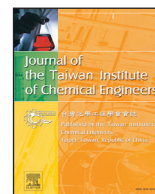




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## Screening of ionic liquids as extractant for 1-butanol extraction from dilute solution

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## ABSTRACT

Extraction of 1-butanol from dilute solution is one of the most popular means for bio-butanol recovery due to its low energy consumption and easy operation. However, the problems of low efficiency, solvent loss, extractant toxicity and *etc.* existed and needed to be solved by finding new extractant. Ionic liquids (ILs) as new material have been the potential extractants due to their special thermo-physical properties of negligible vapor pressure, high stability and strong designability. In this work, 960 ILs formed from 40 cations and 24 anions were evaluated for the selection of suitable extractant using COSMO-RS model with the index of distribution coefficient and selectivity. Finally, [HMIM][FEP] was screened out as a promising extractant for its high distribution coefficient (70.73) and selectivity (200.90). The LLE (liquid–liquid equilibrium) experiments of 1-butanol + water + IL were determined and compared with the result calculated by COSMO-RS model. By comparison, it could be safely concluded that the calculated results were in good agreement with the experimental results generally, which meant the validation of this methodology. Meanwhile interaction energy calculations and hydrogen-bond (H-bond) interactions between 1-butanol or water and the selected IL were also investigated to reveal the working mechanism of the extraction process.

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### 1. Introduction

Fermentation of biomass for bio-butanol using *Clostridium acetobutylicum* or *C. beijerinckii* bacteria also named ABE method attracts increasing interests owing to the considerations of environmental protection and sustainable development [1]. Unfortunately, the promoted application of the ABE method is limited mainly because of the shortcomings in the separation section, like high energy consumption, low processing capacity, low selectivity and *etc.* [2–4]. A lot of efforts were already and also needed to be made further to solve the aforementioned problems and improve the efficiency.

Generally, in the downstream separating section of the fermentation process, the key product 1-butanol requires sustainable and efficient extract from the fermentation broth for the nature that the fermentation cannot keep proceeding when the content of 1-butanol beyond threshold. Several separating methods, such as distillation, gas stripping, reverse osmosis, extracting and adsorption have been investigated. However, issues of high energy cost and azeotropes form between 1-butanol, ethanol and

water can happen when the energy-intensive distillation is used. Disadvantages of low selectivity, low productivity, complicated operation steps also existed in gas stripping, adsorption and reverse osmosis [5]. Liquid–liquid extraction operated at ambient condition with few operating steps potentially provides an alternative. Common chemicals like, butyl lactate, toluene, oleyl alcohol and non-surfactant [6–8]; inorganic salt, such as sodium chloride, potassium pyrophosphate, sodium sulfate [9,10] and some carbohydrates like, glucose, fructose, sucrose [11] or some mixed extractants [12,13] combined by compounds mentioned above have been used to separate 1-butanol. Although aforementioned extractant can be used to remove 1-butanol from aqueous solution effectively, disadvantages including solvent loss, environmental pollution and recycle in difficulty have limited their further applications. To deal with these problems, a lot of watchful eyes have turned to the new material: room temperature ionic liquid (RTIL) also named organic molten salt [14]. In the year of 2001 Fadeev [15] firstly attempted to take imidazolium-based ILs [BMIM][PF<sub>6</sub>] and [OMIM][PF<sub>6</sub>] as extractant to separate 1-butanol from aqueous solution. The result showed that chemical versatility of ILs made them potential extractants for this system. Inspired by the thought, Kenneth and co-workers [16] investigated [PF<sub>6</sub>] anion-based ILs with different 1-alkyl group chain lengths and found that the longer chain length, the better separation effect.

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**Table 1**  
Overviews of the chemical samples.

Chemical name	Source	Purity	Purification method	Analysis method
1-Butanol	Sinopharm Group	≥0.995	None	GC
Ultra-pure water	Synthesized own(Direct-Q3, Merck Millipore)	≥0.995	None	GC
[HMIM][FEP]GC = Gas chromatography	Merck	≥0.99	None	None

Ha et al. [17] intended to select a suitable extractant from 11 kinds of hydrophobic ILs to recover 1-butanol from aqueous solution mainly by investigating the distribution coefficient and selectivity of 1-butanol in water-rich and ILs-rich phase respectively. The result indicated that IL with anions of [Tf<sub>2</sub>N] showed better performance than others and the IL [OMIM][Tf<sub>2</sub>N] with the longest alkyl chain performed the best. Some other imidazolium-based ILs with different anions like [TDI], [BF<sub>4</sub>], [DCA] and [TCB] or functional groups adhered to cations were also selected as extractants to investigate the factors affecting the separation and the results showed that anions play a main role in 1-butanol separation and side chain functional groups were of less significance [18–21]. The ILs based on quaternary ammonium and phosphonium cations have desirable properties of low density and low viscosity which are benefit for separation. Therefore, Rabari and Banerjee [22] investigated two kinds of phosphonium cations based ILs [TDTHP][DCA] and [TDTHP][DEC] for the separation of 1-butanol. The calculated distribution coefficient of 1-butanol to water ranged from 20 to 290 which meant an effective removal could be achieved. Non-fluorinated task-specific ionic liquids used to remove 1-butanol from dilute solution and a conceptual process design in engineering perspective were conducted by Lesly [23] to determine the most promising extractant. The distribution coefficient and selectivity calculated from experimental data were approximately 21 and 274 with [TOAMNaph], which performed much better than the benchmark solvent oleyl alcohol. More than that, researcher Sadowski and co-workers [24] and Zawadzki et al. [25] also investigated IL based on other ring-cation compounds and compared them to the imidazolium-based ones respectively. It was found that the morpholinium-based ILs performed worse while the pyridinium-based ILs performed better when compared with imidazolium-based ones with same anions, respectively. In recently, Doman'ska found that ammonium-based ILs owned a higher selectivity value and a similar distribution ratio when compared with imidazolium-based IL. And a conclusion that rather the length of the alkyl chain has the influence, a longer alkyl chain length, or few of them influence 1-butanol/water selectivity and the distribution ratio was drawn [26].

Although various kinds of ILs have been investigated for 1-butanol separation from dilute solution, some basic patterns or general rules have not been summarized to guide the new and effective extractant selection and furthermore the mechanism between separating components and extractant is still unknown. Only a large scale of trials are made can some basic patterns be found, which consumes a large amounts of time and money when they are conducted by traditionally experimental method. Fortunately, the computer-aided screening method can figure this problem out due to its own advantages.

In this study, a screening among 960 ILs composed of 24 anions and 40 cations with COSMO-RS model was conducted to select a suitable extractant for separating 1-butanol from dilute solution. Prediction of the LLE behaviors of water + 1-butanol + IL ternary system was also investigated and compared with an experimental validation to testify the consistency of COSMO-RS model. After that the mechanism uncovered by interaction energy and hydrogen bond (H-bond) was explored to study the exactly interaction form. Therefore, a regular selecting rule and the nature of interacting

mechanism to guide the subsequently extractants selection and design can be obtained after all these have been done.

## 2. Model and method

### 2.1. Computational details

As an effective thermodynamic predictive model with no need of any experimental data, COSMO-RS [27] (Conductor-like Screening Model for Real Solvent) is the most widely used one in properties prediction. This predictive process generally contains the following two steps. Firstly, the COSMO file contained screening charge density information of each interested compound was generated for the next statistical thermodynamics conduction. In the goal of COSMO files generation, geometry optimization of each component was performed in vacuum to obtain the minimum energy state first. For each component the COSMO file was needed to be calculated only once and stored in a database, which made the prediction fast and efficient. Subsequently, the COSMO files were inputted in the COSMOthermX software to calculate the thermodynamic properties of each component in the system and then the extraction effect of 1-butanol in different ILs can be obtained. In this work, the calculations were conducted using COSMOthermX (C31-1701) with BP-TZVPD-fine calculating level.

### 2.2. Experimental procedure

The suitability and applicability of the IL preselected from COSMO-RS predictions can be finally confirmed by experiments. The [HMIM][FEP] was purchased from Merck. Volatile chemical used in this study was 1-butanol obtained from Sinopharm Group and the ultra-pure water was prepared in our own lab. The chemicals used in this work are summarized in Table 1 in detail as follow.

Liquid–liquid experiments of selected IL validation were carried out in a thermostatic still controlled by the water bath at ambient pressure and 298.15 K with the temperature uncertainty of 0.1 K. Firstly, a certain and precise weight (10 g) of mixtures formed by 1-butanol and water in different mole fractions were prepared. The weight of each mixture was determined by an analytical balance (CAV264C OHAUS America) with an uncertainty of 0.0001 g. Secondly, each mixture was added with the same amounts of IL solvent (2 g) and the mixture was sealed and stirred in the still for 3 h and then standing overnight. Afterwards, a clear phase split could be observed in the next day. At last, samples from upper and lower phase were carefully separated with syringes and weighted. Samples from both phases were analyzed by a gas chromatograph (Agilent 7890A GC, USA) equipped with a headspace sampler (G1888 Network headspace sampler, Agilent Technologies), a 30 m in length, 0.25 mm in diameter and 0.25 μm in thickness capillary column named DB-WAXETR and a TCD detector whose carrier gas is H<sub>2</sub>. The operating conditions: the temperature of oven, injector and detector was 373 K, 433 K and 443 K, respectively. The contents of IL in each phase were obtained by subtracting the sum of 1-butanol and water measured by GC from initial weight of that. Each sample from the mixture was analyzed three times

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