

Phosphonium based ionic liquids: Potential green solvents for separation of butanol from aqueous media

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Abstract—Depleting conventional resources leads to the development of alternate energy sources as a result of rising energy demand. As a result of its high energy content, bio-butanol is an appealing fuel. Yet, a fermentation method of butanol generation by acetone*butanol*ethanol using solventogenic Clostridium has significant limitations. In addition to repressing microbial movement (normally greater than 10 g/L), it also affects their production. In order to separate butanol from aging broth, various separation techniques can be used. As an alternative to traditional solvents, ionic liquids can be used as novel extractants to counter these problems. In the present paper, separation of butanol (simulated) from aqueous media utilizing typical hydrophobic ionic liquids was studied at 298 ± 1 K. Various parameters, such as distribution coefficient (K_d), extraction efficiency ($\% \eta$), diffusion coefficient, solvent-to-feed ratio diffusion coefficient, and number of stages necessary for butanol separation, have been studied. Separation of butanol from aqueous solutions (0.25-2.5 wt%) Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) amide-CYPHOS IL 109 THTDP [NTF₂] ionic liquid, (purity $\geq 95.0\%$), Trihexyltetradecylphosphonium chloride-CYPHOS IL 101 THTDP [Cl] (purity $\geq 95.0\%$), at ambient conditions (298.15 ± 1 K) was carried out. The average separation efficiency of butanol was observed highest ($\%E$ 80.43) with hydrophobic THTDP [NTF₂] ionic liquid. The maximum average distribution coefficient (K_d) 11.055 was found for RTIL ionic liquid THTDP [NTF₂] compared to THTDP [Cl] ionic liquid. Minimum solvent-to-feed ratio was observed for ionic liquid, THTDP [NTF₂], (S/F_{min} 0.3829) and for THTDP [Cl], (S/F_{min} 0.201). Due to excellent/better mixing blending properties with gasoline and diesel fuels, recovery of this prospective butanol by ionic liquid could be utilized in gasoline-driven combustion systems. It would be a more promising alternative to ethanol and gasoline for large-scale applications. Thus, after evaluating the above parameters, it has been determined that butanol would be the most effective renewable biofuel for commercialization using ionic liquids as an extractant.

Keywords: Butanol, Phosphonium Ionic Liquids, Liquid-liquid Extraction, Distribution Coefficient, Green Solvents

INTRODUCTION

Bio-butanol is produced through acetone-butanol-ethanol fermentation using a solventogenic Clostridium bacteria strain. The fermentative method of producing butanol has limitations and significant problems. A concentration above 10 g/L inhibits microbial growth and affects production of bacteria. Compared to conventional petroleum fuels, biobutanol is a potentially viable biofuel. Other fermentation resulting fuels, such as ethanol, do not possess this inherent benefit. However, the energy content of butanol is higher than that of ethanol (HV 21.1 MJ/L). Considering its superior properties, bio-butanol is highly promising due to its high heat value, low volatility, high viscosity, high hydrophobicity, hygroscopicity, and low vapor pressure [1,2]. In comparison to petroleum fuels, biobutanol produces fewer emissions. In addition to reducing overall greenhouse gas emissions, growing sustainable feedstocks balances carbon dioxide released during combustion of biobutanol. Comparative analysis of butanol with conventional petroleum fuels in terms of heating values (MJ/dm^3) is given in Fig. 1.

The Environmental Protection Agency (EPA) states that biobutanol can be blended as an oxygenate in gasoline in concentrations

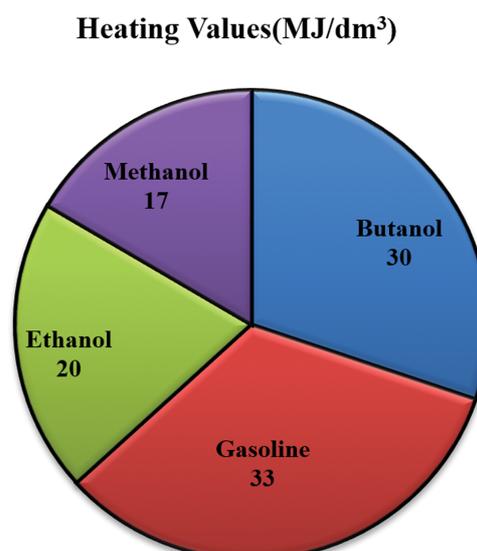


Fig. 1. Comparative analysis of butanol with conventional petroleum fuels in terms of heating values (MJ/dm^3).

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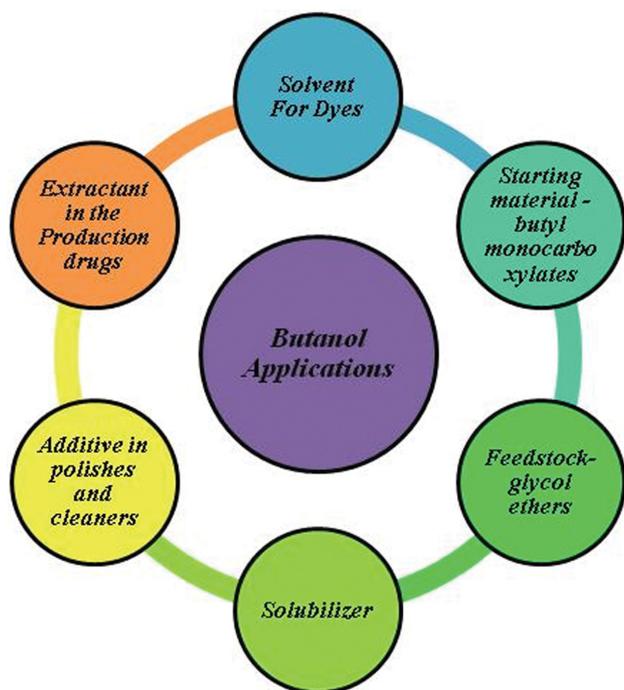


Fig. 2. Applications of butanol.

up to 11.5 percent by volume. To qualify as an alternative fuel, it must be a blend of 85 percent biobutanol and gasoline. With the help of a Department of Education (DOE) Small Business Technology Transfer grant, a company called Butyl Fuel LLC, is working on a process to make biobutanol production economically competitive with petrochemicals [3]. Applications of butanol are presented in Fig. 2.

Generally, biobutanol is produced by means of the acetone butanol ethanol (ABE) method after acidogenesis and solventogenesis are carried out in the ratio 3 : 6 : 1. Biobutanol is produced by ABE fermentation in 10 g/L. The upper limit of convergence of biobutanol inhibits microbial activity and may affect the yield of the product [4,5]. The production of butanol faced many problems after its discovery more than a century ago, which prevented it from becoming a viable market. The first major task that disturbs the anaerobic fermentation process is the hindering phenomenon of microbes over butanol (10 g/L) in the fermentation broth. The second major task involves separating bio-butanol continuously. It disrupts the lipid structure in cell membranes, resulting in changes in lipid-bound enzyme activity, and membrane fluidity in the presence of butanol [6,7].

The liquid-liquid extraction process can be combined with fermentative processes, but the microbe toxicity of these extractants is the biggest challenge. Studies on the process parameters of selectivity, distribution coefficient, and toxicity toward anaerobes were conducted for butanol separation using 36 chemicals. Non-toxic solvents were found in the group of esters with high molecular mass. Solvents with high molar masses can sometimes be toxic or hazardous to microbes [8-10].

Phosphonium based ionic liquids and imidazolium based ionic liquids and their blends also have been explored for the separation

butanol from aqueous phase [11-13]. Garcia-Chavez et al. investigated the use of nonfluorinated ILs for extraction of 1-butanol from water. The results were compared to those obtained when oleyl alcohol and bis(trifluoromethylsulfonyl)imide were used as reference extractants [14]. Rabari et al. investigated alcohol-water mixtures with [TDThP][Phos], [TDTHP][DEC] and [TDTHP][DCA]. A ternary system was studied and compared with NRTL and UNIQUAC [15,16].

A multi-stage continuous extraction system was used by Stoffes et al. [17] to separate n-butanol using imidazolium-based ionic liquid HMIM [TCB]. Experimental data were correlated with NRTL model results. Martak et al. described a model and mechanism of phosphonium ionic liquid extraction of butyric acid [18]. At very low concentrations of butanol (*5% by weight) and water, Fadeev and Meagher investigated the solubilities of hexafluorophosphate and 1-octyl-3-methylimidazolium hexafluorophosphate [Omim][PF₆]. As a result of this study, ionic liquids of a hydrophobic nature have been shown to be effective liquid extractants [19].

The ionic liquid is a mixture of cation and anion, and is in the liquid phase at room temperature; therefore, it is called a room temperature ionic liquid (RTIL). As a result of their ability to alter cations and anions, ionic liquids are also designer solvents. A wide range of applications is possible due to its non-flammability, negligible vapor pressure, and tunable physicochemical properties. Consequently, upcoming research has focused more on developing novel Ionic liquids (ILs) and alternatives for organic solvents in a number of processes. In particular, ILs have been used as alternatives for liquid-liquid extraction [20]. Their negligible vapor pressure allows the extracted products to be separated from ILs by conventional low pressure distillation, thus saving energy [21].

In the present work, separation was carried out of butanol from an aqueous simulated butanol solution (0.309-3.086 mol·kg⁻¹) using pure extractant Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) amide-CYPHOS IL 109 THTDP [NTF₂] ionic liquid, (purity ≥95.0%), Trihexyltetradecylphosphonium chloride-CYPHOS IL 101 THTDP[Cl] (purity ≥95.0%), at ambient conditions (298.15±1 K). We investigated the distribution coefficient (K_d), separation efficiency, minimum solvent-to-feed ratio, and theoretical number of stages for pure extractants such as THTDP[NTF₂], THTDP[Cl]. As an alternative to conventional volatile toxic solvents, ionic liquids can be used as an extractant within the industrial process and can be used as a replacement to overcome problems and challenges associated with conventional solvents. The use of these new sustainable ionic liquids as the designer green solvents, non-volatile, environmental-friendly for separation is of more interest in the present work.

MATERIALS AND METHODS

1. Materials

Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) amide-CYPHOS IL 109 THTDP [NTF₂] ionic liquid, (purity ≥95.0%), Trihexyltetradecylphosphonium chloride-CYPHOS IL 101 (purity ≥95.0%), were procured from Sigma-Aldrich. 1-Butanol was obtained from Sigma-Aldrich (purity 99.9%). All the details about chemicals used in the present work are summarized in Table 1. All

Table 1. Chemical used in the present study

Chemicals	Molecular formula	Molar mass (kg·kmol ⁻¹)	CAS Reg. No.	Supplier	Purity %
1-Butanol	C ₄ H ₁₀ O	74.121	71-36-3	Sigma-Aldrich	99
Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide CYPHOS IL 109	C ₃₄ H ₆₈ F ₆ NO ₄ PS ₂	764	460092-03-9	Sigma-Aldrich	≥95
Trihexyltetradecylphosphonium chloride-CYPHOS-101	C ₃₂ H ₆₈ ClP	519.31	258864-54-9	Sigma-Aldrich	≥95
VOA Stock Solution 1-Butanol	C ₄ H ₁₀ O	74.121	30474	Restek Corporation USA	≥99

substances were utilized with no further pre-treatment.

2. Experimental Section

Generally, biobutanol is produced by means of the acetone butanol ethanol (ABE) method after acidogenesis and solventogenesis are carried out in the ratio 3 : 6 : 1. Biobutanol is produced by ABE fermentation in 10 g/L. The upper limit of convergence of biobutanol inhibits microbial activity and may affect the yield of the product [4,5]. Therefore, model solutions of butanol feed concentrations were taken in the range of 0.25-2.5 wt% in the experiments. Phosphonium based ionic liquids, such as THTDP[NTF₂] and THTDP [Cl], were used for recovery of butanol from aqueous solutions at T=298.15±1 K. We varied the concentration of extractant to diluents between 20 and 80 percent. It was kept at a ratio of 1 : 1 between aqueous and organic phases. Equilibrium was achieved by keeping equal volumes of the two phases in micro centrifuge tubes (Make: REMI; total volume=1.5 mL) and retaining them in orbital incubator shakers (Make: REMI S24-BL) for five hours at 250 RPM. The REMI R12C plus micro centrifuge was used at 15,000 RPM for 5 minutes to assist with stage partition. The experiment was carried out in duplicate, and results are within 0.1% of the average.

3. Analysis Procedure

GC 2010 Plus - Shimadzu Gas Chromatography with a cross bond dimethyl polysiloxane column (ID=0.32 MM, L=30, fused silica) was employed to examine equilibrium aqueous phase butanol concentrations. The experiment was conducted at 40 °C in the oven, 250 °C in the injector, and 280 °C in the FID. The column was calibrated using 1-butanol standard solution obtained from Toshvin Analytical Ltd, Mumbai. As a carrier gas, nitrogen was used at a flow rate of 30 mL/min. A combustion flame was achieved in FID after maintaining hydrogen (H₂(g)) and air in a ratio of 1 : 10 (H₂(g)=40 mL/min; Air=400 mL/min).

4. Standard Deviation

Deviation has been calculated using Eq. (1), with the observed value within $x \pm 0.001$ [22-28].

$$u(E) = \sqrt{\frac{\sum_{i=1}^n (x_i - x'')^2}{(n-1)}} \quad (1)$$

where,

n=Number of data points,

x_i=Each of the values of the data,

x''=mean of x_i

RESULTS AND DISCUSSION

1. Determination of Extraction Efficiency

Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) amide-CYPHOS IL 109 THTDP [NTF₂] ionic liquid, (purity ≥95.0%), Trihexyltetradecylphosphonium chloride-CYPHOS IL 101 (purity ≥95.0%), were used to carry out recovery of butanol from model aqueous solutions at T=298.15±1 K. Experimental investigations were observed for extraction efficiency in the range of 63-96% for CYPHOS 109 >40-76% for CYPHOS 101 using Eq. (2). Extraction. Fig. 3 illustrates the equilibrium plot between organic and aqueous phases in extraction CYPHOS 109 and CYPHOS 101 as extractant at T=298.15±1 K. The results for extraction efficiency are presented in Table 2. Fig. 4 summarizes the results.

A higher extraction efficiency was observed for the THTDP [NTF₂] (%E=80.64) compared to the THTDP [Cl] (%E=60.61). This is a result of an increase in the hydrophobicity of anions as follows: [Cl]⁻ < [NTF₂]⁻. The results are consistent with those found by Freire and colleagues for [NTF₂]⁻ and [Cl]⁻ anion [29,30]. Hydrophobicity of anion can also be defined from distribution coefficient.

$$\eta\% = \frac{K_d}{(K_d+1)} \times 100 \quad (2)$$

A comparison of experimental extraction efficiency ($\eta\%$) and

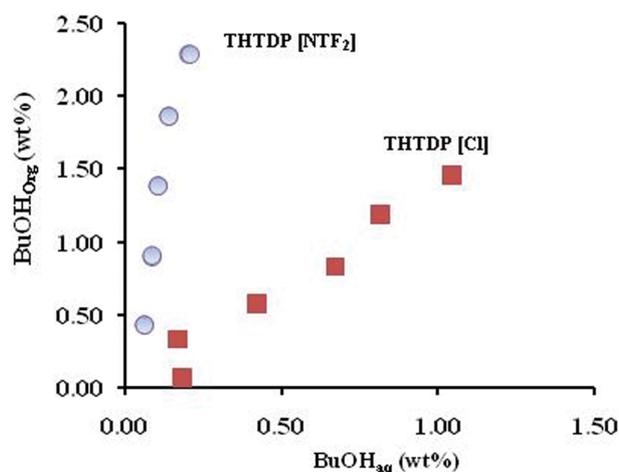
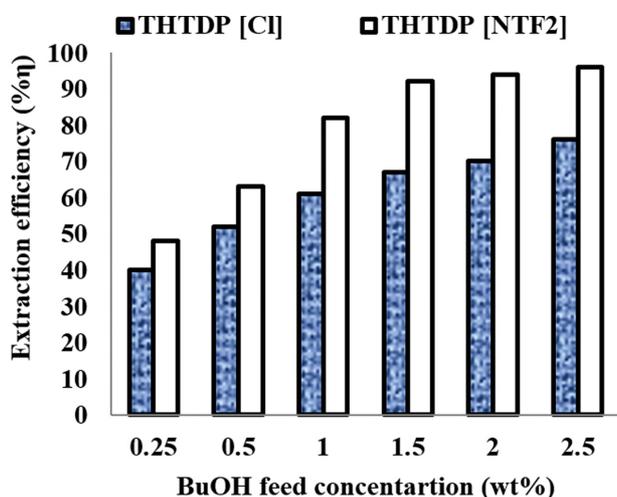


Fig. 3. Extraction equilibrium plot for THTDP [NTF₂] and THTDP [Cl] at 298.15±1 K at 101.325 kPa.

Table 2. Results for extraction efficiency and distribution coefficient of butanol separation using THTDP[NTF₂] nad THTDP [Cl] at T= 298.15±1 K

Extractant	[BuOH] ₀	[BuOH] _{aq}	[BuOH] _{org}	K _d	Avg K _d	E%	Avg E%
THTDP [NTF ₂]	0.25	0.130	0.120	0.92	11.055	48	80.43
	0.5	0.179	0.321	1.79		64	
	1.0	0.173	0.827	4.80		83	
	1.5	0.092	1.408	15.24		94	
	2.0	0.108	1.892	17.45		95	
	2.5	0.098	2.402	24.42		96	
THTDP [Cl]	0.25	0.151	0.099	0.7	4.140	40	60.68
	0.5	0.242	0.258	1.1		52	
	1.0	0.402	0.598	1.5		60	
	1.5	0.502	0.998	2.0		67	
	2.0	0.594	1.406	2.4		70	
	2.5	0.594	1.906	3.2		76	

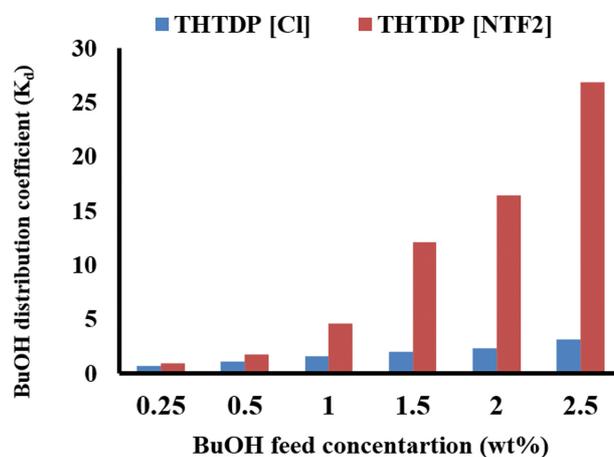
**Fig. 4. Extraction efficiency for recovery of butanol using THTDP [NTF₂] and THTDP [Cl] vs. aqueous butanol concentration at 298.15±1 K.****Table 3. Comparison of experimental distribution coefficients (K_d) and extraction efficiency (%) with literature results of butanol separation using THTDP[NTF₂] nad THTDP [Cl] at T=298.15±1 K**

Ionic liquids	Experimental Avg K _d	Experiemntal Avg %E	Reference
HMIM [NTF ₂] ⁻	1.253	65.84 ¹³	[13]
HMIM [HF ₆] ⁻	0.967	56.64 ¹³	[1]
THTDP [NTF ₂]	11.055	60.68	Present work
THTDP[Cl]	4.140	85.88	Present work

distribution coefficient (K_d) values with those reported in the literature is summarized in Table 3.

2. Estimation of Distribution Coefficient (K_d)

According to the definition, the distribution coefficient (K_d) is equal to the ratio between the organic phase concentration of butanol and its water-rich phase concentration of butanol, respectively.

**Fig. 5. BuOH distribution coefficient vs. BuOH₀ concentration for THTDP [NTF₂] and THTDP [Cl] at 298.15±1 K.**

Distribution Coefficient: $K_d = \frac{\text{conc. of BuOH in IL Rich phase}}{\text{conc. of BuOH in water Rich Phase}}$

$$K_d = \frac{C_{\text{BuOH in IL}}}{C_{\text{BuOH in w}}} \quad (3)$$

where,

$C_{\text{BuOH in IL}}$ - the organic phase concentration of a butanol (BuOH) after equilibrium separation (wt%)

$C_{\text{BuOH in w}}$ - the water-rich phase concentration of a butanol (BuOH) after equilibrium separation (wt%)

A model solution of butanol (0.25-2.5 wt%) was used to determine the distribution coefficient (K_d) values for phosphonium-based ionic liquids. For the extraction of butanol from model solutions of butanol (0.25-2.5 wt%), K_d values were observed by using THTDP [NTF₂] and THTDP [Cl]. As a result of the equilibrium experiments, average distribution coefficients (K_d) were observed as 3.44 for THTDP [NTF₂] and 1.79 for THTDP [Cl], respectively. K_d values were observed in the range of THTDP [NTF₂], (1.73-24.42) > THTDP [Cl], (0.66-3.21), respectively. A graphical representation of BuOH distribution coefficient versus BuOH feed con-

centrations is shown in Fig. 5.

The hydrophobicity of solvents affects the distribution coefficient. K_d values were observed in the order of THTDP [NTF₂] > THTDP [CL] at 298.15 K, respectively, THTDP [NTF₂]. The distribution coefficient and extraction efficiency of THTDP [NTF₂] for the separation of butanol are greater than those for THTDP [CL].

3. Determination of the Minimum S/E, Number of Stages for Pure Solvents

Using counter-current liquid-liquid extraction, butanol was recovered from aqueous feed solutions in concentrations ranging from 0.25 to 2.5 wt% in the current study. To successfully extract butanol at industrial scale using room temperature ionic liquid, it is important to determine the minimum solvent-to-feed ratio and the minimal number of extraction stages. Mass transfer units (theoretical stages, NTS) are used to determine the proportion of extraction dissolvable to nourish stream rates required to achieve the ideal exchange of mass from one stage to the next in a fluid extraction process. Minimum solvent-to-feed ratio for recovery of butanol using different extractants THTDP [NTF₂] and THTDP [CL] vs. aqueous butanol concentration at 298.15±1 is presented in Fig. 6. For industrial scale, it is relevant to estimate capital costs. Therefore, the minimum S/F ratios were determined using Eq. (4) [31].

$$\left(\frac{S}{F}\right)_{min} = \frac{x_{in} - x_{out}}{K_d x_{in} - y_{in}} \quad (4)$$

where,

x_{in} =BuOH concentration in the Feed (mass fraction),

x_{out} =BuOH concentration in the Raffinate (mass fraction)

y_{in} =Initial BuOH concentration in the extract phase (mass fraction)

As a rule of thumb, in the liquid-liquid extraction process, the solvent-to-feed ratio is 1.5 times the minimum ratio. Using modified Kremser equation, the number of theoretical stages (NTS) for counter-current extraction of butanol using THTDP [NTF₂] and THTDP [CL] as extractants was found. Results of the theoretical number of stages for recovery of Butanol at 298.15±1 K are given in Fig. 7.

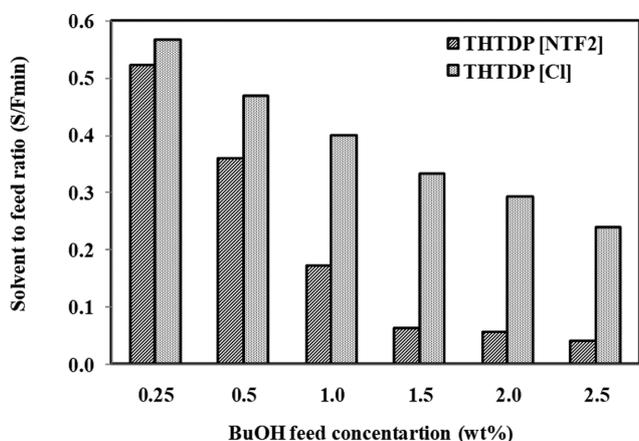


Fig. 6. Minimum solvent-to-feed ratio for recovery of butanol using different extractants THTDP [NTF₂] and THTDP [CL] vs. aqueous butanol concentration at 298.15±1.

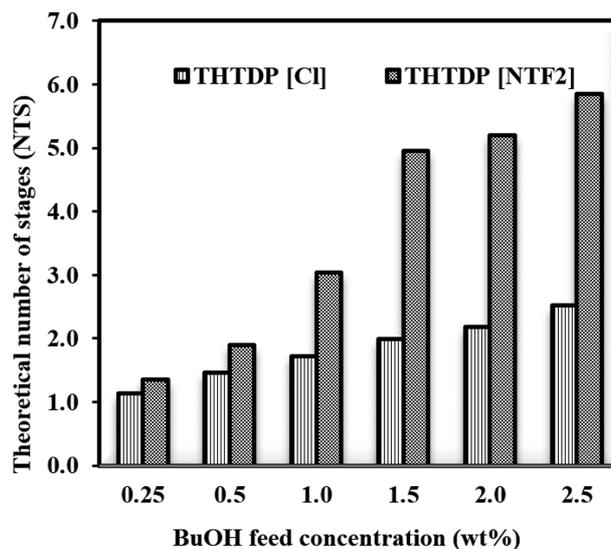


Fig. 7. Theoretical number of stages (NTS) for recovery of butanol using different extractants THTDP [NTF₂] and THTDP [CL] vs. aqueous butanol concentration at 298.15±1.

$$NTS = \frac{\ln \left[\left(\frac{x_{in} - y_{in}/K_D}{x_{out} - y_{in}/K_D} \right) (1 - 1/E_x) + \frac{1}{E_x} \right]}{\ln E_x} \quad (5)$$

Extraction factor: E_x is given by Eq. (6):

$$E_x = K_D \frac{S}{F} \quad (6)$$

4. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR technique is applicable to both organic and inorganic samples. Infrared spectroscopy (FTIR) identifies chemical bonds within a molecule by analyzing its infrared absorption spectrum. A spectrum gives a profile of a sample, a distinctive molecular fingerprint that can be used to screen and detect various components in samples. For detecting functional groups and characterizing covalent bonding, FTIR can be an effective analytical tool. FTIR was used to examine the complex formed by ionic liquid from the

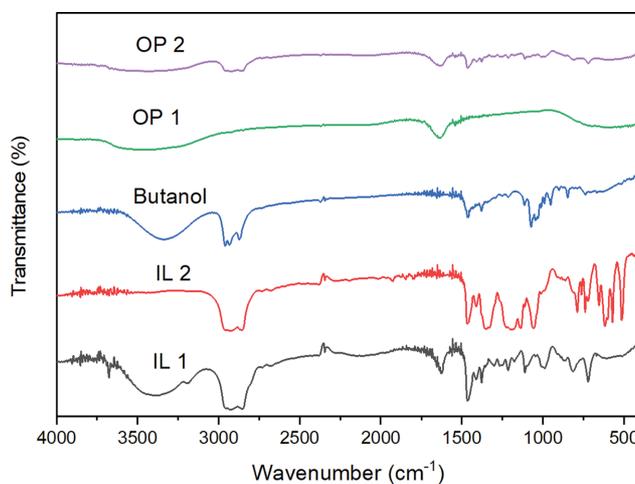


Fig. 8. FTIR spectrum of pure ionic liquids, butanol and organic phase.

Butanol extracted from the aqueous phase (Shimadzu IRAffinity-1). FTIR spectra in the 4,000-400 cm^{-1} region were employed to recognise chemical bonds in a molecule or an interaction system or the presence of particular functional groups. Fig. 8 represents the FTIR spectra of ionic liquid-IL1 (Trihexyltetradecylphosphonium chloride-CYPHOS IL 101 (purity $\geq 95.0\%$)), ionic liquid-IL2 (Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) amide-CYPHOS IL 109 THTDP [NTF₂] ionic liquid, (purity $\geq 95.0\%$)), Butanol, Organic phase-OP1 (Trihexyltetradecylphosphonium chloride-CYPHOS IL 101 and butanol), organic phase-OP2 (Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) amide and butanol) before and after equilibrium extraction. For IL1, IL2 and butanol, FT-IR analysis demonstrated characteristic signals of O-H stretching vibrations pertaining to hydrogen bonds in the range of 2,500-3,300 cm^{-1} . A weak hydrogen bonding, O-H stretch vibration, was observed for OP1 and OP2, which may help in regenerating and reusing ionic liquid for further use.

CONCLUSION

An investigation was carried out to separate butanol from aqueous solutions (0.25-2.5 wt%) using Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) amide-CYPHOS IL 109 THTDP [NTF₂] ionic liquid, (purity $\geq 95.0\%$), Trihexyltetradecylphosphonium chloride-CYPHOS IL 101 THTDP [Cl] (purity $\geq 95.0\%$), at ambient conditions (298.15 \pm 1 K). Ionic liquid, Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) amide, was found an efficient green solvent in terms of maximum separation efficiency, distribution coefficient and minimal solvent-to-feed ratio compared to other ionic liquids. Extraction efficiency was observed in the order of THTDP [NTF₂] > THTDP [Cl], respectively. The average separation efficiency of butanol was observed highest (%E 80.43) with hydrophobic THTDP [NTF₂] ionic liquid. The maximum average distribution coefficient (K_d) 11.055 was found for RTIL ionic liquid THTDP [NTF₂] compared to THTDP [Cl] ionic liquid. Minimum solvent-to-feed ratio was observed for ionic liquid, THTDP [NTF₂], (S/F_{min} 0.3829) and for THTDP [Cl], (S/F_{min} 0.201). Thus, the use of ionic liquids as an extractant can be a promising alternative to conventional volatile, toxic solvents. Because of the excellent blending properties and fewer emissions, biobutanol can be recovered with ionic liquid by gasoline-driven combustion systems. Thus, ionic liquids are novel sustainable green solvents, environment friendly for separation of butanol from aqueous media.

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STATEMENT AND DECLARATIONS

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Author Contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Kalyani A. Motghare.

The first draft of the manuscript was written by Kalyani A. Motghare and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Conception of theory and experiments, supervision, data analysis were performed by Dr. Kailas L. Wasewar and Dr. Diwakar Z. Shende.

Ethics Approval and Consent to Participate

Not applicable

Consent for Publication

Not applicable

Availability of Data and Materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

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