Quantification of Zwitterion Betaine in Betaine Bis(trifluoromethylsulfonyl)imide and its Influence on Liquid-Liquid Equilibrium with Water

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Quantification of Zwitterion Betaine in Betaine Bis(trifluoromethylsulfonyl)imide and its Influence on Liquid-Liquid Equilibrium with Water

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Jaeseong Lee,[a] Melissa Fairley,[b] George S. Goff[b] and Joan F. Brennecke[a]

Ionic liquids (ILs) have been proposed as extractants for separation of metals, including rare earth elements. In particular, protonated betaine bis(trifluoromethylsulfonyl)imide ([HBet][TFSI]) exhibits liquid-liquid phase behavior with water that can be tuned by complexation with various metals. Here we show that previously undetected neutral zwitterionic betaine formed during the IL synthesis can affect the phase behaviour.

Ionic liquids (ILs), molten salts that are liquid under mild temperature conditions, have the potential to play a key role in the development of new technology for metal separation that could be more selective, safer and less waste intensive. Of particular interest are rare earth elements (REE), which are critical in a variety of industries, but hard to separate due to their similar chemical properties. Especially as the demand for REEs increases, ILs may be feasible substitutes for current cumbersome extraction processes, which typically involve the use of concentrated mineral acids or caustic solutions followed by organic solvent extraction steps.[1–5] Both primary recovery and recycling of REEs are viable targets. After Visser et al. showed that ILs can replace traditional organic solvents as the receiving phase in the separation of metal ions from aqueous solutions with an additional extractant,[6] many studies showed that some REEs can be extracted with ammonium-based and phosphonium-based ionic liquids as solvents or extractants.[7–31]

Protonated betaine bis(trifluoromethylsulfonyl)imide ([HBet][TFSI]), shown in **Fig. S1**, is an IL well-known for its ability to dissolve large quantities of metal ions.[32–35] The carboxylic group of [HBet]$^+$ can coordinate with metal ions, dissolving them in the weakly hydrophobic IL.[36] In fact, [HBet][TFSI] is not completely miscible with water up to about 50 °C, which is advantageous for extraction of metals from aqueous solutions. For example, Nockemann et al. showed that numerous metal ions (trivalent REEs, uranium (VI), copper (II), etc.) dissolve in [HBet][TFSI] and can be stripped from the IL with acid.[32] Fagnant et al. found that the Upper Critical Solution Temperature (UCST) of [HBet][TFSI] with water decreases when loaded with neodymium (III), affording another potential separation strategy.[37]

[HBet][TFSI] is generally synthesized through ion exchange in water between lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and betaine hydrochloride (HBetCl), as shown in **Fig. 1**.[34] The [HBet][TFSI] forms a separate dense liquid phase. Researchers generally concern themselves with chloride and lithium ion impurities, washing the IL-rich phase with water until the aqueous extract shows no chloride impurity according to a silver nitrate test. However, another possible “impurity” is neutral zwitterionic betaine, which is formed by deprotonation of the carboxylic acid; this is also shown in **Fig. 1**. Because betaine is zwitterionic and quite a strong acid (pKa=1.83)[35], if synthesis includes solvents less acidic than betaine and a water washing step, generation of deprotonated betaine due to dissociation is inevitable. As will be described herein, we have determined that without the addition of acid, there is significant zwitterion present in the [HBet][TFSI] and that its presence affects the [HBet][TFSI]/water and [HBet][TFSI]/water/REE cloud point curves.

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[a] *J. Lee, J. F. Brennecke*
McKetta Department of Chemical Engineering,
The University of Texas at Austin,
Austin, TX 78712 (USA)
E-mail: jfb@che.utexas.edu

[b] *M. Fairley, G. S. Goff*
Materials Physics and Applications Division
Los Alamos National Laboratory
Los Alamos, NM 87545

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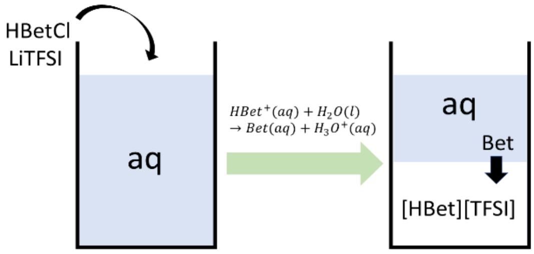

Fig. 1 Protonated betaine bis(trifluoromethylsulfonyl)imide ([HBet][TFSI]) traditional synthesis, along with deprotonation reaction that can occur to form a neutral zwitterion betaine impurity.

To our knowledge, no previous reports have recognized or attempted to quantify in solution the neutral zwitterionic betaine in the as-synthesized [HBet][TFSI] despite the fact it has been recognized as an impurity in the solid-state and verified by single-crystal X-ray diffraction, powder X-ray diffraction, and Infrared spectroscopy.[32,38] Moreover, we are not aware of any researchers adding acid in the synthesis of [HBet][TFSI], which we have found necessary to reduce betaine formation (see SI).[32–35,39–41] Adding acid is a common method to ensure full protonation of carboxylates and reduce zwitterion concentrations.[42,43]

Volia et al.[39] studied the impact of *added* betaine and HCl on the aqueous phase composition of [HBet][TFSI]/water systems at 23 °C. They analysed the aqueous phase, recognized the reprotonation equilibrium to form zwitterionic betaine, and observed partitioning of added betaine into the IL-rich. However, like previous researchers, they did not consider, measure, or account for the betaine in the as-synthesized [HBet][TFSI].

We synthesized three samples of [HBet][TFSI] with an aim towards decreasing Li^+, Cl^- and zwitterion betaine impurities (see SI). The concentrations of Li^+ and Cl^- in the [HBet][TFSI] were determined using Ion Chromatography (IC). Quantitative ^{19}Fluorine Nuclear Magnetic Resonance spectroscopy (q^{19}F-NMR) detected [TFSI$^-$]. The water content was subtracted after determination by Karl Fischer titration (KF) techniques. These measurements were used with the charge balance (equation 1) and the mass balance (equation 2) to determine the amount of [HBet$^+$] and neutral zwitterionic betaine. We also attempted quantification with Raman Spectroscopy and ^{1}H-NMR (as described in the SI); however, these techniques were not sufficiently sensitive, which has likely contributed to this impurity not previously being reported in the literature.

$$[HBet^+] + [Li^+] = [Cl^-] + [TFSI^-] \qquad (1)$$

$$x_{HBet^+} + x_{Li^+} + x_{Cl^-} + x_{TFSI^-} + x_{Bet} = 1 \qquad (2)$$

The results are shown in mole fraction in **Table 1**. Uncertainties in these measurements are discussed in the SI. Washing the IL with water effectively removes Li^+ and Cl^-; however, zwitterion betaine in the least pure sample is a substantial 4.78 mol %. This corresponds to one neutral betaine molecule for every 9.95 [HBet$^+$] cations, as shown in **Table 2**. The second and third samples contain less betaine, with one betaine for every 25.5 [HBet$^+$] cations for the purest sample. Higher purity [HBet][TFSI] was only possible when more HTFSI was added to the solution after the ion exchange reaction (see Supporting Information for more description of the method and the raw results).

Table 1. The mole fraction of species in [HBet][TFSI] samples

	Cl^-	Li^+	$TFSI^-$	$HBet^+$	Bet
1	1.1×10^{-3}	9.3×10^{-5}	0.475	0.476	4.78×10^{-2}
2	7.3×10^{-4}	7.0×10^{-5}	0.485	0.486	2.85×10^{-2}
3	1.5×10^{-3}	8.2×10^{-5}	0.489	0.490	1.92×10^{-2}

Table 2. The molar ratios of species in [HBet][TFSI] samples

	$\frac{[Cl^-]}{[TFSI^-]}$	$\frac{[Li^+]}{[TFSI^-]}$	$\frac{[HBet^+]}{[TFSI^-]}$	$\frac{[TFSI^-]}{[Bet]}$	$\frac{[HBet^+]}{[Bet]}$
1	2.2×10^{-3}	2.0×10^{-4}	1.00	9.93	9.95
2	1.4×10^{-3}	1.4×10^{-4}	1.00	17.0	17.1
3	3.0×10^{-3}	1.7×10^{-4}	1.00	25.4	25.5

More importantly, we found that the cloud point curves (see SI for a description of the turbidity measurements) of different [HBet][TFSI] samples with water are different from one another, as shown in **Fig. 2**. At temperatures below the UCST and overall compositions within the cloud point curve the mixture will split into two phases, with the compositions indicated by the two sides of the curve in the figure. The data for samples in **Fig. 2** are shown along with previously published data for the [HBet][TFSI]/water system reported by Nockemann et al.[32] and Fagnant et al.[37] Note that these [HBet][TFSI] samples were made without any acid added to promote protonation of the betaine. The composition of the IL-rich phase (left side in **Fig. 2**) strongly depends on the amount of betaine impurity, with the purest sample (1.92 mol % betaine) dissolving the most water. From **Fig. 2** one can surmise that the Nockemann et al. [HBet][TFSI] sample contained significantly more than 4.78 mol % betaine impurity. The Fagnant et al. sample displays very similar cloud point values as the 4.78 mol % betaine sample. All of the curves except the Nockemann et al. sample (which appears to contain the largest amount of neutral betaine impurity) are very similar on the water-rich side; i.e.; betaine impurity has less impact on the aqueous phase. This is in agreement with the solid-state structure published by Nockemann et al. with a HBet$^+$:Bet ratio of 3:1.[32] Moreover, the weight percent of water at the UCST increases with increasing IL purity and the UCST itself drops by approximately 3 °C (57 °C and 49 wt % water for Nockemann's sample[32] vs. 54 °C and 62 wt % water for the sample containing the least amount of betaine impurity).

Also shown in **Fig. 2** is the saturated water content at 23 ^{o}C reported by Volia et al. ,[39] for their [HBet][TFSI] sample without any added betaine or HTFSI. Clearly, their as-synthesized sample contained significant amounts of betaine (much greater than our least pure sample, which corresponded to one betaine molecule per every 9.95 [Hbet$^+$]). The neutral zwitterionic betaine in the as-synthesized [HBet][TFSI] sample was not taken into account in their analysis of the influence of betaine on the aqueous phase composition.

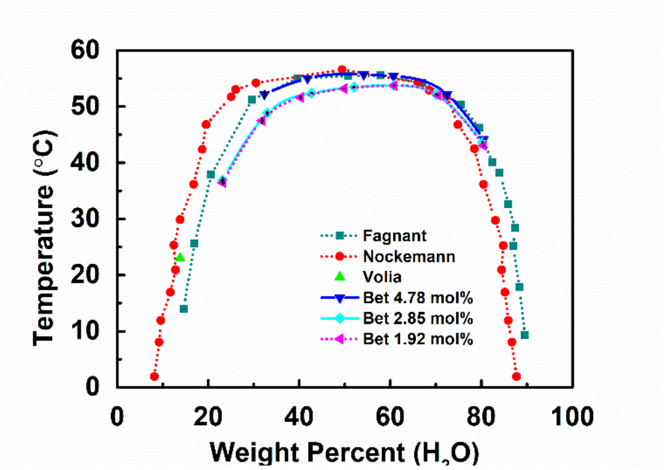

Fig. 2 Cloud point curves of binary water + [HBet][TFSI] mixtures[32,37] For compositions and temperatures beneath the curve, the mixture will split into two liquid phases, one water-rich (right side) and the other IL-rich (left side). Note that the data from Volia (green triangle)[39] is just one point for the solubility of water in the IL-rich phase as room temperature.

Fig. 3 demonstrates the influence of betaine impurity on the cloud point curves of an aqueous [HBet][TFSI] system containing neodymium. For a Nd loading of roughly one Nd for every 4.48 IL cation/anion pair, there is significantly more water in the IL-rich phase for the purer sample (**2**), containing 2.85 mol % betaine, than reported by Fagnant et al.[37] for a similar Nd loading. Moreover, the UCST shifts from ~40 wt % water to ~70 wt % water. The primary difference between the two [HBet][TFSI] samples is the amount of betaine zwitterion: 2.85 mol % for the sample in this work and an estimated ~4.78 mol % for the Fagnant et al.[37] sample. The presence of more betaine impurity shifts the UCST from 32 ^{o}C and 58 wt % water to 36 ^{o}C and 44 wt % water. Thus, it appears that the presence of betaine impurity has an even greater effect on the phase behaviour of [HBet][TFSI] + water mixtures containing dissolved metals (**Fig. 3**) than on [HBet][TFSI] + water mixtures (**Fig. 2**). This suggests that it is also possible that the presence of the betaine impurity in the IL affects the solubility of dissolved metals, which have been reported by multiple researchers.[17,41,44] Therefore, controlling and quantifying the concentration of deprotonated betaine in [HBet][TFSI] and similar ILs is necessary to obtain reliable and reproducible phase equilibrium data in order to exploit this behaviour for advanced separation processes.

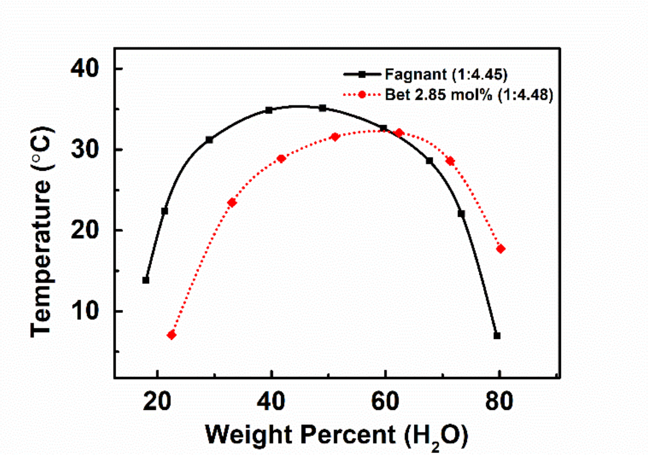

Fig. 3 The UCST change with specific molar ratio of Nd to [HBet][TFSI][37]

We also investigated the influence of residual Li$^+$ in [HBet][TFSI], concluding that Li$^+$ reduces [HBet][TFSI] + water cloud point temperatures, especially for IL-rich mixtures, as shown in the SI, but the magnitude of the effect is significantly less than that for betaine.

In this study, we investigated the effect of the betaine zwitterion impurity on the mutual solubility of [HBet][TFSI] and water, and on the phase equilibrium with dissolved neodymium. Although it is known that added acid and betaine affect the mutual solubility, previous research has neglected the significant amount of betaine in the [HBet][TFSI] itself, when it is synthesized by the standard technique.[32–35,39–41] Acid must be added after ion exchange in order to promote protonation to [HBet$^+$]. A combination of ion chromatography, q^{19}F-NMR and mass and charge balances provide reliable impurity quantification.

Conflicts of interest

There are no conflicts of interest to declare.

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