



Partitioning of butanol between a hydrophobic ionic liquid and aqueous phase: Insights from Liquid-Liquid Equilibria measurements and Molecular Dynamics simulations



Pyarimohan Dehury, Upasana Mahanta, Tamal Banerjee*

Department of Chemical Engineering, Indian Institute of Technology Guwahati, Assam 781039, India

ARTICLE INFO

Article history:

Received 2 March 2016

Received in revised form

14 May 2016

Accepted 5 June 2016

Available online 18 June 2016

Keywords:

Liquid-Liquid Equilibria

MD simulation

Ionic liquids

Butanol

Distribution coefficient

ABSTRACT

This work investigates the effectiveness of 1-methyl-3-octylimidazolium bis (trifluoromethylsulfonyl) imide, [OMIM] [Tf₂N] as a solvent to recover 1-butanol from aqueous stream. The solvent [OMIM] [Tf₂N] (1.320 g/cm³) possessed a higher density and formed two clear and distinct phases after extraction. Both Liquid-Liquid Equilibrium (LLE) experimental studies and Molecular Dynamic (MD) simulation were carried out for [OMIM] [Tf₂N]-1-butanol-water system to explain the effectiveness of the solvent. A type II phase behavior with a large immiscible region was observed for the system at $T = 298.15$ K and $p = 1$ atm. High values of selectivity ranging from 555 to 3583 have been observed for 1-butanol extraction. The distribution coefficients were also found to be greater than unity. The experiments indicated an easier separation of solute from aqueous phase to extract phase. The NMR spectra confirmed the absence of solvent in the water rich phase. NRTL and UNIQUAC models gave root mean square deviation (RMSD) in the range of 0.1%–0.5% for the ternary system. The MD simulations were then performed in an NVT ensemble for a time period of 40 ns using OPLS-AA force field. The first solvation shell for 1-butanol was obtained within 0–4.35 Å and 0–5.75 Å with [OMIM] and [Tf₂N] ions respectively. This highlights the fact that butanol molecules are highly solvated by the presence of both ions.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The reserves of hydrocarbon based fossil fuels being available in few countries are not sufficient for prolonged use. The combustion of these fossil fuels further emits greenhouse gases and threatens the balance of the ecosystem. It invariably becomes a challenge for governments, engineers, scientists and economists to reduce dependence on the conventional fuels. The gradual decrease of fossil fuel resources and ever increasing environmental pollution has thus led us to focus on alternative energy resources such as biomass. According to BP statistical review, the production of bio-fuels has increased by 7.4% in 2014 [1]. To overcome the drawbacks of the conventional fossil fuels, biomass derived 1-butanol as an alternative fuel is gaining importance recently.

In the Acetone-Butanol-Ethanol (ABE) fermentation [2–4] process, bacteria like *Clostridium acetobutylicum* [2,3] and *Clostridium bjerinki* [3,4] ferment biomass under anaerobic conditions and

hence Acetone, Butanol, and Ethanol are being produced with a proportion of 3:6:1. Hence butanol produced from this fermentation process has potential to be used as a fuel. Further the calorific value [2] of butanol (29.2×10^6 kJ/m³) is much higher than that of Ethanol (19.6×10^6 kJ/m³). Butanol also shows lesser flammability and hydrophilicity than ethanol. Furthermore, it is easily miscible with gasoline in any proportion and has industrial applications [5]. However, in the conventional process, butanol concentration inside the broth greater than 10 g/L prevents the growth of the microbial cells during fermentation process [6]. Therefore, to overcome this and to enhance the use of 1-butanol, its separation from water present in the broth is essential.

Methods like pervaporation, extraction, adsorption and gas stripping have been investigated earlier [7–12]. The main disadvantage for the recovery of 1-butanol from fermentation broth through adsorption is that it can only be used in laboratory scale. This is due to the small-capacity of adsorbents which is not economically acceptable on an industrial or semi-industrial scale. Separation by distillation is further complicated since the lower chain alcohol such as butanol forms an azeotropic mixture with water [13]. Membrane separation and pervaporation are not cost

* Corresponding author.

E-mail address: tamalb@iitg.ernet.in (T. Banerjee).

effective as it involves low mass transfer rates and low pressure [2]. Selection of a suitable polymer for the membrane preparation is another crucial issue in this case. In this regard, solvent extraction can be a suitable method particularly with the solvents having high affinity for 1-butanol and hydrophobicity simultaneously.

The selection criteria for a good solvent are namely high selectivity, high capacity and non-toxicity to cells particularly when extraction is carried out inside a fermentation broth. Additionally, it should have low viscosity and should be available commercially. In this regard, Ionic Liquids (ILs) are non-volatile, non-flammable and thermally stable which are better alternative as compared to conventional volatile organic solvents. ILs have been reported earlier [14–17] as effective solvents for 1-butanol extraction from aqueous phase. The rapidly emerging applications of ILs involve their use as solvents but the understanding and study of their physical properties are insufficient. It is very essential to collect a valuable set of physical data which includes phase equilibrium data. The effect of number of carbon atoms in the alkyl chain of the cation and the anion on the basic properties like density, viscosity, surface tension, melting point and thermal stability needs to be computed. In order to satisfy the above requirements, we have chosen the IL: 1-methyl-3-octylimidazolium bis (trifluoromethylsulfonyl) imide [OMIM] [Tf₂N] due to its long alkyl chain length and its anion. The Octyl chain makes the cation [OMIM] hydrophobic in water. Similarly, the anion bis (trifluoromethylsulfonyl) imide [Tf₂N] is also known for its immiscibility with water.

However in most of the earlier work concerning experimental studies, a theoretical approach such as those from MD simulations has not been explored. MD studies on Liquid-Liquid Extraction are very few. An earlier study has been carried out on the interface layering of butanol - [BMIM] [PF₆] by Jawhashi et al., [18]. Further Stephenson et al. [19], has reported ethanol extraction from higher chain alcohols using MD simulations. To study the effectiveness of IL's containing OMIM cation, MD studies were also performed for the extraction of different aliphatic and aromatic hydrocarbons by Santiago et al., [20]. Taha et al. [21], has further studied the buffer induced phase separation of water and alcohols with the help of Molecular Dynamics simulation.

2. Materials and methods

2.1. Materials

Butanol having purity of 99% and bis (trifluoromethanesulfonyl) lithium salt of purity >99% have been purchased from Sigma Aldrich. 1-Methyl Imidazole of reported purity >99% and 1-Bromooctane of purity >98% were purchased from Spectrochem Pvt. Ltd., Mumbai. Dimethyl Sulfone Oxide-D₆ (DMSO-D₆) and Chloroform-D (CDCl₃) were used as NMR solvent and were supplied by Merck, Germany. All the chemicals were used without further purification for experimental studies. The densities were measured by Anton Paar Density Meter (DMA 4500 M) so as to compare the manufacturer specification. The measured densities were within ±1%.

2.2. Experimental details

2.2.1. Synthesis of IL

The method for synthesis of [OMIM] [Tf₂N] has been adopted from literature [22]. The pictorial representation of the process has been shown in Fig. 1. To confirm the composition of the Ionic Liquid, ¹H (Fig. 2), ¹³C (Fig. 3) and ¹⁹F (Fig. 4) NMR spectroscopy were performed. Further HSQC (Heteronuclear Single Quantum Coherence) 2D-NMR spectroscopy (Fig. 5) has been carried out to confirm the corresponding carbon and hydrogen bonding and the carbon peaks present in Tf₂N. The ¹H-NMR spectra for [OMIM] [Tf₂N] consists of the following peaks: ¹H NMR (600 MHz, DMSO-d₆) δ_H 9.10 (1H, s), 7.73–7.67 (1H, m), 4.16 (2H, t), 3.86 (3H, s), 1.79 (2H, quin), 1.26 (10H, sex), 0.85 (3H, t).

The ¹³C NMR results (ppm) include: ¹³C NMR (600 MHz, DMSO-d₆) δ_C 13.80, 22.00, 25.45, 28.30, 28.43, 29.36, 31.12, 35.66, 48.80, 118.42, 122.21, 123.57 and 136.47.

The ¹⁹F NMR results (ppm) include: ¹⁹F NMR (600 MHz, DMSO-d₆) δ_F which gave a single peak at –78.84 for all six fluorine atoms. The density of the IL was measured by Anton Paar Densitometer (DMA 4500M) at *T* = 298.15 K (*ρ* = 1.320 g/cc), which compared well with literature [23].

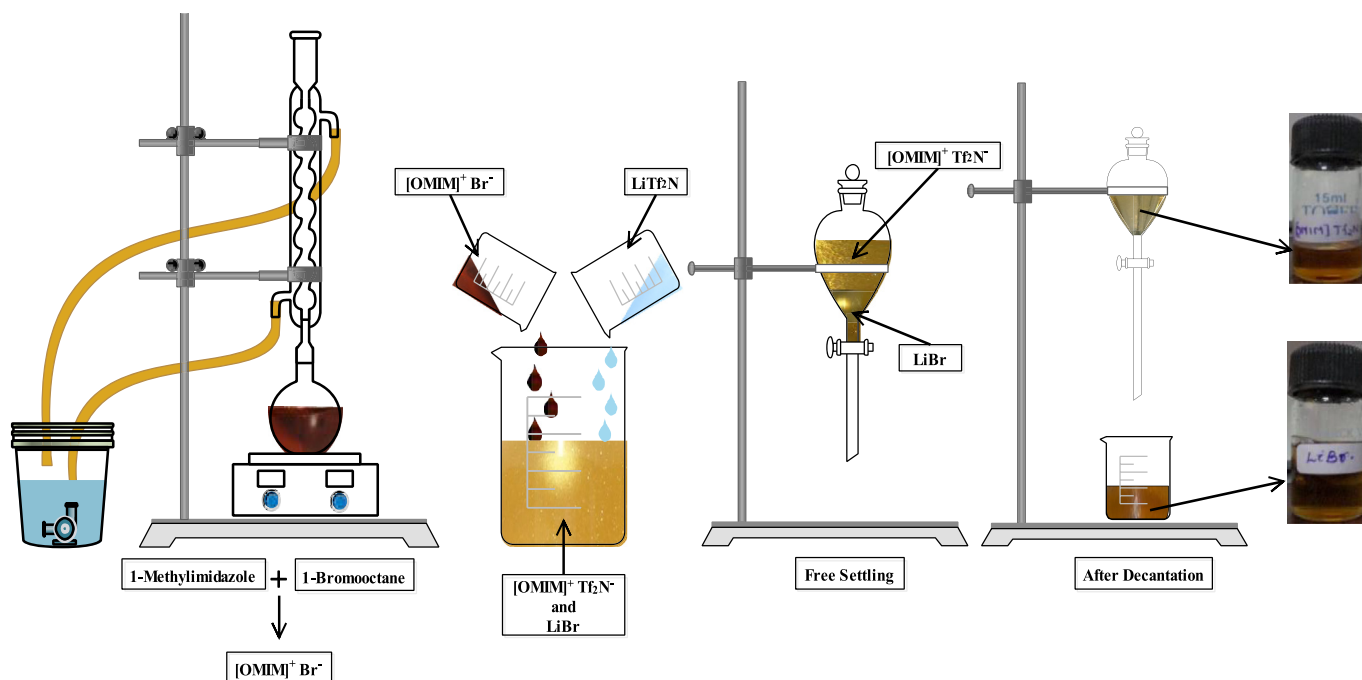


Fig. 1. Synthesis of ionic liquid [OMIM] [Tf₂N].

Download English Version:

<https://daneshyari.com/en/article/201128>

Download Persian Version:

<https://daneshyari.com/article/201128>

[Daneshyari.com](https://daneshyari.com)