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Fluid Phase Equilibria

Modeling of liquid–liquid equilibrium in the quinary system of water, acetone, *n*-butanol, ethanol, and ionic liquid

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A R T I C L E   I N F O

A B S T R A C T

Acetone–butanol–ethanol (A–B–E) fermentation is the most common way to produce biobutanol. This valuable product may be removed from the fermentation broth by extraction using a convenient hydrophobic solvent such as ionic liquid, which is suggested in this study. A proper design of the extraction unit requires an experimentally validated model of thermodynamic liquid–liquid equilibrium in the two-phase mixture containing all components of the aqueous fermentation broth and extracting solvent. Here, for modeling of LLE, the NRTL model was employed. The equation parameters were determined from data measured for three hydrophobic ionic liquids: 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [Bmim][Tf$_2$N], 1-hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF$_6$], and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide [Bmp][Tf$_2$N].

1. Introduction

N-Butanol (further referred to as butanol) is an important bulk chemical with many current and potential industrial and non-industrial applications. It is a colorless liquid with a distinct odor, highly miscible with organic solvents, *e.g.*, alcohols, ketones, aldehydes, ethers, glycols, aliphatic and aromatic hydrocarbons. However, its miscibility with water is restricted. Selected physicochemical properties of butanol are shown in Table 1.

Vast majority of butanol finds applications in the broadly defined chemical sector, including coatings, enamels and lacquers, pharmaceutical, automotive, textile and cosmetics industries, and others [2,3]. However, one of the most promising applications of butanol, thanks to its encouraging physicochemical properties, would be using it as a fuel additive or even as a direct replacement for gasoline in existing spark-ignition engines. Butanol offers several advantages over widely used ethanol, which are described elsewhere [4–7] but, first of all, it has a much higher energy content and lower heat of vaporization [8]. It also provides much better miscibility with both diesel fuel and gasoline. For economic reasons, since, the 1950s butanol has been produced mostly by the petrochemical process called "oxo synthesis" [9,10]. Nevertheless, the traditional fermentative method of butanol production, which was practised in the first half of the 20th century, is based on

biological processing of organic substrate [11,12]. Currently, the greatest efforts to recommercialize biobutanol, driven mostly by the unbalanced demand, are being undertaken in China, where the industrial A–B–E fermentation was revived in 2006 [12–16]. Traditional ABE fermentation yields butanol and acetone as main metabolites of anaerobic *Clostridium* bacteria. Both of these may be deemed valuable intermediate products for other chemical processes. The concentration of ethanol in the broth is usually much lower – typical final molar ratio of A–B–E equals approximately 3:6:1 [15]; however, specific fermentation performance is a function of the microbe, process conditions and substrate type [17–24].

As reported by [5], there are five major obstacles in introducing an economically competitive biological solvent production:

- high substrate costs,
- low solvent concentration in the broth caused by the inhibition of bacterial cells,
- low solvent productivity,
- low solvent yield due to heterofermentation,
- high cost of solvent recovery from low-concentration yields.

While the first four issues are rather biotechnical in nature, the last one deals strictly with downstream processing of the fermentation broth. The problem of efficient separation of solvents from aqueous media has been tackled by many authors. Various unit operations such as gas stripping, vacuum flash, adsorption, liquid–liquid extraction, membrane-assisted solvent extraction

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Nomenclature

List of symbols
α activity
m mass [g]
n amount of substance [mol]
R universal gas constant [J/(mol K)]
T temperature [K]
w mass fraction
x mole fraction
γ activity coefficient

Subscripts
i, j, k, m, n component identifiers
E extract (organic, IL-rich phase)
F feed solution
R raffinate (aqueous, water-rich phase)
S solvent (IL)
T total mass in the system
W water

(perstraction), pervaporation, thermo-pervaporation, membrane distillation or reverse osmosis have been investigated for this purpose [17,25–28].

The simplest, yet highly energy-intensive, method is based on the traditional distillation process. Small concentration of solvents in the fermentation broth is the main culprit for high energy demand during distillation. However, VLE behavior displayed by acetone, ethanol, and butanol in aqueous solutions makes the separation process feasible. Among other proposed methods a few deserve a closer look. Opinions vary but, in general, adsorption and liquid–liquid extraction combined with distillation as well as other hybrid processes involving extraction or pervaporation are mentioned as the most promising solvent recovery techniques [25,27,29].

Liquid–liquid extraction of butanol from ABE fermentation broths can be performed in two ways – either inside or outside the fermenter. However, for the efficient in situ recovery non-toxic extractants must be selected, insoluble in the aqueous phase. Also, a few other general conditions should be met by the extracting agent [27] used for industrial purposes, such as:

- possibly high selectivities and distribution coefficients of ABE,
- density significantly different from that of the broth for efficient phase separation,
- possibly low viscosity for the reduction in energy consumption,
- sufficient chemical and thermal stability for further regeneration and recycling,
- low volatility and high boiling point,
- availability and low cost.

Table 1
Physicochemical properties of n-butanol (according to [1,2]).

Property	Unit	Value
Molar mass	g/mol	74.12
Boiling point (at 1013 hPa)	°C	117.7
Melting point (at 1013 hPa)	°C	−88.6
Density (at 20 °C)	g/cm^3	0.810
Lower heating value	MJ/kg	33.10
Latent heat of evaporation	kJ/kg	585
Solubility of n-butanol in water (at 20 °C)	% w/w	≈7.7
Solubility of water in n-butanol (at 20 °C)	% w/w	≈20.1

For a few reasons, one of them being the extractant potential toxicity towards microbial cells, in situ recovery may not be convenient for industrial large-scale production. If an external extraction column is used, the flow of extractant through the bioreactor is eliminated or greatly reduced, which makes more solvents applicable [26,27,29].

Ionic liquids (in particular, a separate class named room temperature ionic liquids RTILs) may possess many favorable traits making them potentially useful in liquid–liquid extraction. The desired qualities commonly attributed to RTILs include:

- very low volatility (at temperatures up to 450 K) [30,31],
- high thermal stability (at temperatures up to 370 K) [32],
- wide liquidus regions (ranging from below ambient to over 570–670 K) [33],
- ability to dissolve various substances, both organic and inorganic [34], as well as hydrophilicity or hydrophobicity, depending on the anion and cation structure [35].

Overall, the number of available anion–cation combinations constituting ionic liquids is estimated at 10^{18}, hence the term "designer solvents" [25]. It means that their properties may be adjusted or "tuned" to suit specific process requirements.

In view of the recent studies on biobutanol recovery from aqueous solutions using RTILs, the effort was made by the authors to model liquid–liquid equilibrium in the five-component system of water, acetone, butanol, ethanol, and ionic liquid. Apparently, this kind of approach has not been taken up thus far, as the vast majority of available papers deal with extraction in ternary systems. For the purpose of modeling, the NRTL equation was chosen, which has proved very accurate in describing ternaries, also containing ionic liquids [36–39]. The unknown NRTL parameters characterizing binary interactions between ionic liquid, and the rest of constituents, i.e., water and ABE, were regressed from the experimental LLE data. The model was then validated and used to predict the extraction equilibrium in the investigated system, yielding encouraging results.

2. Materials and methods

Acetone, n-butanol, and ethanol (analytical grade) were used in the experiments. Three hydrophobic ionic liquids, , 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [Bmim][Tf$_2$N], 1-hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF$_6$], and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [Bmp][Tf$_2$N], whose chemical structures are shown in Figs. 1–3 were employed as extracting agents. All the chemicals were used without prior purification. Their purities are given in Table 2.

For the purpose of calculating the NRTL equation parameters, 45 experiments at temperatures of 10, 30, and 50 °C were performed for each of the ionic liquids studied. ABE contents in the aqueous feed solutions were chosen according to the three-factor central composite design with 1.0 and 5.0 wt% as the low and high levels, 0.5 and 5.5 wt% as the axial points, and 3.0 wt% as the center point (15 experiments at each temperature).

Volumes of the feed solutions were approximately equal to 1 cm^3. Then, roughly 1 cm^3 of ionic liquid was added to each feed solution. Afterwards, the mixtures were placed in a thermostated water bath and shaken for about 1.5–2.0 h. At the end of that period they were centrifuged to expedite phase separation. Preliminary experiments had been done ensuring that the accepted mixing times were sufficient to reach the equilibrium state.

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