

LIQUID-LIQUID EXTRACTION IN SYSTEMS CONTAINING BUTANOL AND IONIC LIQUIDS – A REVIEW

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Room-temperature ionic liquids (RTILs) are a moderately new class of liquid substances that are characterized by a great variety of possible anion-cation combinations giving each of them different properties. For this reason, they have been termed as designer solvents and, as such, they are particularly promising for liquid-liquid extraction, which has been quite intensely studied over the last decade. This paper concentrates on the recent liquid-liquid extraction studies involving ionic liquids, yet focusing strictly on the separation of *n*-butanol from model aqueous solutions. Such research is undertaken mainly with the intention of facilitating biological butanol production, which is usually carried out through the ABE fermentation process. So far, various sorts of RTILs have been tested for this purpose while mostly ternary liquid-liquid systems have been investigated. The industrial design of liquid-liquid extraction requires prior knowledge of the state of thermodynamic equilibrium and its relation to the process parameters. Such knowledge can be obtained by performing a series of extraction experiments and employing a certain mathematical model to approximate the equilibrium. There are at least a few models available but this paper concentrates primarily on the NRTL equation, which has proven to be one of the most accurate tools for correlating experimental equilibrium data. Thus, all the presented studies have been selected based on the accepted modeling method. The reader is also shown how the NRTL equation can be used to model liquid-liquid systems containing more than three components as it has been the authors' recent area of expertise.

Keywords: extraction, ionic liquids, butanol, liquid-liquid equilibrium, NRTL equation

1. INTRODUCTION

Ionic liquids (ILs) are liquid organic salts with melting points below 373 K (Brennecke and Maginn, 2001). However, a separate group termed as room-temperature ionic liquids (RTILs), liquid at room temperature, can also be distinguished. Although the first RTIL – ethylammonium nitrate – was synthesized already in 1914 (Earle and Seddon, 2000), the intensive investigation of ionic liquids started only in the 1990s. An important breakthrough came with the discovery of chloroaluminate ionic liquids based on the ethylmethylimidazolium cation (Wilkes and Zaworotko, 1992).

One of the possible and interesting applications of ILs is the liquid-liquid extraction of *n*-butanol from aqueous media. *n*-Butanol, nowadays produced chiefly by the petrochemical industry, can also be synthesized biologically in the process of Acetone-Butanol-Ethanol (ABE) fermentation (Ezeji et al., 2007; García et al., 2011; Qureshi and Blaschek, 2006). This traditional method was exploited at the

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beginning of the 20th century by the military industry, but almost completely abandoned in the 1950s and early 1960s (Dürre, 2007; Jones and Woods, 1986; Lütke-Eversloh and Bahl, 2011).

n-Butanol has numerous commercial uses; moreover, it can be successfully blended with both gasoline and diesel fuel. Because of convenient combustion characteristics it was even suggested that butanol be used directly in the existing engines (García et al., 2011; Kumar and Gayen, 2011; Lee et al., 2008; Ramey, 2007; Siwale et al., 2013). In light of the Stanford Research Institute statistical data, in 2010 the global consumption of petrochemical *n*-butanol amounted to ca. 3 million tons along with a production capacity exceeding 3.5 million tons. The world's two largest *n*-butanol manufacturers are now BASF and Dow Chemical Company. The top ten manufacturers, including companies, such as Oxea Group, Formosa Plastics Group and Eastman Chemical Company, provide about 78% of the world's production capacity. The three most developed regions in terms of production ability are Asia, North America and Western Europe (38, 31 and 18%, respectively). At the same time, Asia is the biggest consumer of butanol being responsible for 53% of the world's total consumption. North America and Western Europe use up to 22 and 19% of *n*-butanol respectively. In view of the SRI predictions, further growth of *n*-butanol demand and production is expected up to the year 2020 (Liu and Xue, 2012).

Currently, China is an undisputed leader in commercial ABE fermentation. Between 2000 and 2006, China imported over 50% of butanol required to satisfy growing domestic needs. Thus, there was a niche to be filled by an alternative technology. Up to the end of 2008, over a dozen Chinese fermentation plants had been built or retrofitted for the purpose of restarting the ABE production, offering a total capacity exceeding 300,000 tons per year, but with further plans to enhance the solvent production to about 1,000,000 tons per year within the next few years (Ni and Sun, 2009). Similar initiatives are also being undertaken in other countries such as Brazil and the United States (Huang et al., 2014; Natalense and Zouain, 2013).

At this point, ABE fermentation is less economical than petrochemical synthesis. The achievable total concentration of solvents in conventional batch reactors fluctuates around 20 g/dm³ (depending on the bacterial strain and substrate type), of which butanol is barely about 13 g/dm³. For this reason, recovery of ABE has to be particularly efficient. Theoretically, a few unit operations are capable of separating fermentation products from the broth. However, they are not equally encouraging in terms of energy demand and costs. As reported by several authors, liquid-liquid extraction is considered to be one of the most promising methods (Abdahagh et al., 2014; Ha et al., 2010; Huang et al., 2014; Kraemer et al., 2011; Stoffers et al., 2013; Vane, 2008).

2. SOLVENTS INVESTIGATED FOR THE RECOVERY OF BUTANOL

Initially, the majority of studies devoted to the recovery of *n*-butanol via liquid-liquid extraction dealt with batch fermentation (*in situ* extraction), thus the appropriate extracting agents were selected based on their non-toxicity towards the fermentation bacteria. Consequently, two main groups of extracting agents were distinguished, i.e. alkanes and alcohols. As it transpired, alcohols usually provided high distribution ratios of butanol ($D > 5$) and moderate selectivities. On the other hand, alkanes, although highly selective, displayed rather low affinity for butanol ($D < 0.5$) (Kraemer et al., 2011; Matsumura et al., 1988).

The benchmark solvent for butanol is oleyl alcohol, whose density (0.845–0.855 g/cm³) is favorable for further separation of the extract from the raffinate. Promising results of extracting butanol with oleyl alcohol were presented already in 1985 (Davison and Thompson, 1993; Ishii et al., 1985; Roffler et al., 1988) and the reported distribution ratios fell in the range between 3.0 and 4.1. However, the main fault of oleyl alcohol is its low separation ability with regard to acetone and ethanol (0.45 and 0.22 according

to Ishii et al., 1985), which, in the case of extractive ABE fermentation, may lead to high solvent demand in order to prevent from excessive accumulation of acetone in the broth (Kraemer et al., 2011).

The other solvents that have been tested with the intention of recovering biobutanol include substances such as glyceryl tributyrate, methylated crude palm oil and other modified plant oils, biodiesel, gasoline, decyl alcohol, mesitylene, surfactants and ionic liquids (Adhami et al., 2009; Evans and Wang, 1988; Huang et al., 2014; Ishizaki et al., 1999; Kraemer et al., 2011). Decanol and mesitylene provide satisfying separation performance but they are toxic and thus capable of being used only in *ex situ* extraction. Kraemer et al. (2011) simulated integrated extraction-distillation of butanol assuming either mesitylene or oleyl alcohol as the extracting agent. The estimated energy demand was 5.7 MJ/kg_{BuOH} in the case of mesitylene and 15 MJ/kg_{BuOH} in the case of oleyl alcohol. When traditional distillation was simulated instead, the energy demand increased to 19 MJ/kg_{BuOH}.

3. EXTRACTION OF N-BUTANOL WITH IONIC LIQUIDS

Over the last decade, liquid-liquid extraction employing room-temperature ionic liquids has become a very popular topic. Among the advantages of RTILs the following are most often mentioned: negligible vapor pressure (Earle and Seddon, 2000; Ji et al., 2012; Sowmiah et al., 2009), thermal stability (Kosmulski et al., 2004), wide liquidus regions (Brennecke and Maginn, 2001; Johnson, 2007), ability to dissolve both organic and inorganic compounds (Simoni et al., 2010) as well as hydrophobicity or hydrophilicity (Klähn et al., 2010).

The potential ability of ionic liquids to extract *n*-butanol from aqueous solutions has also been intensely studied. The properties of ionic liquids determining their separation performance towards butanol vary considerably from one to another. Depending on the anion and the cation structures, the achievable distribution ratios range from a few to several hundred while selectivities vary from a few tens to over a thousand (Domańska and Królikowski, 2012; Garcia-Chavez et al., 2012; Ha et al., 2010; Huang et al., 2014; Marciniak et al., 2016; Rabari and Banerjee, 2013; Simoni et al., 2010; Stoffers and Górak, 2013).

Currently, high prices of ionic liquids are the main obstacle to their application in the extraction process. One should also keep in mind that additional energy is required to regenerate the used-up solvent and, in the case of ABE fermentation, separate the mixture of the extracted substances, which is most easily done through distillation. Butanol is a dominant product of fermentation and, depending on the type of fermenting bacteria, its amount in the broth constitutes between 60 and 80% of the total ABE product (Ezeji et al., 2004; Green, 2011; Qureshi and Blaschek, 2001). Acetone is the second most important component of the broth while the fraction of ethanol in total ABE usually does not exceed 10%.

4. SELECTED ASPECTS OF LIQUID-LIQUID EQUILIBRIUM IN SYSTEMS CONTAINING N-BUTANOL, WATER AND IONIC LIQUID

In order to design a commercial extraction process, it is necessary to know the dependence of thermodynamic equilibrium in the mixture of the feed solution and the extracting agent on its initial composition and physical parameters such as temperature and pressure. This knowledge allows further simulation of multi-stage extraction and, consequently, integrated extraction-distillation. To approximate the equilibrium, one of the available mathematical models can be employed. Due to proven accuracy in approximating liquid-liquid equilibria, the most popular equations are NRTL and UNIQUAC (based on the 'local composition' concept), which enable estimation of activity coefficients of the respective components in both liquid phases. Often, the NRTL equation provides more precise

results as well as enables modeling liquid-liquid systems containing both water and uncommon organic substances such as ionic liquids (Cheruku and Banerjee, 2012; Domańska and Lukoshko, 2015; Haghazadeh et al., 2013; Haghtalab and Paraj, 2012; Królikowski, 2016; Liu et al., 2016; Mohsen-Nia et al., 2008; Rabari and Banerjee, 2013; Zhang et al., 2010). The crucial question in applying the NRTL equation is the determination of its binary parameters related to the interactions between the respective constituents of the system. Thus, experimental data, describing the equilibrium in a model system, are required for further considerations.

Domańska and Królikowski (2012) studied the extraction of *n*-butanol from aqueous solutions at 308.15K using three tetracyanoborate-based ionic liquids, i.e. 1-hexyl-3-methylimidazolium tetracyanoborate [hmim][TCB], 1-decyl-3-methylimidazolium tetracyanoborate [dmim][TCB], and trihexyltetradecylphosphonium tetracyanoborate [P_{14,6,6,6}][TCB], and obtained very encouraging results. The authors measured the compositions of both liquid phases using gas chromatography. They used mole fractions to calculate distribution ratios of butanol and selectivities, and correlated the experimental LLE data by means of the NRTL equation. In order to estimate the unknown binary parameters, they used an objective function minimizing the squared differences between the experimental and calculated concentrations. The approximation proved very accurate. The root-mean-square deviation (*RMSD*) values calculated for each of the ternary systems were equal to 0.0024, 0.0022 and 0.0034, respectively.

All three ionic liquids displayed low solubility in water, [P_{14,6,6,6}][TCB] being the least soluble due to its long alkyl chain, while [dmim][TCB] and [P_{14,6,6,6}][TCB] provided the best separation performance. Density of [P_{14,6,6,6}][TCB], equal to 0.885 g/cm³ at 308.15 K, is the most favorable for the extraction from aqueous solutions. Densities of [hmim][TCB] and [dmim][TCB] at the same temperature are 0.983 and 0.956 g/cm³. Table 1 presents the minimum and maximum values of the experimental distribution ratios and selectivities together with the lowest and the highest measured solubilities of water in the organic phase and ionic liquid in the aqueous phase.

Table 1. Minimum and maximum experimental values of the distribution ratios (*D*) and selectivities (*S*) towards butanol in the systems [hmim][TCB] or [dmim][TCB] or [P_{14,6,6,6}][TCB] + *n*-butanol + water at 308.15 K and mutual solubility of the ionic liquids and water (Domańska and Królikowski, 2012)

Ionic liquid	Distribution ratio D_{BuOH}	Selectivity S_{BuOH}	Mole fraction		
			H ₂ O in the organic phase	IL in the aqueous phase	
[hmim][TCB]	min	25.6	45.9	0.502	0.000
	max	33.5	66.5	0.560	0.002
[dmim][TCB]	min	24.0	51.1	0.23	0.00
	max	48.0	137.9	0.46	0.00
[P _{14,6,6,6}][TCB]	min	35.6	96.3	0.134	0.000
	max	127.0	903.0	0.364	0.003

Rabari and Banerjee (2013) extracted *n*-butanol from water using trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate [TDTHP][Phosph]. In the article, they present the experimental data that were used to estimate the NRTL and UNIQUAC parameters. To determine the compositions of both the organic and the aqueous phases, they employed nuclear magnetic resonance spectroscopy (NMR). According to the authors, the investigated ionic liquid practically does not dissolve in water although certain solubility of water in the ionic liquid can be observed. Density of [TDTHP][Phosph], lower than the density of water, is convenient for the separation of butanol from aqueous feeds. The

calculated values of the distribution ratio and selectivity as well as mutual solubility of the ionic liquid and water are given in Table 2.

Table 2. Minimum and maximum experimental values of the distribution ratio (D) and selectivity (S) towards butanol in the system [TDTHP][Phosph] + n -butanol + water at 298.15 K and mutual solubility of the ionic liquid and water (Rabari and Banerjee, 2013)

Ionic liquid		Distribution ratio D_{BuOH}	Selectivity S_{BuOH}	Mole fraction	
				H ₂ O in the organic phase	IL in the aqueous phase
[TDTHP][Phosph]	min	18.89	80.18	0.1559	0
	max	377.75	2138.16	0.2279	0

The mean *RMSD* values comparing the experimental and predicted concentrations of butanol were equal to 0.002809 and 0.005552 for the NRTL and UNIQUAC equations, respectively. Therefore, better results were obtained with the NRTL equation.

Marciniak et al. (2016) studied phase equilibria in three ternary systems containing n -butanol, water and one of the following ionic liquids: 1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide [bmPIP][NTf₂], 1-(2-methoxyethyl)-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide [COC₂mPIP][NTf₂] or 1-(2-methoxyethyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [COC₂mPYR][NTf₂] at 298.15K. They measured equilibrium compositions using gas chromatography.

All the ionic liquids tested by the authors displayed low solubility in water; although they provided lower distribution ratios and selectivities than the ionic liquids investigated by Domańska and Królikowski (2012). The calculated root-mean-square errors of approximation (*RMSD*) with the NRTL equation were 0.002, 0.008 and 0.007 for the systems containing [bmPIP][NTf₂], [COC₂mPIP][NTf₂] and [COC₂mPYR][NTf₂], respectively. The minimum and maximum recorded distribution ratios and selectivities as well as mutual solubilities of the ionic liquids and water are gathered in Table 3.

Table 3. Minimum and maximum experimental values of the distribution ratios (D) and selectivities (S) towards butanol in the systems [bmPIP][NTf₂] or [COC₂PIP][NTf₂] or [COC₂PYR][NTf₂] + n -butanol + water at 298.15 K and mutual solubility of the ionic liquids and water (Marciniak et al., 2016)

Ionic liquid		Distribution ratio D_{BuOH}	Selectivity S_{BuOH}	Mole fraction	
				H ₂ O in the organic phase	IL in the aqueous phase
[bmPIP][NTf ₂]	min	14.7	48.2	0.265	0.000
	max	25.7	61.2	0.523	0.001
[COC ₂ PIP][NTf ₂]	min	14.9	37.0	0.352	0.000
	max	26.5	49.8	0.586	0.002
[COC ₂ PYR][NTf ₂]	min	11.6	28.6	0.360	0.000
	max	22.2	55.4	0.597	0.002

As demonstrated by Ha et al. (2010), mutual solubility of the imidazolium-based ionic liquids and water, being a very important factor in the extraction process, increases with temperature. Altogether, the authors studied eleven ionic liquids containing 1-alkyl-3-methylimidazolium cations and four types of anions such as trifluoromethanesulfonate [OTf], hexafluorophosphate [PF₆],

bis(trifluoromethylsulfonyl)imide [NTf₂] and tetrafluoroborate [BF₄]. Table 4 shows mutual solubilities of the ionic liquids and water in binary systems at 298.15K and 323.15K expressed in mass fractions and recalculated to mole fractions for convenient comparison. The significant differences between the mass fraction and the mole fraction are typical for the systems containing ionic liquids, whose molecular masses are usually relatively high. Likewise, distribution ratios and selectivities calculated using mole fractions are commonly about one order of magnitude higher.

Table 4. Mutual solubility of selected 1-alkyl-3-methylimidazolium ionic liquids and water at 298.15K and 323.15K (Ha et al., 2010)

Ionic liquid	T [K]	Mass fraction		Mole fraction	
		H ₂ O in IL	IL in H ₂ O	H ₂ O in IL	IL in H ₂ O
[hmim][PF ₆]	298.15	0.0269	0.0170	0.3036	0.0011
	323.15	0.0338	0.0221	0.3555	0.0014
[bmim][NTf ₂]	298.15	0.0175	0.0051	0.2930	0.0002
	323.15	0.0202	0.0114	0.3242	0.0005
[hmim][NTf ₂]	298.15	0.0147	0.0023	0.2703	0.0001
	323.15	0.0152	0.0047	0.2771	0.0002
[omim][OTf]	298.15	0.2603	0.0109	0.8706	0.0006
	323.15	0.2699	0.0126	0.8760	0.0007
[hmim][BF ₄]	298.15	0.1793	0.0664	0.7549	0.0050
	323.15	0.1987	0.0687	0.7776	0.0052

According to Kubiczek and Kamiński (2013), who studied the extraction equilibrium in quinary systems comprising water, acetone, butanol, ethanol and ionic liquid, mutual solubility of ionic liquids and water increases also in the presence of acetone, butanol and ethanol. A similar correlation can be observed in the above-mentioned studies concerning ternary systems containing butanol. The minimum recorded solubilities of water in the organic phase given in Tables 1–3 essentially occur in ionic liquid + water binary systems when butanol is not present. Increasing the concentration of butanol in the mixture raises the equilibrium concentration of water in the organic IL-rich phase, which reduces the extractant's selectivity. This phenomenon is illustrated in Figs. 1–3 using the data taken from Marciniak et al. (2016) and Domańska and Królikowski (2012).

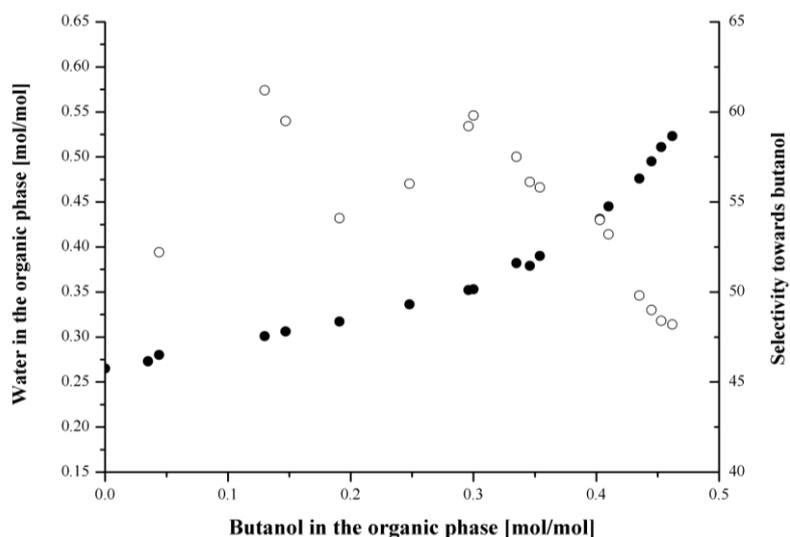


Fig. 1. Solubility of water in the organic phase (●) and selectivity of the IL towards butanol (○) in the system [bmPIP][NTf₂] + *n*-butanol + water (based on the data taken from Marciniak et al., 2016)

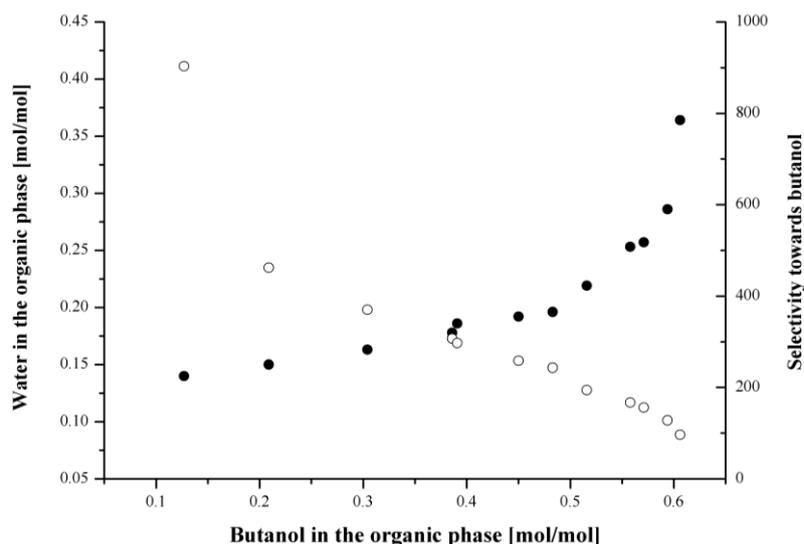


Fig. 2. Solubility of water in the organic phase (●) and selectivity of the IL towards butanol (○) in the system $[P_{14,6,6,6}][TCB] + n\text{-butanol} + \text{water}$ (based on the data taken from Domańska and Królikowski, 2012)

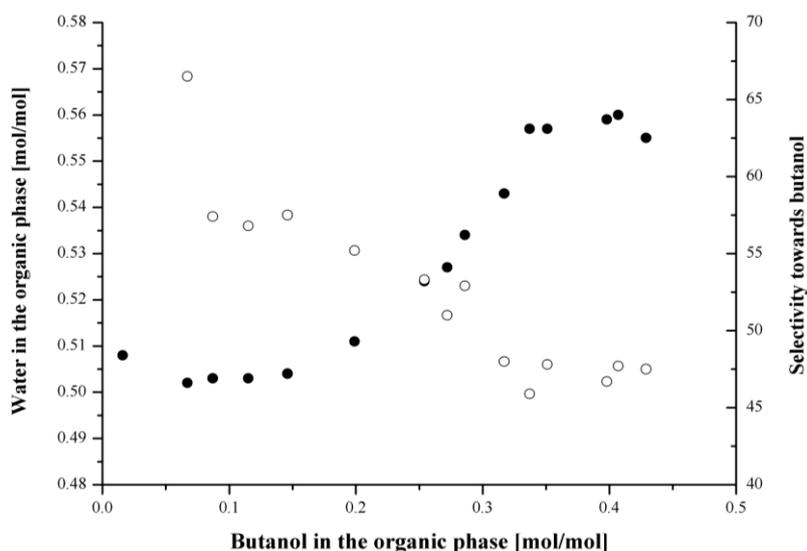


Fig. 3. Solubility of water in the organic phase (●) and selectivity of the IL towards butanol (○) in the system $[hmim][TCB] + n\text{-butanol} + \text{water}$ (based on the data taken from Domańska and Królikowski, 2012)

Kubiczek and Kamiński (2013), using non-linear regression, determined correlations describing mutual solubility of the investigated ionic liquids and water as a function of temperature and concentrations of acetone, butanol and ethanol in the respective phase, which corroborated the observations made by Ha et al. (2010). Figs. 4 & 5 present exemplary relations concerning quinary systems containing 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[bmim][NTf_2]$ as the extracting agent. At each point on the x axis, the concentrations of acetone, butanol and ethanol are assumed as equal and range from 0 to 3 wt%.

An increase in temperature, enhancing mutual solubility of the extractant and water, causes the extractant's selectivity towards the separated components to drop. However, as reported by Kubiczek (2015), this effect is to a certain degree compensated by growing distribution ratios, because higher temperatures favor dissolving acetone, butanol and ethanol in the organic phase.

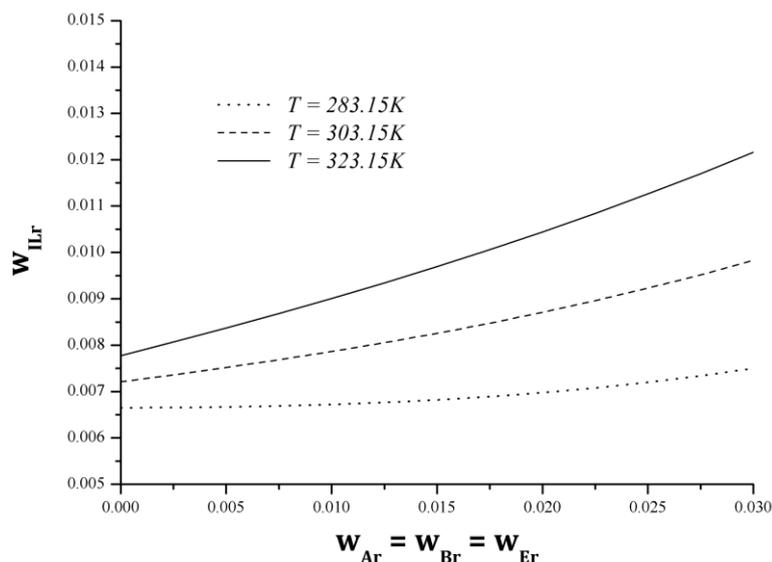


Fig. 4. Mass fraction of the ionic liquid in the raffinate (aqueous phase) vs. mass fractions of ABE in the raffinate in the system [bmim][NTf₂] + acetone + *n*-butanol + ethanol + water (Kubiczek, 2015)

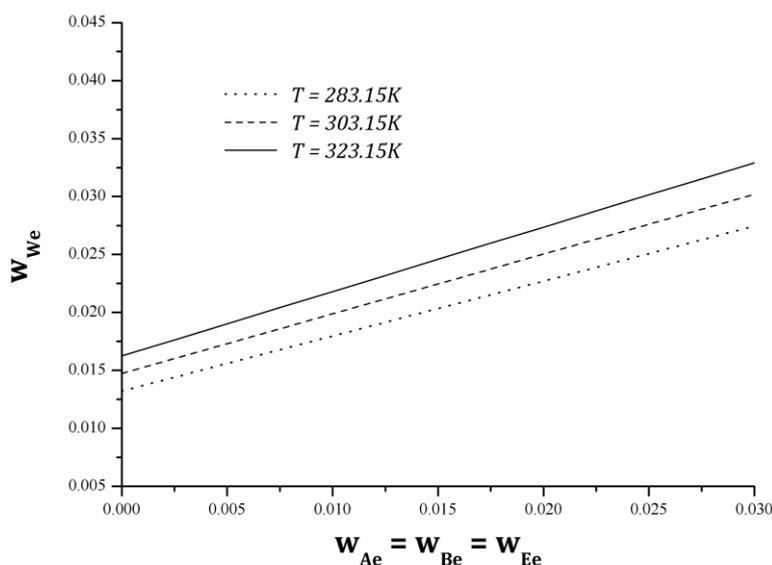


Fig. 5. Mass fraction of water in the extract (organic phase) vs. mass fractions of ABE in the extract in the system [bmim][NTf₂] + acetone + *n*-butanol + ethanol + water (Kubiczek, 2015)

Still, the increased amount of an extractant in the raffinate negatively affects the extraction economics, especially when the price of the ionic liquid is high. It leads to the conclusion that heating the feed before the extraction step in order to improve the separation efficiency serves no useful purpose.

5. APPLICATION OF THE NRTL EQUATION IN DESIGN OF THE EXTRACTION PROCESS

The majority of studies on the extraction equilibrium, not only those dealing with butanol and ionic liquids, focus on ternary systems comprising a feed solution, an extracting agent and a separated solute. These studies can help to determine the extractant's ability to recover a specific substance from a given feed solution although, in reality the systems subject to liquid-liquid extraction are more complex. In the case of extractive separation of the ABE fermentation broth, the feed contains not only butanol, but

also acetone, ethanol and other organic products, which can be transferred into the extract to different extents. This phenomenon can be either favorable or unfavorable for the quality of the process. For example, acetone present in the broth can be considered a valuable intermediate improving the economics of fermentation. Some of the other products can be considered as impurities, which should be disposed of after extraction. Taking the above into account, it is helpful if the accepted mathematical model takes these products into consideration. In the system containing water, acetone, butanol, ethanol and an extractant, binary parameters of the NRTL equation are available with regard to the common constituents, i.e. water, acetone, butanol and ethanol. The unknown parameters between these components and the extracting solvent (e.g. ionic liquid) must be determined with the aid of optimization algorithms using experimental data.

Stoffers and Górak (2013) employed the experimental data of Domańska and Królikowski (2012) concerning the [hmim][TCB] + *n*-butanol + water system in order to calculate the missing NRTL parameters and simulate a liquid-liquid extraction process. To validate the model, the authors performed experiments in a three-stage counter-current mixer-settler unit and then simulated the unit using the Aspen Plus software. Consequently, they obtained good agreement between the experimental and simulated results. As reported by the authors, equilibrium was reached in each extraction stage. When using a solvent-to-feed ratio of 0.91 g/g, about 99% of butanol was recovered from the feed solution.

Some of the experiments in the mixer-settler unit were performed using a feed containing butanol, acetone, ethanol, acetic acid and butyric acid, normally present in the fermentation broth. During the first experiment, the feed solution contained 6 wt% butanol and 0.87 g/g of fresh [hmim][TCB] was used. During the second experiment, regenerated [hmim][TCB] was employed in an amount of 0.27 g/g and the concentration of butanol in the feed was reduced to 2 wt%. The recorded efficiencies of recovery were equal to 99 and 85% respectively. The simulated concentrations of butanol in the raffinate and the extract in the respective extraction stages were in close agreement with the experimental results.

The authors of this paper investigated three quinary systems containing water, acetone, butanol, ethanol and one of the following ionic liquids: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][NTf₂], 1-hexyl-3-methylimidazolium hexafluorophosphate [hmim][PF₆] or 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [bmp][NTf₂]. The experiments were conducted at 283.15 K, 303.15 K and 323.15 K with concentrations of acetone, butanol and ethanol in the feed varied from 0.5 to 5.5 wt%. The minimum and maximum distribution ratios of acetone, butanol and ethanol and selectivities of the investigated ionic liquids, calculated using mole fractions, are summarized in Table 5.

Table 5. Minimum and maximum experimental values of the distribution ratios (*D*) and selectivities (*S*) towards acetone, butanol and ethanol in the systems [bmim][NTf₂] or [hmim][PF₆] or [bmp][NTf₂] + acetone + *n*-butanol + ethanol + water at 283.15 K - 323.15 K (Kubiczek, 2015)

Ionic liquid		Distribution ratio			Selectivity		
		<i>D_A</i>	<i>D_B</i>	<i>D_E</i>	<i>S_A</i>	<i>S_B</i>	<i>S_E</i>
[bmim][NTf ₂]	min	10.54	14.77	1.87	34.83	54.60	6.81
	max	19.02	24.05	3.32	65.67	80.41	10.98
[hmim][PF ₆]	min	6.92	7.53	0.71	28.29	30.05	2.91
	max	15.08	17.38	2.58	53.61	56.81	8.26
[bmp][NTf ₂]	min	9.80	11.85	1.34	31.96	49.61	4.69
	max	16.18	23.30	3.15	60.35	78.91	11.35

The equilibrium data were further used to estimate the unknown NRTL parameters related to the interactions between the ionic liquids and the remaining components of the mixture. It was achieved with two different tools, i.e. Matlab and Aspen Plus software. As a result, two different sets of parameters were obtained for each binary system but, subsequently, they provided comparable results when predicting the equilibrium state. The exact description of the experimental and calculation methods can be found in the works of Kamiński et al. (2014), Kubiczek (2015) and Kubiczek et al. (2016).

The root-mean-square errors of prediction calculated for acetone, butanol and ethanol are given in Table 6. They are close to the errors concerning ternary systems, presented by the other authors.

Table 6. Root-mean-square errors of equilibrium prediction in the systems [bmim][NTf₂] or [hmim][PF₆] or [bmp][NTf₂] + acetone + *n*-butanol + ethanol + water expressed in mole fractions and calculated using the NRTL parameters estimated with Matlab and Aspen Plus

Ionic liquid	Calculation method	RMSD		
		A	B	E
[bmim][NTf ₂]	Matlab	0.00136	0.00157	0.00143
	Aspen Plus	0.00130	0.00054	0.00124
[hmim][PF ₆]	Matlab	0.00252	0.00161	0.00232
	Aspen Plus	0.00162	0.00122	0.00138
[bmp][NTf ₂]	Matlab	0.00225	0.00239	0.00231
	Aspen Plus	0.00147	0.00105	0.00158

The main advantage of applying the NRTL equation to quinary systems comes from the possibility to simulate simultaneous extraction of acetone, butanol and ethanol from aqueous solutions. Simulations of this kind were performed by the authors of this paper using Aspen Plus and enabled a comparison of ABE purification systems based on both traditional distillation and integrated extraction-distillation. In each case, the following feed parameters were assumed:

- a temperature of 308.15K (typical fermentation conditions),
- a feed flow rate of 100kg/s,
- concentrations of acetone, butanol and ethanol in the feed solution equal to 0.005, 0.010 and 0.001 g/g, respectively.

The aim of the process was to obtain butanol purer than 99.9%, acetone purer than 99% and ethanol 92-94% pure. The system based on direct distillation of the feed comprised 5 distillation columns and its ABE production rates were estimated at 3600 kg/h butanol, 1815 kg/h acetone and 380 kg/h ethanol. Considering the heat supplied to the columns, the estimated energy demand amounted to 37.46 MJ/kg_{BuOH} or 23.28 MJ/kg in relation to the total ABE product.

The simulated integrated extraction-distillation system comprised a counter-current extraction column containing 12 theoretical stages. The solvent-to-feed ratio was so adjusted that 90% of butanol was removed from the feed (0.618 g/g). Moreover, the purification system included an ionic liquid regeneration step and 5 distillation columns. Considering the heat necessary for distillation and regeneration (performed via flash evaporation) the energy demand was reduced to 10.82 MJ/kg_{BuOH} or 7.76 MJ/kg_{ABE}. The resulting production rates were equal to 3218 kg/h butanol, 1228 kg/h acetone and 41.5 kg/h ethanol.

In the case of integrated extraction-distillation, the additional cost related to the recycling and partial losses of the extracting solvent through the raffinate stream can be reduced by applying an ionic liquid providing a higher distribution ratio and higher hydrophobicity or directing part of the raffinate back to the fermentation process. The latter solution is possible if the ionic liquid is non-toxic to the

fermentation bacteria. Additional waste heat recovery can significantly decrease the overall energy consumption in the purification process. At the same time, the price of ionic liquid remains a crucial factor shaping the cost level.

6. SUMMARY AND CONCLUSIONS

Ionic liquids are a new class of solvents with a great potential for liquid-liquid extraction because of their negligible vapor pressure and adjustable properties being a function of their chemical structure. For instance, ionic liquids can be employed to recover biobutanol produced via ABE fermentation.

The paper provides an overview of the latest research concerning the application of different ionic liquids in liquid-liquid extraction of butanol from aqueous media and additionally presents and interprets the authors' own data concerning quinary systems containing acetone, butanol and ethanol.

In the referenced studies, their authors approximate phase equilibrium with the help of the NRTL equation and optionally the UNIQUAC equation. The analysis of statistical indicators, however, proves that the former gives closer agreement between the experimental and predicted compositions of both liquid phases at equilibrium.

In addition, the paper discusses mutual solubility of ionic liquids and water, which is not only a function of temperature but also concentrations of acetone, butanol and ethanol in the liquid mixture. It is an important issue in terms of potential losses and regeneration of the extracting agent. Finally, the paper points at the possibility of predicting multi-stage extraction results thanks to the application of proper calculation methods.

SYMBOLS

D	distribution ratio
$RMSD$	root-mean-square deviation
S	selectivity
T	absolute temperature, K
w	mass fraction

Subscripts

A	acetone
B	butanol
e	extract (organic phase)
E	ethanol
IL	ionic liquid
r	raffinate (aqueous phase)
W	water

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