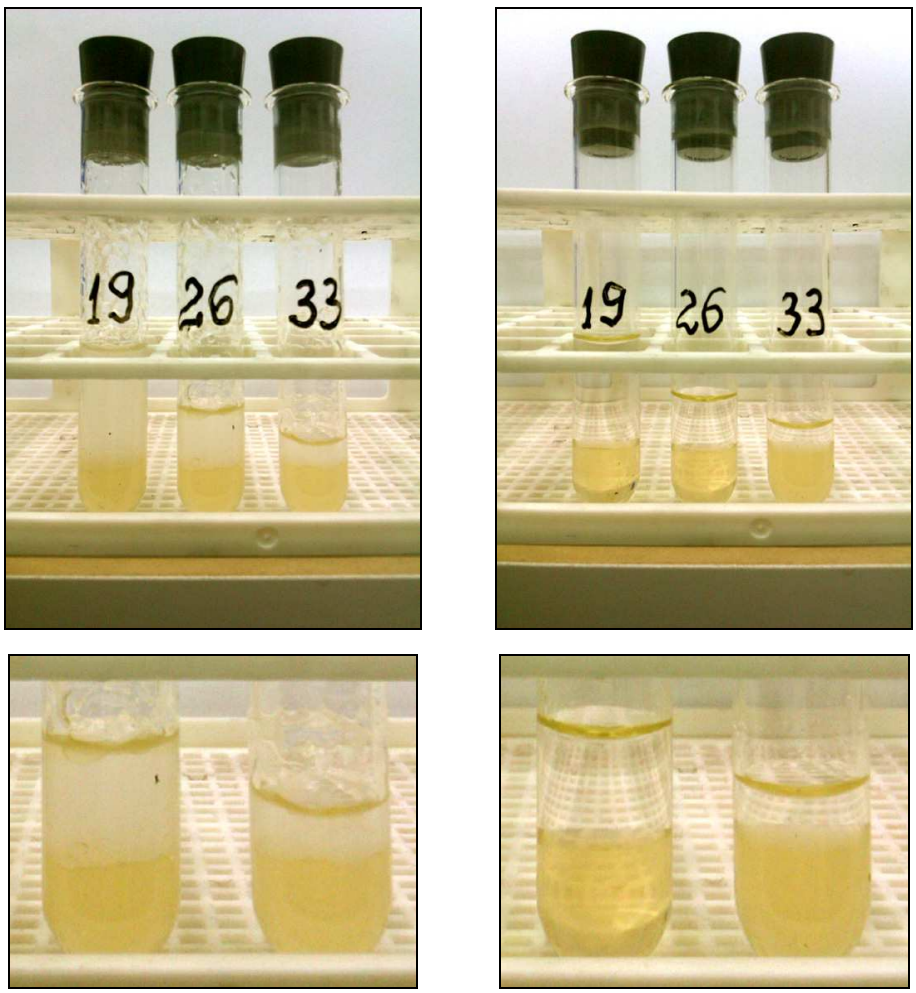
Water content in the extract (IL-rich phase) was determined by Karl-Fischer titration (*Mettler Toledo T70 Titrator*).

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 = 116-118ºC). 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.



After mixing After centrifugation

Fig. 3. Mixtures containing water, 1-hexyl-3-methylimidazolium hexafluorophosphate, acetone, butanol and ethanol

Results

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

- Extraction efficiency

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

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

$$\alpha = \frac{C_{IL}}{C_W} \tag{2}$$

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

$$\beta = \frac{\alpha}{\alpha_w} \tag{3}$$

where: α - distribution coefficient of a component, α_W - distribution coefficient of water.

The results are shown in Tables 2-5, where m_{IL}/m_W is a mean ionic liquid and water mass ratio for a given set of experiments.

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 0.5, 1.0 and 2.0 cm^3 volumes of feed solutions.

Table 2

Distribution coefficients of acetone, butanol, ethanol and water after extraction by [Hmim][PF_6]

Temperature [°C]	m_{IL}/m_W	α_A	α_B	α_E	α_W
10.0	0.609	1.043	1.089	0.183	0.024
10.0	1.201	0.917	0.889	0.125	0.023
10.0	2.575	0.998	0.912	0.111	0.020
30.0	0.625	1.122	1.371	0.200	0.029
30.0	1.221	1.110	1.242	0.162	0.027
30.0	2.478	1.081	1.178	0.169	0.024
50.0	0.601	1.269	1.810	0.236	0.032
50.0	1.206	1.176	1.546	0.214	0.031
50.0	2.475	1.205	1.492	0.191	0.028

Table 3

Distribution coefficients of acetone, butanol, ethanol and water after extraction by [Bmim][Tf2N]

Temperature [°C]	m_{IL}/m_W	α_A	α_B	α_E	α_W
10.0	0.789	0.907	1.153	0.146	0.024
10.0	1.574	1.064	1.329	0.155	0.023
10.0	3.140	0.934	1.247	0.123	0.019
30.0	0.792	1.124	1.695	0.215	0.028
30.0	1.577	1.037	1.516	0.192	0.026
30.0	3.169	1.040	1.464	0.169	0.024
50.0	0.789	1.167	2.054	0.256	0.032
50.0	1.578	1.097	1.869	0.228	0.031
50.0	3.165	1.249	1.970	0.240	0.028

Table 4

Selectivity and efficiency of extraction (in [%]) of acetone, butanol and ethanol by [Hmim][PF_6]

Temperature [ºC]	m_{IL}/m_W	β_A	β_B	β_E	η_A	η_B	η_E
10.0	0.609	44.52	46.15	7.28	36.7	37.8	6.8
10.0	1.201	40.15	38.72	5.36	49.7	48.7	7.8
10.0	2.575	50.52	46.97	5.42	69.3	67.0	14.0
30.0	0.625	39.17	44.98	6.98	38.8	43.9	7.4
30.0	1.221	40.97	46.98	6.00	54.6	57.9	11.1
30.0	2.478	45.20	46.46	7.10	70.2	72.4	22.1
50.0	0.601	40.61	57.67	7.35	41.4	50.7	9.1
50.0	1.206	38.34	50.07	6.91	56.4	63.2	15.2
50.0	2.475	43.76	54.28	6.88	72.8	76.9	24.5

Table 5

Selectivity and efficiency of extraction (in [%]) of acetone, butanol and ethanol by [Bmim][Tf_2N]

Temperature [ºC]	m_{IL}/m_W	β_A	β_B	β_E	η_A	η_B	η_E
10.0	0.789	38.87	48.90	6.09	39.1	45.4	6.6
10.0	1.574	47.42	59.36	6.91	60.2	65.7	13.5
10.0	3.140	48.86	66.08	6.36	72.5	78.0	20.3
30.0	0.792	39.44	59.29	7.55	44.7	55.5	10.4
30.0	1.577	39.05	56.51	7.26	59.6	68.7	17.3
30.0	3.169	43.80	61.03	7.07	74.7	80.9	27.2
50.0	0.789	36.54	64.06	7.92	45.7	60.4	12.6
50.0	1.578	36.04	61.14	7.45	60.8	73.2	20.5
50.0	3.165	44.99	71.47	8.63	78.1	85.2	36.3

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 for both ILs studied, ca 77% and 85% respectively, were reached at 50ºC 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).

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.

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CIECZE JONOWE W EKSTRAKCJI *n*-BUTANOLU Z ROZTWORÓW WODNYCH

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Abstrakt: Przedmiotem artykułu jest proces ekstrakcji *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 do tego perspektywa wyczerpania dostępnych zapasów paliw kopalnych, jak również podejmowane na szeroką skalę próby wdrażania zasad czystej produkcji i korzystania z odnawialnych źrodeł 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 za pomocą metod biochemicznych może mieć zatem ogromny wpływ na rozwój technologii produkcji paliw płynnych. 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 zainteresowania pojawiają się niskolotne i stabilne termicznie ciecze jonowe nierozpuszczalne w roztworach wodnych. Właściwości cieczy jonowych jako substancji stosunkowo nowych nie są jeszcze dokładnie poznane, jednak z uwagi na szeroki wachlarz potencjalnych zastosowań budzą one coraz większe zainteresowanie, a możliwości ich "projektowania" mogą wydawać się nieograniczone. Przeprowadzono badania równowagi ekstrakcyjnej w układach zawierających wodę, aceton, butanol, etanol i ciecz jonową. Wykorzystano w tym celu dwie ciecze jonowe: heksafluorofosforan 1-heksylo-3-metyloimidazolu oraz bis(trifluorometylosulfonylo)imid 1-butylo-3-metyloimidazolu. Wyniki eksperymentów potwierdzają wysoką skuteczność procesu ekstrakcji *n*-butanolu przy zbliżonych objętościach roztworu surowego i ekstrahenta.

Słowa kluczowe: ekstrakcja ciecz-ciecz, ciecze jonowe, biobutanol, odnawialne źrodła energii