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Investigation of Ionic Liquids for the Separation of Butanol and Water

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Abstract: With the continual rise in the cost of fossil fuel based energy, research into economic and sustainable alternatives is of increasing importance. One significant source of increased cost and demand is the consumption of fossil fuels for automotive fuels. While ethanol has received the most attention as a fuel additive; butanol could be a better direct fuel alternative owing to its physical properties and energy value when compared to ethanol. Commercial butanol is nearly exclusively produced from petroleum feedstocks currently; however, some recent interest has begun to refocus on its generation via fermentation. Unfortunately, this production is limited due to the nature of the process and the use of energy-intensive separation techniques. Ionic liquids are novel green solvents that have the potential to be employed as an extraction agent to remove butanol from the aqueous fermentation media. A hurdle to this potential is the limited availability of solubility data for ionic liquids. This research investigates the phase behavior of two ionic liquids, butanol, and water. Additionally, issues related to the implementation of the investigated ionic liquids are discussed.

Keywords: Butanol, ionic liquid, liquid-liquid equilibrium, liquid-liquid extraction, separation, water

INTRODUCTION

As the cost of crude oil rises, research to develop alternatives to fossil fuels is becoming increasingly relevant. One set of alternatives to petroleum derived fuels is biofuels and more specifically fuels produced

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from a fermentation process. Biofuels are generally used as fuel additives rather than petroleum substitutes. The advantage of adding biofuels to gasoline is an overall decrease in the release of carbon dioxide (CO_2) to the atmosphere. While the combustion of biofuels releases roughly the same amount of CO_2 as the combustion of petroleum, the plants used in the production of biofuels consume CO_2 as they grow. Thus, the overall volume of CO_2 released to the atmosphere is lower than that of conventional fuels. The most commonly used biofuel is ethanol. Biologically derived ethanol is currently used as a gasoline additive in several countries, including the United States and the United Kingdom.

Although bioethanol is the most common biofuel currently in use, biobutanol has several advantages which may make it a more desirable fuel additive. The two main advantages are a higher energy content and relatively easy integration into the present fuel infrastructure. The energy content of butanol is approximately 110,000 BTU per gallon, as opposed to ethanol's 84,000 BTU per gallon. The energy content of conventional gasoline is about 115,000 BTU per gallon. Other physical properties of butanol, such as density and heat capacity, are very similar to those of ethanol (Table 1).

The low vapor pressure of butanol allows it to be directly added to gasoline without concern about evaporation and subsequent related complications. While vehicles require modifications in order to use gasoline containing higher concentrations of ethanol, no such modifications are necessary for the burning of butanol (1). The nature of butanol makes blending with gasoline less susceptible to separation in the presence of water than other biofuel/gasoline blends. For this reason, butanol can be easily integrated into the present fuel delivery and storage infrastructure. Thus, the potential for quick and widespread introduction of biobutanol into the market exists.

Currently, butanol is mainly produced from petroleum products in a process known as oxo-synthesis (2). This method, employed since the 1950s to produce the majority of butanol, is receiving increased scrutiny for two main reasons:

1. regulatory pressure to reduce greenhouse gas emissions and,
2. increasing crude oil prices.

Table 1. Selected physical properties for gasoline, ethanol, and butanol

	Gasoline	Ethanol	Butanol
Density (g/cm^3)	0.7–0.8	0.789	0.8098
Boiling Point (°C)	27–221	78	118
Energy Content (BTU/gal)	115,000	84,000	110,000

The other well-defined method of butanol production utilizes a bacterial fermentation process developed in 1913 (3). This biological method is not currently viable for a number of reasons, including cost, yield, and difficulty in separation (4). The fermentation process used in the production of butanol is economically inefficient due to the great cost associated with the separation of butanol from the fermentation broth. The cost of producing butanol from this fermentation process is roughly three times that of gasoline; the cost of production of butanol from the petroleum process runs around $3 per gallon (1).

Currently, the butanol fermentation process is a batch process or a pseudo-continuous process. Toxicity and separation issues prevent the process from operating continuously. Most fermentation processes utilized Clostridium acetobutylicum, the traditional bacterium for the Acetone-Butanol-Ethanol (ABE) fermentation that produces butanol. Toxicity issues are present for this bacterium at concentrations of butanol near 15 to 20 grams per liter (approximately 2% by weight) (3). To mitigate the toxicity and allow the fermentation process to be continuous the process must be improved such that the organism's resistance to butanol is increased or the butanol must be constantly extracted from the fermentation broth to remain below the toxicity threshold. Extracting the butanol has its own obstacles. Butanol is partially miscible in water with a solubility of 74 grams per liter (approximately 7% by weight) (1,2). A distillation technique could be employed to separate butanol from water; however, it is energy intensive and thus expensive. This is primarily due to the fact that water is the low boiler and the amount of energy necessary to complete the separation is very high due to the absolute concentration of water in the fermented broth (4). If a method of extraction could be developed to continuously extract the butanol from the fermentation broth, the process may be able to be transformed from a batch process to a continuous process and therefore more economically viable.

A potentially cost effective method for the separation of butanol from water would involve the use of a liquid extracting agent. Ionic liquids could be potential extracting agents for this application (5); however the literature data relating to these compounds are limited. Ionic liquids comprise a broad yet relatively new field of study (6–10). Limited data exists in terms of thermophysical properties and multi-component equilibrium data for the use of ionic liquids as extraction agents. What data does exist primarily describes the binary equilibria between selected ionic liquids and alkanols with a pair of studies reporting limited ternary equilibrium data for butanol-water-ionic liquid systems.

Wu et al. investigated the binary liquid-liquid equilibrium of butanol and various ionic liquids, 1-alkyl-3-methylimidazolium hexafluorophosphate, [Rnmim][PF_6], where Rn=butyl, pentyl, hexyl, heptyl, and octyl (11).

The results were considered typical for partially miscible systems with upper critical solution temperatures (UCST). The study found that the higher the organic content, i.e. length of alkyl chain, the higher its solubility in butanol. Another report by Sahandzhieva and coworkers on the binary liquid-liquid equilibrium of [bmim][PF6] and three alkanols, ethanol, 1-propanol, and 1-butanol, over a range of temperatures demonstrated a rise in UCST with a rise in chain length on the alkanol (12). The region of concentrations in which two phases are formed in mixtures of ionic liquid and alkanol also increases as the length of the chain on the alkanol increases. Bendova and Wagner have also investigated the binary equilibrium of [Bmim][PF_6] and 1-butanol (13) and were in good agreement with the work of Wu et al Sand Sahandzhieva et al. Heintz et al. reported similar results regarding the increased in UCST with increasing alkyl chain length for the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf2N]) and 1-propanol, 1-butanol, and 1-pentanol (14,15).

Fadeev and Meagher have investigated the solubilities of 1-butyl-3-methylimidazolium ([bmim][PF_6]) and 1-octyl-3-methylimidazolium hexafluorophosphate ([omim][PF_6]) with butanol and water at very low concentrations of butanol ($<5\%$ by weight) (5). This study provided evidence that ionic liquids of a hydrophobic nature have the potential as liquid extraction agents, but those studied were not ideally suited for pervaporative separation of butanol from water. In another study, Hu et al. investigated the ternary liquid-liquid equilibrium of 1-(2-Hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([C_2OHmim][BF_4]) and 1-(2-Hydroxythyl)-2,3-dimethylimidazolium ([C_2OHdmim][BF_4]) with butanol and water (16). The applications of this research were for drying butanol; thus, ionic liquids which are hygroscopic were chosen. The results of this analysis show that both systems phase separate into an upper butanol-rich phase and a lower ionic-liquid rich phase. The calculated distribution ratios show a greater concentration of water in the ionic liquid-rich phase than in the butanol-rich phase. The selectivity data shows that both [C_2OHmim][BF_4] and [C_2OHdmim][BF_4] have suitable efficiencies for extracting water from butanol when the water is at low concentrations.

It is clear even from the limited literature data that ionic liquids have potential as liquid extraction agents for the separation of butanol and water. Several concerns exist regarding their use for extraction from fermentation systems,

1. toxicity of the ionic liquid toward any bioorganisms present,
2. need for high selectivity of butanol over water, and
3. reduction of the loss of ionic liquid to the aqueous fermentation broth phase.

The first concern, toxicity, has been generally addressed by Scammells et al. and the development of a biodegradable ionic liquid (8). The second concern will only be resolved when there exists sufficient understanding of butanol-water-ionic liquid systems to predict and produce an "ideal" ionic liquid. Our research presented in this article explored the ternary liquid equilibrium of butanol, water, and a pair of ionic liquids, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf2N]) and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf2N]), in order to quantify the usefulness of the ionic liquids in performing the extraction. The liquids were selected for their increased hydrophobicity over those studied in earlier work (5) and should further mitigate concern number three.

EXPERIMENTAL

Materials

This study investigated the ternary solubility of butanol, water, and each of two ionic liquids: [bmim][Tf2N] and [hmim][Tf2N]. Both ionic liquids used in this study were synthesized our laboratory. All ionic liquid precursors, 99% 1-methylimidazole (CAS# 616-47-7), 99 + % 1-bromobutane (CAS# 109-65-9), 99 + % 1-bromohexane (CAS# 111-25-1), and 99.5% lithium bis(trifluoromethylsulfonyl)imide (CAS# 90076-65-6), were purchased from Sigma-Aldrich and used as received. The 1-butanol used in this study was obtained from Sigma-Aldrich as Chromasolv® Plus, HPLC grade, with purity $>99.7\%$. Methanol used as a dilutant and a carrier during liquid chromatography was obtained from Fisher Scientific as HPLC grade and purity $>99.9\%$.

Ionic Liquid Synthesis

The ionic liquids used in this study were synthesized by two slightly different methods. [bmim][Tf2N] was synthesized first by preparing [bmim][Br] using an ultrasonic approach similar to that utilized by Namboodiri and Varma (17). 1-methylimidazole was reacted with a small molar excess of 1-bromobutane in a 2510 Branson Ultrasonic Cleaner for six hours followed by purification at elevated temperature ($<80°C$) under vacuum (<10 torr) for more than 72 hours. The purified [bmim][Br] was further reacted with lithium bis(trifluoromethylsulfonyl)imide to form the desired ionic liquid [bmim][Tf2N] via a metathesis reaction yielding a water soluble salt, LiBr, and a water insoluble ionic liquid in sufficiently high yield ($>85\%$).

[hmim][Tf2N] was synthesized via a "slow-reaction" method. 1-methylimidazole and excess 1-bromohexane were placed in a constant temperature oven at temperatures between 30 and 40°C for approximately 3 weeks to yield [hmim][Br]. This primary ionic liquid was then purified at elevated temperature (<80°C) under vacuum (<10 torr) for more than 72 hours. The purified [hmim][Br] was further reacted with lithium bis(trifluoromethylsulfonyl)imide to form the desired ionic liquid [hmim][Tf2N] via a metathesis reaction yielding a water soluble salt, LiBr, and a water insoluble ionic liquid. This method has the added advantage of reducing the initial degree of discoloration of the ionic liquid that can occur when the ionic liquids are subjected to elevated temperatures during synthesis.

The ionic liquids were tested for purity using both NMR and HPLC analysis, the results of which indicated that any impurities (residual reactants) were below detectable limits. Prior to each use the ionic liquids were purified at elevated temperature (<80°C) and under vacuum ($\sim$1.0e-4 torr) for a minimum of 24 hours. The ionic liquids were stored under dry air in a dessicator after purification and when not in use.

Experimental Method

To determine the nature (phases, tie-lines, and phase compositions) of the ternary systems at equilibrium, varying amounts of butanol, water, and ionic liquid were placed in 4 mL vials. The vials were shaken vigorously to ensure complete contacting of the phases. The vials were placed in a 25°C constant temperature bath for 24 + hours and allowed to reach equilibrium. When the vials where at equilibrium and multiple phases were observed, 35 µL samples of each phase were acquired and subsequently diluted in 1 mL of methanol for HPLC and GC analysis.

The concentration of ionic liquid present in each sample was determined using an Agilent 1100 Series High Performance Liquid Chromatograph (HPLC) with a Supelco ODP-50 15 cm column. The method used a methanol/water gradient with methanol concentration increasing from 10% to 100% at a flowrate of 1.1 mL/min. The column temperature was set to 25°C. Each sample was analyzed using an injection volume of 3 µL (determined to give the best signal and calibrated for accuracy). The ionic liquid peaks were observed at 230 nm. [bmim][Tf2N] had a typical retention time of approximately 4.7 minutes while [hmim][Tf2N] was observed at a retention time near 5.1 minutes. As butanol is not easily detectable in the HPLC UV/Vis detector, a Varian 3900 Gas Chromatograph (GC) was used to determine the concentration of butanol present in each sample. The column used was a Stabilwax Carbowax column

(30 m × .53 mm). The method employed a temperature ramp from 40°C to 180°C and an injection volume of 1 µL. The water concentration was determined through a mass balance based on determined ionic liquid and butanol values.

RESULTS AND DISCUSSION

This study investigated the ternary solubility of two ionic liquids, [bmim][Tf2N] and [hmim][Tf2N], with butanol and water. The equilibrium concentrations of both phases were determined over a range of concentrations, and selectivity coefficients and distribution ratios were determined.

When designing a system to extract one liquid from another, an important factor for determining the viability of a given solvent is the selectivity of that solvent for the solute of interest. Selectivity, is defined as a solvent's ability to separate the components of a given mixture (18). Selectivity measures the possibility of separating solute A from carrier solvent B using extraction solvent C. In a system consisting of butanol (BuOH) and water (H_2O) and an ionic liquid (IL) as the extracting solvent, the relationship for selectivity is defined as:

$$S = \frac{\left(w_{BuOH} \middle/ w_{H_2O} \right)^{IL-rich\ phase}}{\left(w_{BuOH} \middle/ w_{H_2O} \right)^{H_2O-rich\ phase}} \tag{1}$$

where S = selectivity and w = mass fraction of component (subscript) in each phase (superscript). The distribution ratio (β) is another important parameter when evaluating extracting agents. This quantity measures the mass fraction of the solute in the solvent rich phase (in this case, butanol in the ionic liquid phase) versus that in the carrier rich phase (water) (18). The higher the distribution ratio, the greater the efficiency the extraction solvent displays in separating the solute from the carrier solvent. It is commonly understood that solute distribution ratios greater than unity indicate a potentially favorable extraction. The distribution ratio is defined as:

$$\beta_{BuOH} = \frac{\left(w_{BuOH} \right)^{IL-rich\ phase}}{\left(w_{BuOH} \right)^{H_2O-rich\ phase}} \tag{2}$$

The experimental tie-line data, selectivity, and distribution ratio for the water + butanol + [bmim][Tf2N] and water + butanol + [hmim][Tf2N] ternary mixtures are given in Table 2 and 3, respectively. The experimental

Table 2. Experimental data for water (1) + butanol (2) + [bmim][Tf_2N] (3) at 298.15 K

H_2O-rich phase			[bmim][Tf2N]-rich phase				
w_1	w_2	w_3	w_1	w_2	w_3	S	β_{BuOH}
0.9396	0.0604	0.0000	0.0418	0.2674	0.6908	99.49	4.43
0.9314	0.0686	0.0000	0.0715	0.3317	0.5968	62.99	4.84
0.9177	0.0682	0.0141	0.1131	0.4520	0.4350	53.77	6.62
0.9071	0.0801	0.0128	0.0802	0.3237	0.5961	45.70	4.04
0.9267	0.0733	0.0000	0.1278	0.4610	0.4111	45.62	6.29
0.9303	0.0697	0.0000	0.1379	0.4698	0.3922	45.49	6.74
0.9267	0.0733	0.0000	0.1623	0.5134	0.3243	39.99	7.00
0.9294	0.0706	0.0000	0.1725	0.5237	0.3038	39.94	7.41
0.9337	0.0663	0.0000	0.1112	0.3118	0.5770	39.49	4.70
0.9268	0.0732	0.0000	0.1734	0.5124	0.3142	37.43	7.00
0.9047	0.0953	0.0000	0.1007	0.3903	0.5090	36.80	4.09
0.9306	0.0694	0.0000	0.1409	0.3613	0.4978	34.37	5.20
0.8662	0.0797	0.0541	0.0733	0.2210	0.7057	32.78	2.77
0.9876	0.0124	0.0000	0.5717	0.1744	0.2540	24.36	14.10
0.9951	0.0049	0.0000	0.5613	0.0591	0.3796	21.25	11.98
0.9358	0.0642	0.0000	0.1399	0.1739	0.6862	18.13	2.71
0.9405	0.0595	0.0000	0.1581	0.1635	0.6783	16.34	2.75
0.9571	0.0430	0.0000	0.1306	0.0936	0.7758	15.97	2.18
0.9794	0.0206	0.0000	0.1010	0.0278	0.8712	13.09	1.35
0.9559	0.0441	0.0000	0.1181	0.0617	0.8202	11.31	1.40
0.9527	0.0473	0.0000	0.1264	0.0669	0.8067	10.65	1.41

ternary diagrams for the water + butanol + [bmim][Tf2N] and water + bubutanol + [hmim][Tf2N] systems are presented in Figs. 1 and 2, respectively. Additionally, plots of the selectivity and distribution ratio relative to each ionic liquid are provided in Figs. 3 and 4.

As can be seen from the provided data, the two ionic liquids tested, [bmim][Tf2N] and [hmim][Tf2n], do have promise for use as liquid-liquid extraction solvents for the separation of butanol from water. Several important items should be noted for each system. The selectivity, being an indication of extraction potential, is favorable for high concentrations of butanol in the ionic liquid phase. Both ionic liquids have similar distribution ratios and selectivity over the bulk of the measured global mixture composition; however, neither ionic liquid truly demonstrates an obvious superiority. The slope of the tie-lines is a good indication that ionic liquids would not be necessary as extraction solvents for concentrations greater than the saturation concentration of butanol in

Table 3. Experimental data for water (1) + butanol (2) + [hmim][Tf_2N] (3) at 298.15 K

H_2O-rich phase			[bmim][Tf2N]-rich phase				
w_1	w_2	w_3	w_1	w_2	w_3	S	β_{BuOH}
0.9342	0.0658	0.0000	0.0997	0.5286	0.3717	75.27	8.04
0.9370	0.0630	0.0000	0.0518	0.2341	0.7141	67.27	3.72
0.9301	0.0699	0.0000	0.1239	0.4545	0.4216	48.81	6.50
0.9282	0.0718	0.0000	0.1419	0.5227	0.3353	47.59	7.28
0.9389	0.0611	0.0000	0.1102	0.3399	0.5499	47.42	5.56
0.9292	0.0708	0.0000	0.1292	0.4649	0.4059	47.23	6.57
0.9290	0.0710	0.0000	0.1299	0.4555	0.4146	45.93	6.42
0.9294	0.0706	0.0000	0.1643	0.5060	0.3297	40.55	7.17
0.9403	0.0598	0.0000	0.1084	0.2516	0.6400	36.52	4.21
0.9258	0.0742	0.0000	0.1585	0.4243	0.4173	33.43	5.72
0.9276	0.0724	0.0000	0.1238	0.3172	0.5589	32.84	4.38
0.9502	0.0498	0.0000	0.1362	0.1853	0.6784	25.97	3.72
0.9349	0.0651	0.0000	0.1311	0.2310	0.6379	25.30	3.55
0.9629	0.0371	0.0000	0.1208	0.0651	0.8141	14.00	1.75
0.9638	0.0362	0.0000	0.2054	0.0573	0.7373	7.42	1.58
0.7993	0.2007	0.0000	0.0522	0.0790	0.8689	6.03	0.39
0.9390	0.0610	0.0000	0.3560	0.0360	0.6080	1.56	0.59
0.9239	0.0761	0.0000	0.8728	0.0452	0.0821	0.63	0.59

water ($\sim$7 wt%). This is not true for concentrations below the butanol-water solubility limit (consequently the range of concentrations relevant to butanol fermentation systems), where both ionic liquids have demonstrated effective potential recovery of butanol. For most of the data observed there exists negligible (below detectable limits) ionic liquid in the water phase, the exception being a few points in the [hmim][Tf2N] system. It is likely that with an improved calibration and HPLC method the actual quantity of ionic liquid in the aqueous would become clearer.

During our exploration of the two-phase region we observed the existence of two unique phase separations, for both systems:

1. the presence of a three phase region for global compositions in the region to the upper left hand side of the ternary diagram, and
2. the replacement of the ionic liquid-rich phase with a butanol-rich phase that contained significant quantities of ionic liquid.

Additionally, for the three phase samples an opposite interface shape (convex versus concave) was observed for the [bmim][Tf2N] system

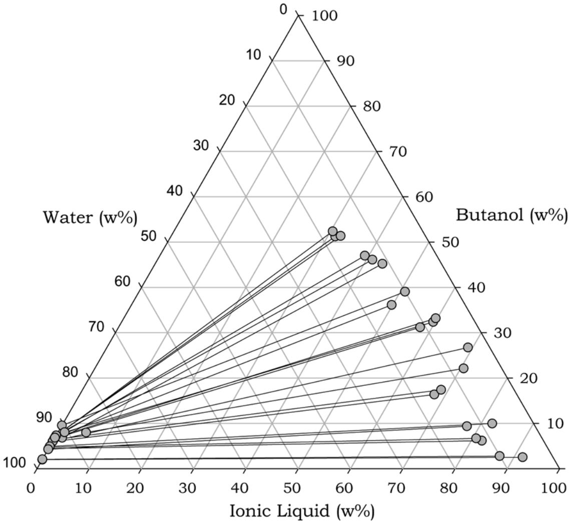

Figure 1. Ternary liquid-liquid equilibrium of water (1) + butanol (2) + [bmim][Tf_2N] (3) at 298.15 K.

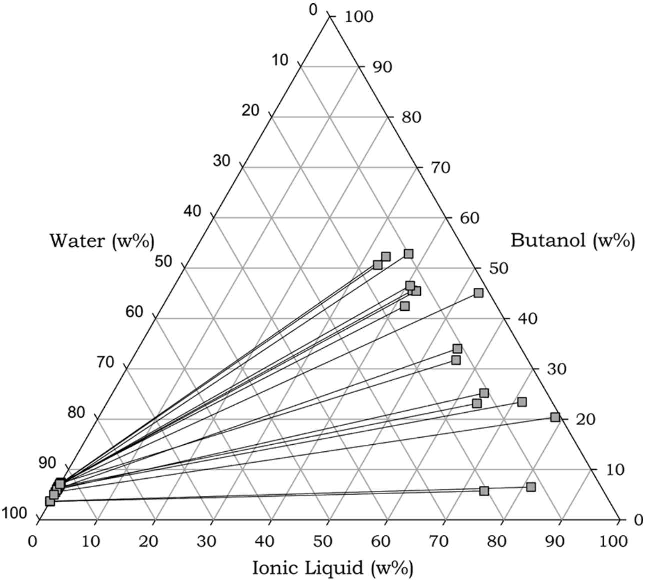

Figure 2. Ternary liquid-liquid equilibrium of water (1) + butanol (2) + [hmim][Tf_2N] (3) at 298.15 K.

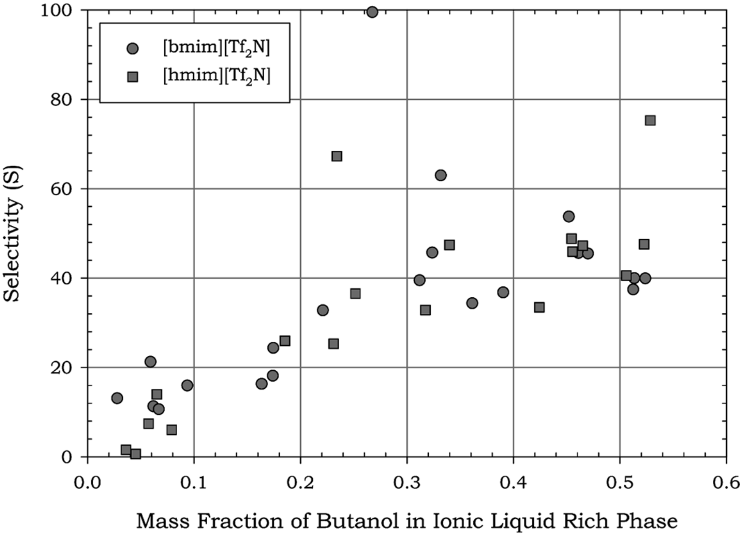

Figure 3. Selectivity of extracting butanol.

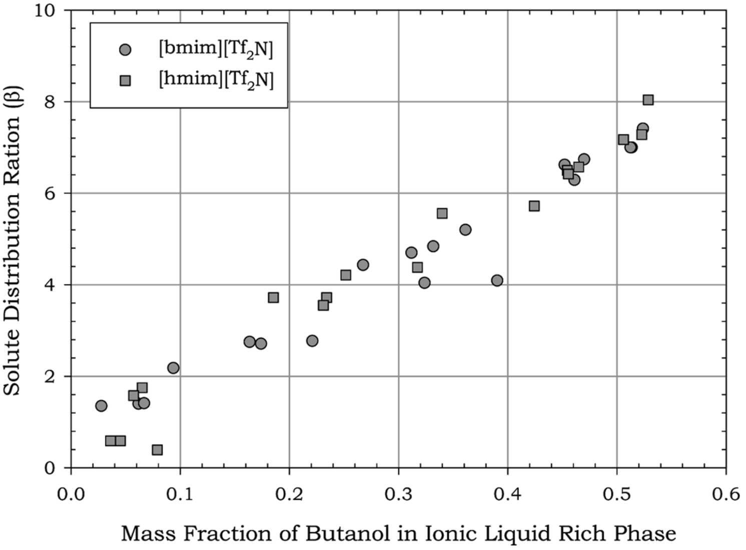

Figure 4. Solute distribution ratios.

compared to the [hmim][Tf2N]. Since data indicates that both ionic liquids are favorable extraction solvents, the choice of selection between would be driven by three factors:

1. cost of the ionic liquid solvent,
2. the hydrophobicity and water solubility of the ionic liquid, and
3. the toxic effect of the ionic liquid on any bacteria employed in the generation of butanol.

CONCLUSIONS

The ternary liquid-liquid equilibrium data for two ionic liquid + water + butanol systems has been presented. The data shows that [bmim][Tf2N] and [hmim][Tf2N] exhibit high selectivity for butanol when low concentrations of butanol are present in the initial aqueous phase. The hydrophobic properties of [bmim][Tf2N] and [hmim][Tf2N] are not strong enough to overcome the miscibility of butanol and water; thus, the ionic liquid rich phases contain some water. The nature of the tie-lines, the distribution ratio, and the selectivity all lend credence to the further investigation of primarily hydrophobic ionic liquids for the separation of butanol from fermentation systems. More information is needed to identify an ideal ionic liquid for extractions of this type and is the subject of our ongoing work.

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