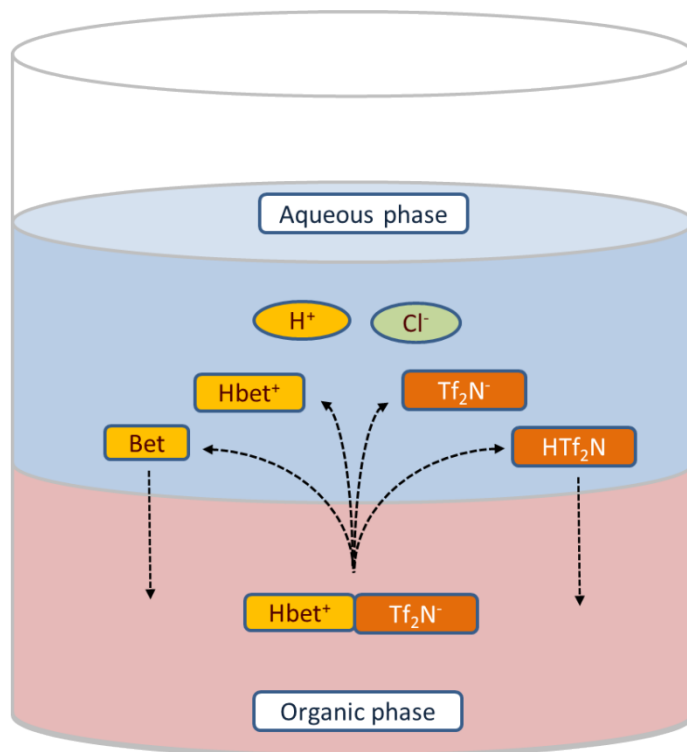


Effect of Aqueous Hydrochloric Acid and Zwitterionic Betaine on the Mutual Solubility between a Protic Betainium-based Ionic Liquid and Water

Highlights:

- The presence of acid increased the aqueous solubility of the IL cation while its effect on the IL anion was the opposite.
- The transfer of [Hbet⁺] species into the aqueous phase is most likely associated with the transfer of water molecules in the same direction.
- Zwitterionic betaine was partially distributed between the two phases.
- A mathematical model to determine the conditional solubility product constant (K_{sp}') of [Hbet][Tf₂N] ionic liquid in DCI was developed.

Graphical Abstract



Effect of Aqueous Hydrochloric Acid and Zwitterionic Betaine on the Mutual Solubility between a Protic Betainium-based Ionic Liquid and Water

Merinda F. Volia^{a, b}, Evgeny E. Tereshatov^{a*}, Valérie Mazan^c, Charles M. Folden III^{a, d}
and Maria Boltoeva^c

^aCyclotron Institute, Texas A&M University, College Station, Texas 77843, USA

^bDepartment of Nuclear Engineering, Texas A&M University, College Station, Texas
77843, USA

^cUniversité de Strasbourg, CNRS, IPHC UMR 7178, F-67000 Strasbourg, France

^dDepartment of Chemistry, Texas A&M University, College Station, Texas 77843, USA

* Corresponding Author:

E-mail: etereshatov@tamu.edu

Address: Cyclotron Institute, Texas A&M University, TAMU 3366, College Station,
Texas 77843-3366, USA

Abstract

The solubility of hydrophobic betainium *bis*(trifluoromethylsulfonyl)imide ionic liquid in an aqueous phase with controlled acidity has been investigated by a standard liquid–liquid extraction technique. The effect of zwitterionic betaine added into the aqueous phase has

also been studied. Quantitative NMR was employed to characterize the distribution behavior of the ionic liquid constituents between the two phases. A mathematical model to describe the ionic liquid solubility in the aqueous phase was developed. This approach was utilized to estimate the conditional solubility product constant of the ionic liquid. The possibility of the transfer of some dissociation products back into the organic phase was investigated.

Keywords: Ionic liquid, mutual solubility, betainium *bis*(trifluoromethylsulfonyl)imide, zwitterionic betaine, hydrochloric acid.

1. Introduction

Ionic liquids (ILs) are a class of solvents composed of salts having a melting temperature below 100 °C [1]. Generally, ILs are composed of discrete organic cations and weakly coordinating anions. The common cation moieties of the ILs are alkyl-substituted ammonium, phosphonium, imidazolium, pyridinium, and pyrrolidinium, while the anions are usually halides, hexafluorophosphate, tetrafluoroborate, trifluoromethanesulfonate, and *bis*(trifluoromethanesulfonyl)imide. The physicochemical properties (thermal stability, hydrophobicity, viscosity, and conductivity) [2, 3] of ILs can be tuned by varying the cation-anion combination [4]. This is why the ILs are often described as “designer solvents” [5, 6].

Ever since ILs were developed, they have emerged as the most studied solvent in the last two decades owing to their unique characteristics [7, 8]. ILs have found applications in various fields such as organic synthesis [9-12], catalysis [13-16], electrochemistry [17], electrocatalysis [18], solid support [19], nanoparticle formation [20], and solvent extraction [21-23]. In particular, ILs gained interest as an alternative to conventional molecular solvents due to their wide liquid range, very low vapor pressure, non-flammability, and ability to solubilize various solutes [24].

Among this wide variety of ILs, we studied betainium *bis*(trifluoromethylsulfonyl)imide (herein denoted as [Hbet][Tf₂N] or betainium bistriflimide). This is a hydrophobic compound categorized as a task-specific ionic liquid (TSIL), which is a subclass of IL with a functionalized group incorporated into its cation and/or anion. The presence of the functionalized group has an advantage over conventional ILs due to its ability to coordinate with a metal ion [25]. The synthesis of TSILs generally involves multistep processes, but [Hbet][Tf₂N] can be prepared easily with relatively inexpensive raw materials. The building block of the [Hbet⁺] cation is zwitterionic glycine betaine, a natural and biodegradable material. The functionalized group of the [Hbet][Tf₂N] is a carboxylic group covalently bounded to its cationic part [25]. Figure 1 shows the structural formulas and respective acronyms of the ions constituting [Hbet][Tf₂N] ionic liquid.

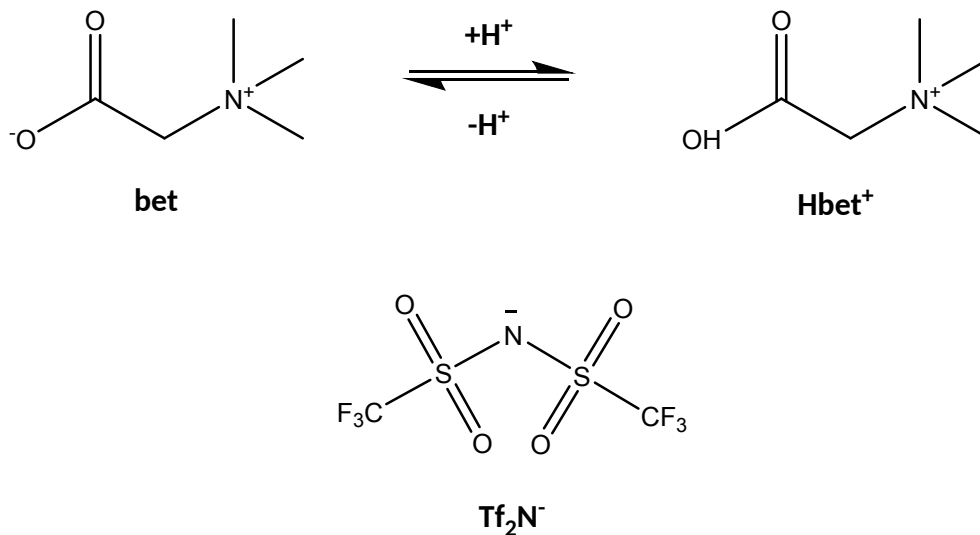


Figure 1. Chemical structure of the ions constituting [Hbet][Tf₂N] IL studied in this work: zwitterionic betaine and betainium cation (top) and *bis*(trifluoromethanesulfonyl)imide anion (bottom).

The cationic part of this ionic liquid, [Hbet⁺], is the protonated form of betaine ($pK_a = 1.83$) [26, 27]. The [Hbet][Tf₂N] IL was developed by Nockemann *et al.*, who successfully used it to dissolve various metal oxides in large quantity [25]. Some interesting properties of this IL were reported, such as temperature- and pH-dependent phase separation between [Hbet][Tf₂N] and water. Hoogerstraete *et al.* later reported that the [Hbet][Tf₂N] and water mixture exhibits an upper critical solution temperature (UCST) of 55° C [27]. The latter group explored the UCST property of the mixture to extract trivalent rare-earths, In, and Ga by phase-transition extraction. They showed that above the UCST, the mixture forms only one phase, while below the UCST, phase separation occurs. This extraction technique was reported to be advantageous in reducing the high viscosity of the IL (*i.e.*, 351 cP at 60° C for dry [Hbet][Tf₂N]) [25].

Despite being a somewhat hydrophobic IL, [Hbet][Tf₂N] is known to be mutually soluble with water [26, 28]. It was suggested that mutual solubility between the IL and the aqueous phase poses several consequences, especially in the solvent extraction process. Among others, there is the possibility of phase reversal which can cause pollution of the product stream due to the presence of unwanted IL ions and the loss of valuable organic materials [29]. On the other hand, the mutual solubility of the IL and the aqueous phase was shown to be the basis for the extraction of metal ions into the organic phase [30, 31]. Consequently, understanding the mutual solubility of the ionic liquid with the aqueous phase is an important step not only to obtain the most effective extraction system for the solute of interest, but also to elucidate the mechanism of its extraction.

There are several reports of [Hbet][Tf₂N] solubility in water with and without acid present, and they are primarily focused on the cation behavior [25, 26, 32]. In this paper, we extend the study of mutual solubility of this IL with water and hydrochloric acid media, paying attention to the most probable species that were produced due to [Hbet][Tf₂N] dissociation and their interactions in the aqueous phase. The results obtained in this study give further insight for designing [Hbet][Tf₂N]-based extraction systems and explaining the solute extraction mechanism.

2. Experimental Section

2.1. Overview of the experiment

All experiments on the mutual solubility of [Hbet][Tf₂N] with water and hydrochloric acid media were carried out by the conventional liquid–liquid extraction technique. It is noteworthy that neat and dry [Hbet][Tf₂N] IL is highly hygroscopic and viscous in nature,

which makes it difficult to handle.[26] Therefore, preconditioning of the organic phase was carried out. In the current study, [Hbet][Tf₂N] was initially saturated with pure water to avoid further water uptake during the partition trials, to minimize changes in the phase ratio, and to lower the viscosity of the organic phase.

To perform the partition experiment, equal volumes of water-saturated IL and aqueous phase (typically 0.8 mL) were placed into Eppendorf centrifugation tubes (2 mL). The required IL mass was calculated using the density and taken precisely by weighing. The aqueous solution was added into the tube by an Eppendorf Research precision pipette. The biphasic samples were vigorously mixed for 5 min at 1,500 rpm on a mechanical shaker (IKA vibrax VXR basic) at 23 ± 2 °C and then, centrifuged for 5 min at 3,000 rpm (Micro Star 12, VWR) in order to promote phase separation. Then, aliquots of the equilibrium organic and aqueous phases were taken for further analysis. Subsequently, the aqueous phase was analyzed to determine the equilibrium concentration of the IL cation and anion, proton, and chloride ions in the aqueous phase using techniques described below. Meanwhile, the organic phase was analyzed to determine the equilibrium concentration of water.

Concentrations given below are expressed as molarities (mol/dm³). Throughout the text, the subscripts “init” and “eq” denote the initial and equilibrium concentrations, respectively. The initial concentration specifically refers to the concentration of a species prior to phase contact. Meanwhile, the equilibrium concentration is used to describe the concentration of a species after the formation and separation of the biphasic system. Hereinafter, the subscripts “org” and “aq” denote the species in the IL and aqueous phase, respectively. Both deuterium (²H, D) from deuterated solvents and proton (¹H) from the

solutes are present in the aqueous phase. For simplicity, a generic notation H^+ is used to address the acidic proton from either source.

2.2. Chemicals

High purity grade betaine anhydrous (*N,N,N*-trimethylammonium acetate, abbreviated as bet, $\geq 99.0\%$), betaine hydrochloride (HbetCl, $\geq 99\%$) and analytical grade deuterium chloride (deutero-hydrochloric acid, DCl, 99 atom% D, 35 wt% in D_2O) were purchased from Sigma-Aldrich. High purity grade IL 1-butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide ($[C_4mim][Tf_2N]$, 99.5%) and its salt lithium *bis*(trifluoromethylsulfonyl)imide ($LiTf_2N$, 99.9%) were obtained from Solvionic. Deuterium oxide (deuterated water, D_2O , 99 atom% D) was purchased from Eurisotop. Sodium acetate (99.0%) and sodium trifluoroacetate (98.0%) were ordered from Merck and Alfa Aesar, respectively. Sodium hydroxide (NaOH) standard solutions were purchased from Carlo Erba. Deionized water (ELGA PURELAB DV25) with a resistivity of 18.2 $M\Omega$ cm was used for preparing the aqueous solutions, whereas the NMR samples were prepared by using deutero-hydrochloric acid and/or deuterium oxide. Chemicals were used as received without further purification.

2.3. Sample preparation

Betainium *bis*(trifluoromethylsulfonyl)imide IL was synthesized following a procedure in the literature [33]. The aqueous acidic phase was prepared by appropriate dilution of concentrated deutero-hydrochloric acid with D_2O to the required concentrations. The use of deuterated compounds was necessary to avoid interference between proton signals originating from H_2O and the target analytes, namely betaine-bearing species and an internal standard present in the quantitative 1H -NMR sample. It

was assumed that the use of deuterium in place of light hydrogen does not change the solute partition behavior in the biphasic system under study.

In all solubility experiments, the IL forms the denser phase. The density of [Hbet][Tf₂N] saturated with pure water was determined by weighting it in a 1 mL volumetric microflask. The measured density is 1.439 ± 0.014 g/cm³, and is in good agreement with the literature data (1.453 g/cm³) [34].

For quantitative ¹H-NMR and ¹⁹F-NMR measurements, an aliquot of the equilibrium aqueous phase was taken and mixed with sodium acetate and sodium trifluoroacetate solutions as internal standards ($\delta_{\text{H}} = 1.90$ ppm and $\delta_{\text{F}} = -76.5$ ppm, respectively). Then, this solution was diluted with deuterated water to the required volume, shaken in order to assure homogeneity and placed into the NMR tube.

2.4. Instruments and analytical techniques

The aqueous chloride anion concentration was measured by the Mohr method (direct precipitation titration with AgNO₃ using potassium dichromate as an indicator) [35]. The aqueous hydrogen cation concentrations were determined by acid–base titration (SCHOTT Instruments TitroLine easy). Proton (¹H) and fluorine (¹⁹F) measurements for aqueous [Hbet][Tf₂N] solubility were performed with quantitative nuclear magnetic resonance (qNMR) spectroscopy as described in the literature [29]. The aqueous concentrations of the analytes were calculated using the following equation:

$$C_x = \left(\frac{I_x}{I_{std}}\right)\left(\frac{N_{std}}{N_x}\right)\left(\frac{V_{std}}{V_x}\right)C_{std} \quad \text{Eq. 1}$$

where C , I , N , and V are concentration, integral area, number of nuclei per molecule, and volume of the analyte (“x”) and internal standard (“std”), respectively [36].

The total water content in the IL phase was measured by the coulometric Karl Fischer technique (Hydranal®-Coulomat E, Fluka). The performance of the Karl Fischer titrator (Toledo 32 Coulometer) was tested using a standard solution (Hydranal®-Water Standard, Fluka), containing 1,000 or 10,000 ppm of water. The pH of the aqueous solutions was measured with a pH meter (VWR Symphony SB70P). An analytical balance (Sartorius, model BP 2215) with an accuracy of ± 0.1 mg was used for weighing the components.

2.5. Uncertainty of the measurements

The uncertainties of the analytical techniques used in the current study are presented in Table 1.

Table 1. The uncertainties of the analytical techniques used in this study

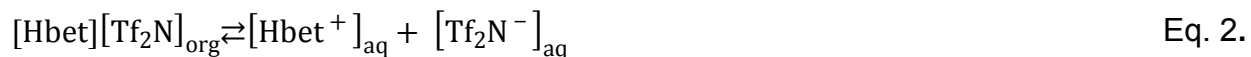
Phase	Species	Technique	Uncertainty (%)
Aqueous	H ⁺ , D ⁺	Acid-base titration	2
	Cl ⁻	Argentometry	10
	[Hbet ⁺]	Quantitative ¹ H-NMR	10
	[Tf ₂ N ⁻]	Quantitative ¹⁹ F-NMR	5
Organic	Water	Karl Fischer	5

3. Results and discussion

The techniques described above typically measured the cumulative concentrations of several species rather than the concentrations of individual species. The acid-base titration gives the concentration of all protonated species in the equilibrium aqueous phase, and includes the sum of protons originating from hydrochloric acid, betainium cations and HTf₂N acid. Additionally, the qNMR technique allowed us to measure the aqueous equilibrium concentrations of betaine and fluorinated species, which both contained protonated and deprotonated forms. Using these data, we determined the equilibrium concentrations of the individual species that were present in the aqueous phase as described in the following section.

3.1. Solubility of [Hbet][Tf₂N] in water

First, the aqueous solubility of [Hbet][Tf₂N] was evaluated as a function of the hydrochloric acid concentration with and without the presence of bet. The distribution of [Hbet][Tf₂N] IL in the aqueous phase is described by its physical partition into the aqueous phase followed by dissociation into betainium and bistriflimide ions:



Betainium dissociates to form proton and zwitterionic betaine (bet):



Moreover, the IL constituent anions and aqueous protons in the aqueous phase form HTf₂N acid (pK_a = 0.16) [30] *via* protonation of the imide nitrogen sites:



A system of equations to evaluate the concentrations of individual species was developed based on the mass balance of the reactions mentioned above. It also includes the dissociation constants of [Hbet⁺] and [HTf₂N] from Eq. 3 and Eq. 4 and uses the mean ionic activity coefficient of HCl ($\gamma_{HCl\pm}$) for the activity coefficient of the protons (assuming that this quantity is independent of the presence of other dissolved ions) [37, 38]. Proton-, betaine-, fluorine-bearing species are referred to as H_{Titrated}, Bet_{NMR}, and F_{NMR}, respectively.

$$\left\{ \begin{array}{l}
 [H^+]_{aq} + [Hbet^+]_{aq} + [HTf_2N]_{aq} = [H_{Titrated}] \\
 [Hbet^+]_{aq} + [bet]_{aq} = [Bet_{NMR}] \\
 [Tf_2N^-]_{aq} + [HTf_2N]_{aq} = [F_{NMR}] \\
 \frac{\gamma_{HCl\pm} [H^+]_{aq} [bet]_{aq}}{[Hbet^+]_{aq}} = K_{a[Hbet^+]} \\
 \frac{\gamma_{HCl\pm} [H^+]_{aq} [Tf_2N^-]_{aq}}{[HTf_2N]_{aq}} = K_{a[HTf_2N]} \\
 \gamma_{HCl\pm} = f([H^+]_{aq})
 \end{array} \right. \quad \text{Eq. 5}$$

The dependence of the activity coefficient $\gamma_{HCl\pm}$ on the H⁺ concentration in the system of equations 5 was implemented using a lookup table based on literature data combined with linear interpolation [37]. In the presence of hydrochloric acid, [Hbet]Cl (one of the precursors of [Hbet][Tf₂N]) was considered to be completely dissociated and was not included in Eq 5.

Table 2 displays the calculated equilibrium concentrations of individual species in the aqueous phase after the pre-equilibrated [Hbet][Tf₂N] was in contact with pure water and with water containing initially 15 % (w/v) bet (1.28 M). Hereinafter, the measured concentrations refer to the experimentally measured values and the calculated concentrations refer to the concentration of individual species evaluated by Eq 5.

Table 2. Experimentally measured values and the calculated concentrations of individual species in the equilibrium aqueous phase. These systems do not contain hydrochloric acid.

Experimentally measured values			Calculated values		
Species	Water (M)	Water + bet (M)	Species	Water (M)	Water + bet (M)
[H ⁺] _{aq}	0.045 ± 0.004	(3.35 ± 0.33)·10 ⁻³	[H ⁺] _{aq}	0.048 ± 0.005	(6.2 ± 0.6)·10 ⁻³
[H _{Titrated}]	0.313 ± 0.031	0.296 ± 0.030	[Hbet ⁺] _{aq}	0.251 ± 0.025	0.288 ± 0.029
[Bet _{NMR}]	0.344 ± 0.017	1.030 ± 0.100	[bet] _{aq}	0.093 ± 0.009	0.750 ± 0.080
[F _{NMR}]	0.274 ± 0.014	0.260 ± 0.013	[Tf ₂ N ⁻] _{aq}	0.259 ± 0.013	0.258 ± 0.013

$$[\text{HTf}_2\text{N}]_{\text{aq}} \quad (1.47 \pm 0.07) \cdot 10^{-2} \quad (2.10 \pm 0.11) \cdot 10^{-3}$$

The uncertainties of the calculated values in Table 2 were estimated by using the values of uncertainties of the corresponding species in Table 1.

In Table 2, the experimentally measured hydrogen cations concentration in water ($[\text{H}^+]_{\text{aq}} = 0.045 \pm 0.004 \text{ M}$) is in a good agreement with the calculated one ($[\text{H}^+]_{\text{aq}} = 0.048 \pm 0.005 \text{ M}$), and suggests that the system of equations (Eq. 5) is adequate to describe the real concentration of the species. The calculated values in Table 2 show that the equilibrium concentrations of cationic and anionic species, $[\text{Hbet}^+]$ and $[\text{Tf}_2\text{N}^-]$, in water containing 15 % (w/v) bet are comparable to those in the pure water system. Meanwhile, the equilibrium concentration of bet in the aqueous phase containing water and 15 % (w/v) bet is lower than the initial one, indicating the transfer of this species into the IL phase. This phenomenon has been observed by Shkrob *et al.*, who suggested that neat $[\text{Hbet}^+][\text{Tf}_2\text{N}^-]$ is able to dissolve up to 60 mol % of zwitterionic betaine [39]. Furthermore, it also can be seen in Table 2 that the amount of HTf_2N species in water containing 15 % (w/v) bet is lower than that in the pure water system. This is most likely due to the low amount of free proton that was available to protonate $[\text{Tf}_2\text{N}^-]$ in the former system. The presence of bet in excess would suppress the dissociation of the cationic species $[\text{Hbet}^+]$ according to Eq. 3. As the result, the amount of free proton that would be available for the protonation of $[\text{Tf}_2\text{N}^-]$ has decreased, and consequently decreased the amount of HTf_2N in the aqueous phase.

The solubility of an IL in the aqueous phase is commonly determined through the measurement of the aqueous equilibrium concentration of the IL cation [26, 30, 32]. The reported value of the solubility of [Hbet][Tf₂N] based on ¹H-NMR measurement is 14 ± 0.5 wt % [26], which is equal to 0.371 ± 0.010 M (assuming the density of the pre-equilibrated IL is 1.453 g/cm³). The experimental result on [Hbet][Tf₂N] solubility in water obtained in this work is 0.344 ± 0.034 M, in good agreement with the literature data.

The system of equations (Eq. 5) was also used to evaluate the concentrations of the individual species in the aqueous phase after the dissolution of [Hbet][Tf₂N] in pure DCI and in DCI containing 15 % (w/v) bet. In the presence of DCI in the aqueous phase, [Bet_{NMR}] increased with increasing aqueous phase acidity (Figure 2a), and both [Hbet⁺] and bet exist at [DCI] < 0.5 M. Above this concentration, all betaine is protonated. bet was also added into DCI as shown in Figure 2b. For low aqueous acidity (< 1 M), [Bet_{NMR}] is independent of the DCI concentration and its concentration is lower than the initial [bet]_{aq}, indicating the transfer of betaine from the aqueous into the IL phase. Above 1 M [DCI], [Bet_{NMR}] notably increases with increasing DCI concentration and becomes even greater than the initial concentrations. This indicates that the addition of neutral betaine into the system significantly increases the dissolution of the IL in a highly acidic aqueous phase.

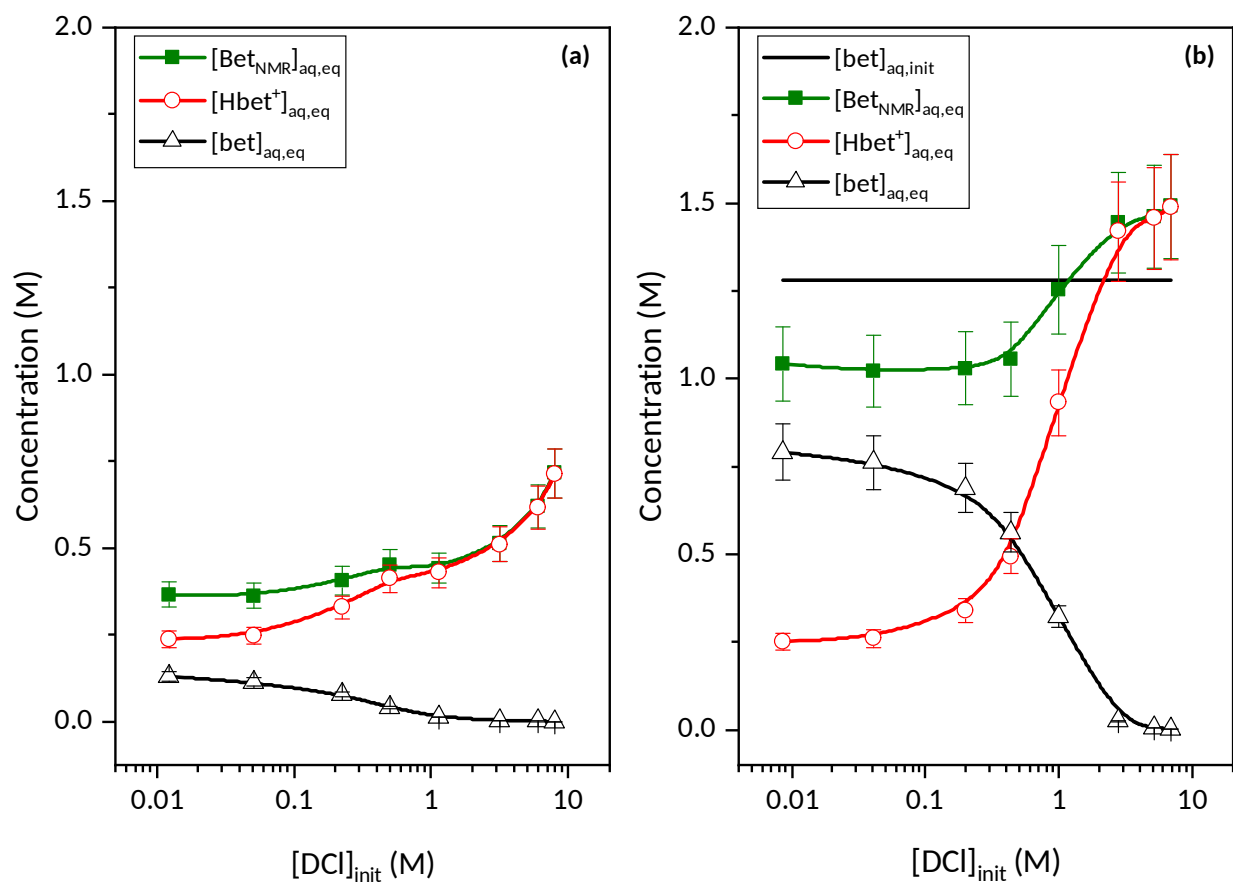


Figure 2. Acid dependency of the betaine-containing species concentration in the aqueous phase: DCI **(a)**, DCI and $[\text{bet}]_{\text{aq,init}} = 15\% \text{ w/v}$ (1.28 M) **(b)**. The closed and open symbols are experimental data and calculation results obtained by using Eq. 5, respectively. The lines are drawn to guide the eye.

The variation of $[\text{F}_{\text{NMR}}]$ due to the presence of DCI is shown in Figure 3a. The equilibrium concentration of this species slowly decreases in the whole range of $[\text{DCI}]$.

Considering the speciation, $[\text{Tf}_2\text{N}^-]$ and $[\text{HTf}_2\text{N}^-]$ are the dominant species at 0.01 – 0.5 M and above 1 M $[\text{DCI}]$, respectively. Comparing these data to the system with betaine added (Figure 3b), it can be seen that the increase of initial aqueous DCI concentration results in a more pronounced decline of $[\text{F}_{\text{NMR}}]$ in the latter system.

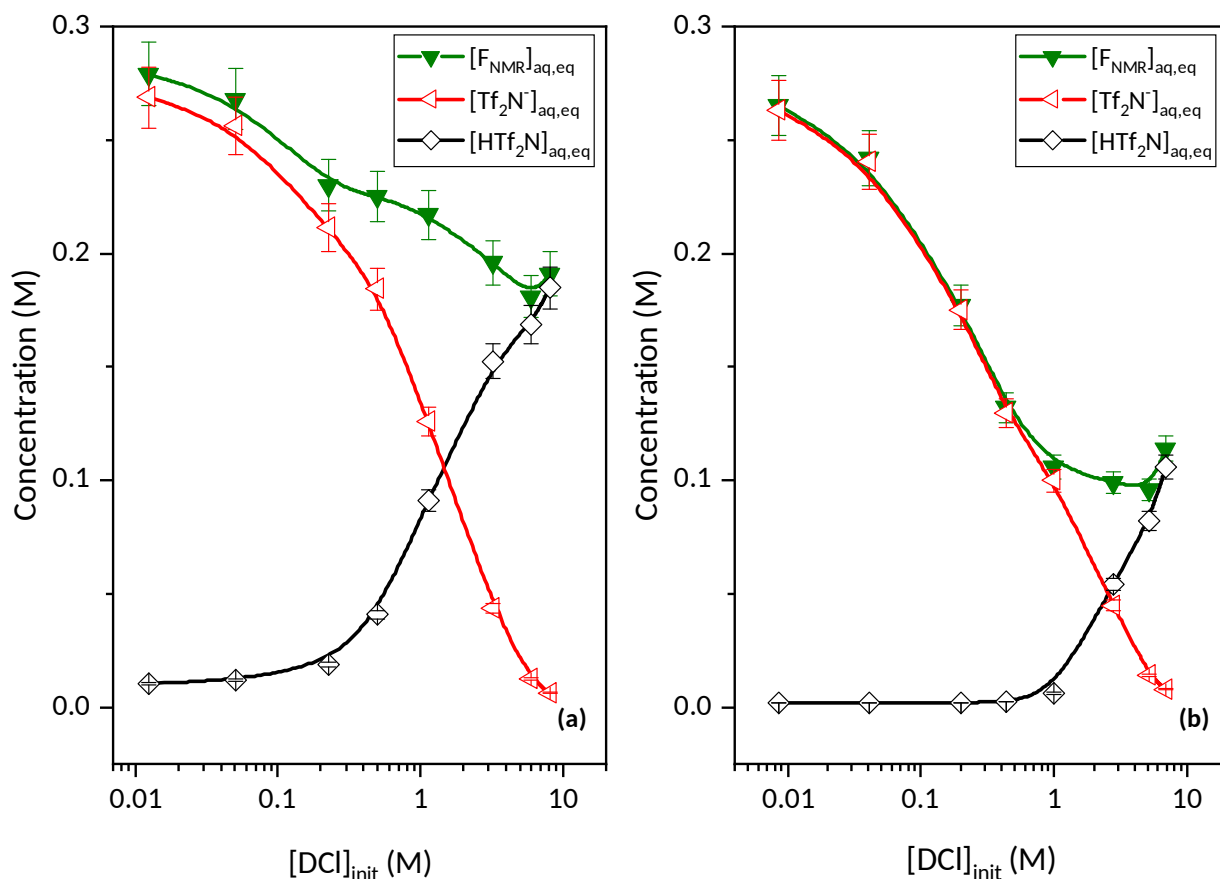


Figure 3. The measured and calculated concentrations of fluorinated species in DCI (a) and in DCI containing 15 % (w/v) bet (b). The closed and open symbols are experimental data and calculation results obtained by using Eq. 5, respectively. The lines are drawn to guide the eye.

In this study, it was observed that at a given acidity, F_{NMR} is lower than Bet_{NMR} (Figures 2 and 3). Meanwhile, the concentrations of both species in pure water are equal (Table 2). Similar data were reported for liquid-liquid systems composed of an imidazolium-based IL and hydrochloric or nitric acid [29, 40]. In the case of added acid, the difference between the aqueous concentrations of species containing IL-constituent ions is probably the result of transfer of the bistriflimide species in its protonated form ($[\text{HTf}_2\text{N}]$) into the organic phase.

We attempted to explain the effect of betaine addition into the aqueous phase containing DCI based on Eq. 2-4. At low acidity (<1 M), the dominant form of betaine is the neutral one (bet, see Figure 2b). Thus, we suggest that the observed transfer of aqueous betaine occurs via dissolution of neutral betaine into the IL phase. At higher DCI concentrations, betaine exists in the protonated $[\text{Hbet}^+]$ form. According to Eq. 2, the presence of aqueous $[\text{Hbet}^+]$ will lower the solubility of $[\text{Hbet}][\text{Tf}_2\text{N}]$ in the aqueous phase. As the result, the amount of bistriflimide species in the aqueous phase is also lower compared to the system with only DCI (Figures 3a and 3b).

The $\text{H}_{\text{Titrated}}$ results show that the solubility of $[\text{Hbet}][\text{Tf}_2\text{N}]$ in DCI, without and with the presence of 15 % (w/v) bet, led to an increase of total proton concentration at low acidity (Figure 4). As shown in the figure, this increment is contributed by the amount of $[\text{Hbet}^+]$ from the IL that dissolved in the aqueous phase. The concentration of free H^+ species is generally lower than the initial DCI concentration. However, Figure 4a shows that equilibrium concentration of free H^+ at 0.01 M DCI is greater than the corresponding initial acid concentration, most likely due to IL dissolution and $[\text{Hbet}^+]$ deprotonation.

Partial protonation of betaine in DCI prior to the biphasic system formation decreased the amount of free H^+ in the initial aqueous solution (Figure 4b).

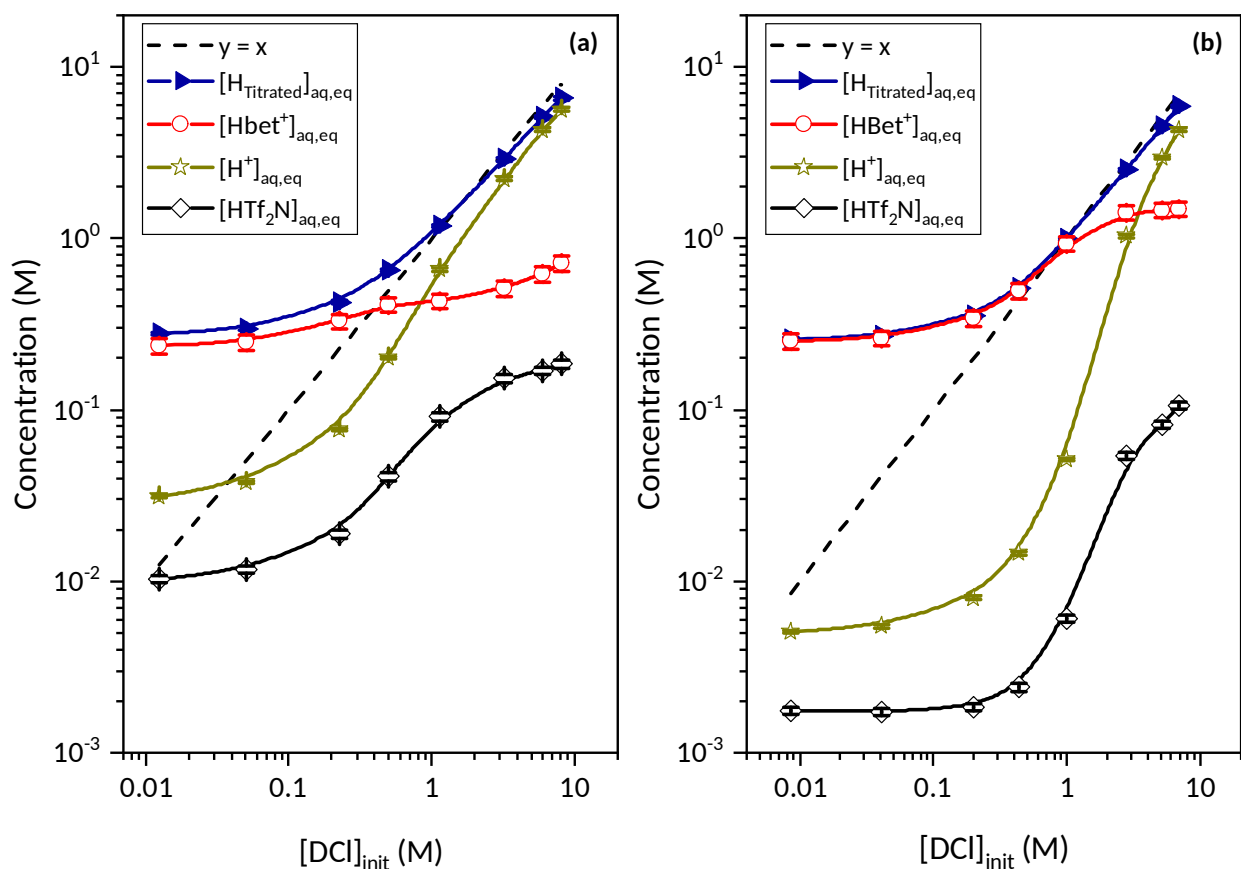


Figure 4. The measured and calculated concentrations of proton-bearing species in DCI (a) and in DCI containing 15 % (w/v) bet (b). The dashed line ($y = x$) indicates the reference value when the initial and equilibrium H^+ concentrations are equal. The closed and open symbols are experimental data and calculation results obtained by using Eq. 5, respectively. The lines are drawn to guide the eye.

3.2. Water solubility in [Hbet][Tf₂N]

In our work, the water-saturated [Hbet][Tf₂N] contained 13.8 ± 0.5 wt % water; this is consistent with literature data [26, 27, 32]. In the presence of 15 % (w/v) bet, the equilibrium concentration of water was found to be 13.9 ± 0.5 wt %. Comparing the results obtained in the presence and absence of betaine, the solubility of water in the IL is not affected by addition of this compound.

In the presence of DCl, water content in [Hbet][Tf₂N] was constant up to 1 M DCl but it decreased with increasing acid concentration (Figure 5). The addition of 15 % (w/v) bet into DCl generally reduced the equilibrium water content in the IL phase for the whole range of DCl concentrations. The amounts of water were approximately constant for 0.01 – 3 M DCl, while above 3 M DCl, water content in the IL phase is decreased.

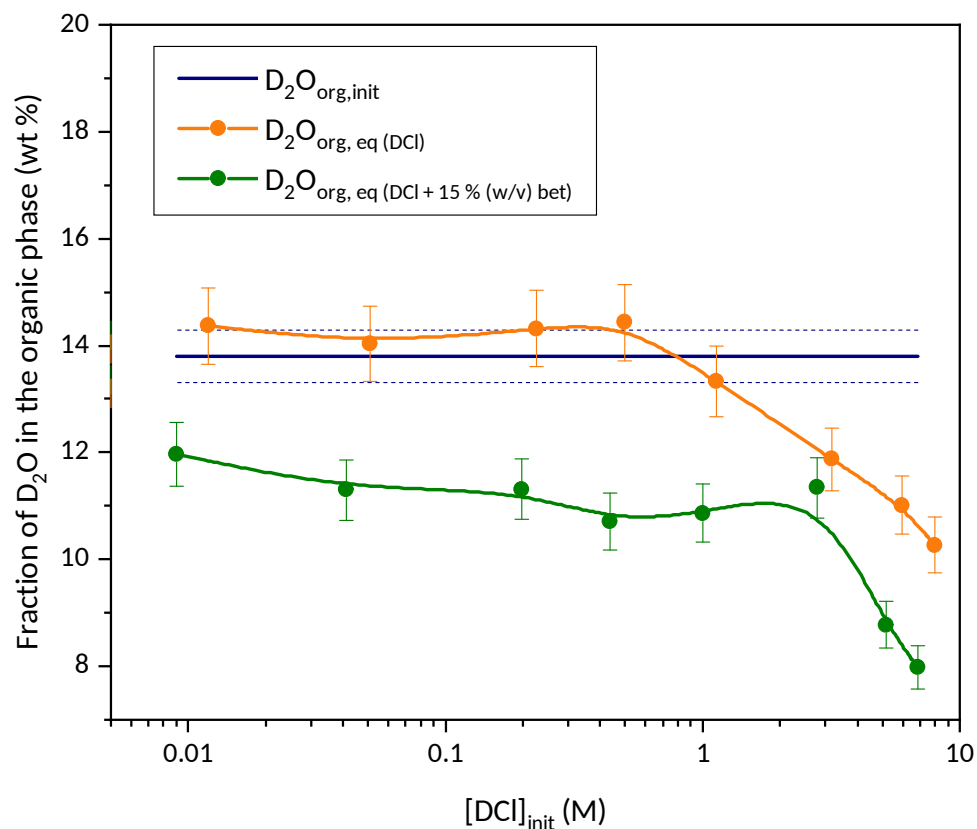


Figure 5. Water content in pre-equilibrated [Hbet][Tf₂N] as a function of initial aqueous DCl concentration. The solid horizontal line represents the water content in pre-equilibrated [Hbet][Tf₂N] (initial water concentration), while the dashed horizontal lines represent its error values. The lines are drawn to guide the eye.

A theoretical study done by Civera *et al.* suggested that a high concentration of zwitterionic betaine in the aqueous phase is likely to increase water solvation around betaine's molecules [41]. Betaine is a small-size molecule, bearing both hydrophilic carboxylate and hydrophobic methyl groups [42, 43]. The carboxylic acid group is strongly

bonded to water molecules through the hydrogen atoms [43, 44]. Meanwhile, chloride ion has a very high charge density and is strongly solvated by water molecules [32]. The presence of concentrated DCl and betaine in the aqueous phase most likely increases the attraction of water molecules from the IL into the aqueous phase, resulting in a decrease of equilibrium water concentration in the majority of the DCl region that was studied.

Figures 6a and 6c show $[\text{Bet}_{\text{NMR}}]_{\text{aq,eq}}$ and $[\text{D}_2\text{O}]_{\text{aq,eq}}$, the concentration of water that was transferred into the aqueous phase, in the presence of pure DCl. It can be seen in the figure that both $[\text{D}_2\text{O}]_{\text{aq}}$ and $[\text{Bet}_{\text{NMR}}]$ are nearly constant in the concentration range of 0.01 – 1 M of the initial DCl. Above 1 M DCl, the amount of water transferred into the aqueous phase was increased. Water likely moved to the aqueous phase to compensate for the substantial reduction in free water available after solvation of H^+ and Cl^- in the aqueous phase. Interestingly, in the same acid region where water transfer was increased, an increase of $[\text{Bet}_{\text{NMR}}]$ was also observed.

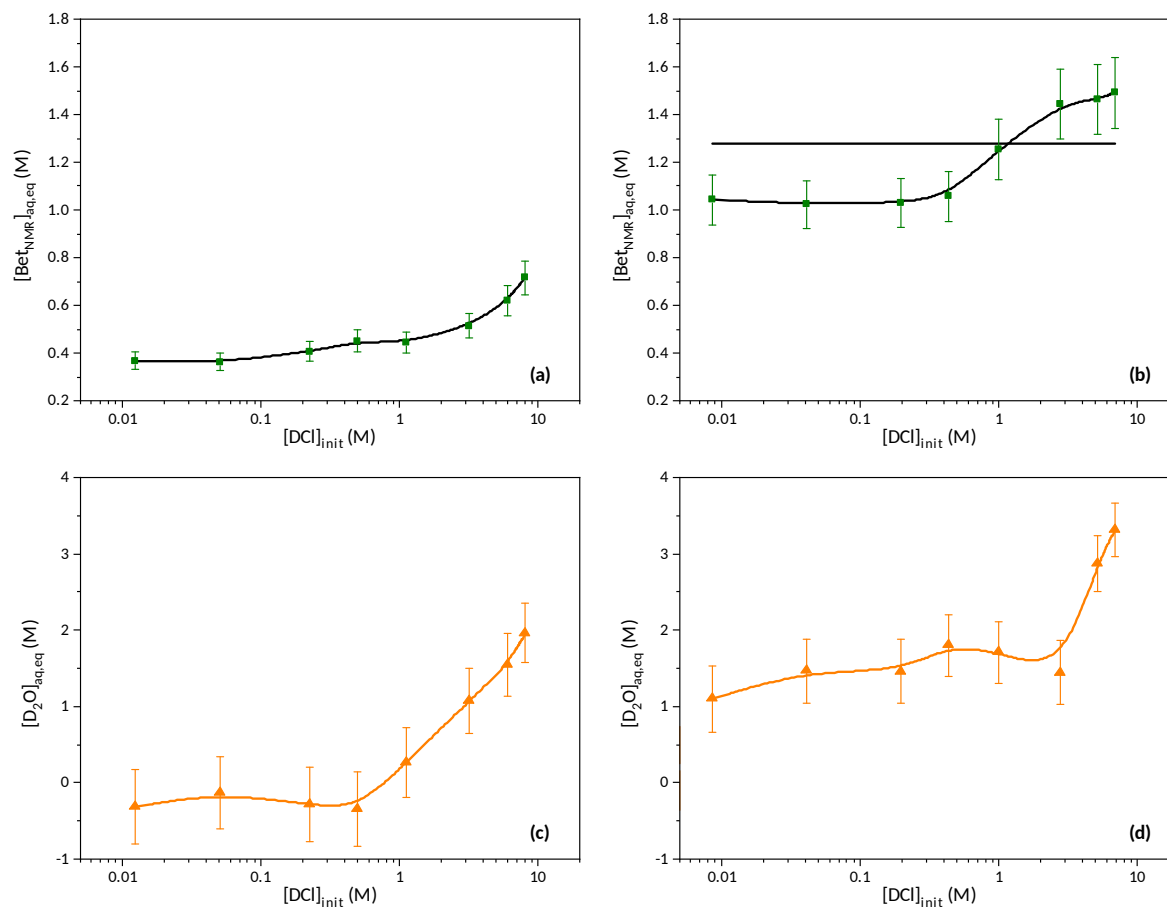


Figure 6. The measured equilibrium concentration of betaine species ($[Bet_{NMR}]_{aq,eq}$) and water content in the aqueous phase ($[D_2O]_{aq,eq}$) due to water transferred from pre-equilibrated $[Hbet][Tf_2N]$ in DCI **(a) and (c)** and in DCI containing 15 % (w/v) bet **(b) and (d)**. The lines are drawn to guide the eye.

As shown in Figure 6d, the amount of water transfer into the aqueous phase is generally higher in the presence of 15 % (w/v) bet than in pure DCI (Figure 6c). Over much of the range of [DCI], the presence of a high concentration of bet in the aqueous phase results in more water transfer to the aqueous phase. Increases in both $[D_2O]_{aq}$ and $[Bet_{NMR}]$ are observed in 5 – 7 M DCI, which is similar to the system in pure DCI. At a very high DCI concentration, the amount of free water in the aqueous phase containing DCI and 15 % (w/v) bet becomes much lower due to the need to solvate betaine and the large concentrations of H^+ and Cl^- . Consequently, the amount of water transfer into the aqueous phase in high DCI concentrations increased, and the overall concentration of betaine species in the aqueous phase increased, as $[Hbet][Tf_2N]$ dissolved in the aqueous phase.

3.3. Extraction of species into $[Hbet][Tf_2N]$

In addition to transfer of water, the mutual solubility of $[Hbet][Tf_2N]$ and water also resulted in the partition of zwitterionic betaine and HTf_2N between the two liquid phases. This was evident from the difference in the equilibrium concentrations of betaine- and bistriflimide species based on the quantitative NMR measurements discussed above. To evaluate the amount of bet and HTf_2N that was transferred into the organic phase, several chemical reactions were considered. It was assumed that the interfacial interaction in the organic phase is weak; therefore the activity coefficients of betaine- and bistriflimide species were not taken into account in the calculation.

The inequality of the measured $[Bet_{NMR}]$ and $[F_{NMR}]$ values is considered to be evidence of extraction of some dissociation products back into the organic phase. Moreover, the divergent trends of the measured parameters (see Figures 2 and 3)

indicate that with increasing DCl concentration, more cations of the IL are transferred from the organic phase while less the IL anions remain in the aqueous phase.

Thus, a cation exchange process is considered to have taken place in the system:



as well as extraction of [HTf₂N] species into the organic phase:



Additionally, analysis of the calculated data (see Figure 2b) shows that betaine is also extracted. As a result, the difference between [Bet_{NMR}] and [F_{NMR}] values represents the concentrations of species that were transferred into the organic phase:

$$[Bet_{NMR}]_{aq,eq} - [F_{NMR}]_{aq,eq} = [H^+]_{org,eq} + [HTf_2N]_{org,eq} + [bet]_{org,eq} \cdot \left(1 + \frac{\gamma_{HCl\pm} \cdot [H^+]_{aq,eq}}{K_a[Hbet^+]} \right) \quad \text{Eq. 8}$$

The parameter in parenthesis (Eq. 8) takes the protonation of betaine into account, which leads to lower amounts of betaine species in the aqueous phase available for extraction.

The amount of proton and [HTf₂N] species that were extracted can be evaluated based on the difference in [Bet_{NMR}] and [F_{NMR}] in the presence and absence of acid:

$$[H^+]_{org,eq} = [Bet_{NMR}]_{aq,eq, DCl} - [Bet_{NMR}]_{aq,eq, D_2O} \quad \text{Eq. 9}$$

$$[HTf_2N]_{org,eq} = [F_{NMR}]_{aq,eq, D_2O} - [F_{NMR}]_{aq,eq, DCl} \quad \text{Eq. 10}$$

Taking into account the results from solving Eq. 9 and Eq. 10, the concentration of [bet] that was extracted into the organic phase can be obtained from Eq. 8:

$$[\text{bet}]_{\text{org,eq}} = \left([\text{Bet}_{\text{NMR}}]_{\text{aq,eq}} - [\text{F}_{\text{NMR}}]_{\text{aq,eq}} - [\text{H}^+]_{\text{org,eq}} - [\text{HTf}_2\text{N}]_{\text{org,eq}} \right) \cdot \left(1 + \frac{\gamma_{\text{HCl}\pm} \cdot [\text{H}^+]_{\text{aq,eq}}}{K_a[\text{Hbet}^+]} \right)^{-1}$$

Eq. 11

The calculated concentrations of proton, HTf₂N, and bet species that were extracted based on Eqs. 9 - 11 are presented in Figure 7.

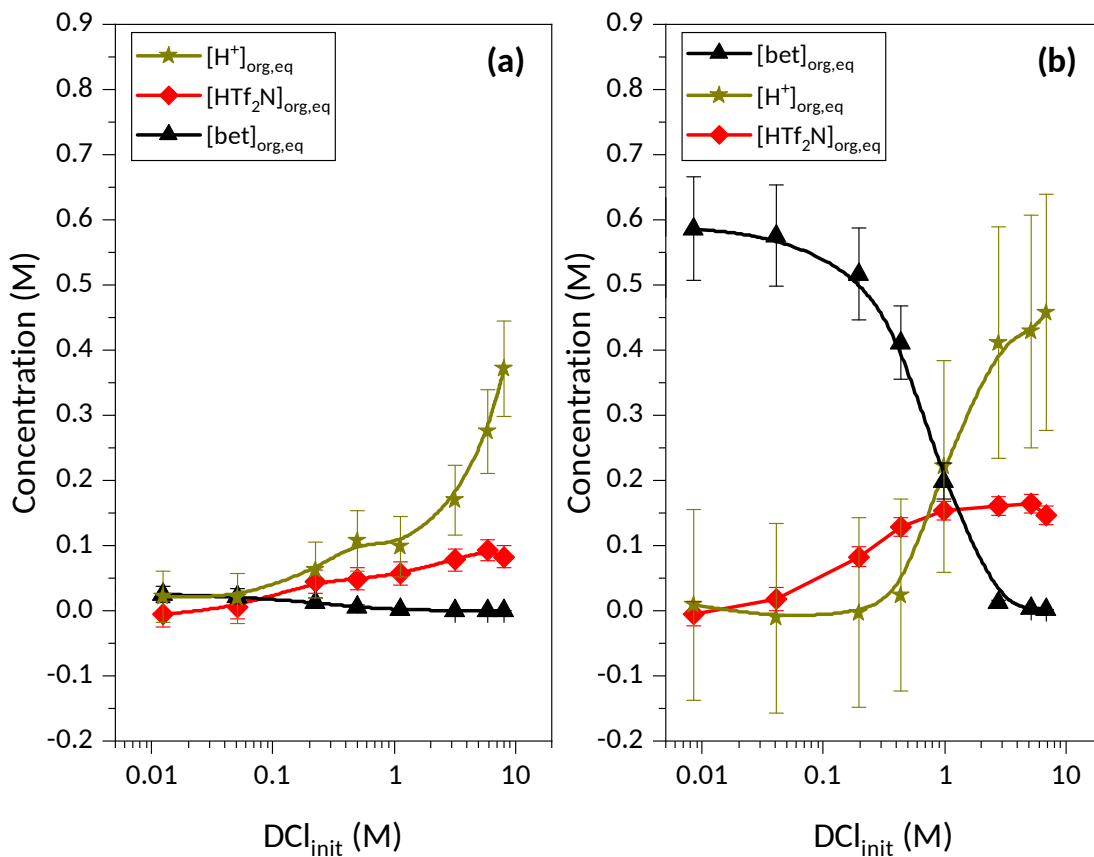


Figure 7. The concentrations of proton, HTf_2N , and bet species that were extracted into the organic phase as a function of initial acid concentrations from pure DCI **(a)** and DCI containing 15 % (w/v) bet **(b)**. The lines are drawn to guide the eye.

The results in Figure 7 show that the concentrations of the extracted protons and HTf_2N in the system with and without betaine increased with increasing acid concentration, while the opposite trend was observed for the extraction of bet species. For example, now it can be easily seen how 1.28 M betaine added to pure water (see Figure 2b) were distributed, namely 0.750 ± 0.080 M in the aqueous phase (see Table S2) and 0.560 ± 0.080 M in the organic phase (see Table S6 in the Supplementary Information).

3.4. Conditional solubility product constant

The solubility product constant (K_{sp}) is a property of an IL that is often used to determine the aqueous concentration of the IL cation and anion [45]. This quantity has been also used to explain the mechanism of metal extraction into an IL [30, 31, 36, 45]. Based on Eq. 2, the K_{sp} of [Hbet][Tf₂N] in the aqueous phase is expressed as:

$$K_{sp} = [\text{Hbet}^+]_{\text{aq}} [\text{Tf}_2\text{N}^-]_{\text{aq}} \quad \text{Eq. 12}$$

Owing to the deprotonation of [Hbet⁺] and the protonation of [Tf₂N⁻] in the aqueous phase, the information obtained on the distribution behavior of [Hbet][Tf₂N] products in this study allowed us to estimate only the value of the *conditional* solubility product constant (K_{sp}'):

$$K_{sp}' = ([\text{Hbet}^+]_{\text{aq,eq}} + [\text{bet}]_{\text{aq,eq}}) ([\text{Tf}_2\text{N}^-]_{\text{aq,eq}} + [\text{HTf}_2\text{N}]_{\text{aq,eq}}) \quad \text{Eq. 13}$$

Taking the dissociation constants of [Hbet⁺] and HTf₂N into account along with activity coefficients for all charged species ($\gamma_{IL\pm}$), we have:

$$K_{sp}' = \gamma_{IL\pm}^2 \cdot [\text{Hbet}^+]_{\text{aq,eq}} \left(1 + \frac{K_{a[\text{Hbet}^+]}}{\gamma_{\text{HCl}\pm} \cdot [\text{H}^+]_{\text{aq,eq}}} \right) \left(1 + \frac{\gamma_{\text{HCl}\pm} \cdot [\text{H}^+]_{\text{aq,eq}}}{K_{a[\text{HTf}_2\text{N}]}} \right) [\text{Tf}_2\text{N}^-]_{\text{aq,eq}} \quad \text{Eq. 14}$$

The charge balance in the aqueous solution at equilibrium can be expressed as:

$$[\text{H}^+]_{\text{aq,eq}} + [\text{Hbet}^+]_{\text{aq,eq}} = [\text{Tf}_2\text{N}^-]_{\text{aq,eq}} + [\text{Cl}^-]_{\text{aq,eq}} \quad \text{Eq. 15}$$

Thus, combining Eqs. 14 and 15, one can get a quadratic equation either for [Hbet⁺]_{aq,eq} or [Tf₂N⁻]_{aq,eq} species, for example:

$$K_{sp}' = \gamma_{IL\pm}^2 \cdot [\text{Hbet}^+]_{\text{aq,eq}} \left(1 + \frac{K_a[\text{Hbet}^+]}{\gamma_{\text{HCl}\pm} \cdot [\text{H}^+]_{\text{aq,eq}}} \right) \left(1 + \frac{\gamma_{\text{HCl}\pm} \cdot [\text{H}^+]_{\text{aq,eq}}}{K_a[\text{HTf}_2\text{N}]} \right) \left([\text{H}^+]_{\text{aq,eq}} + [\text{Hbet}^+]_{\text{aq,eq}} - [\text{Cl}^-]_{\text{aq,eq}} \right)$$

Eq. 16

The solution to the previous equation is

$$[\text{Hbet}^+]_{\text{aq,eq}} = \frac{[\text{Cl}^-]_{\text{aq,eq}} - [\text{H}^+]_{\text{aq,eq}} + \sqrt{([\text{Cl}^-]_{\text{aq,eq}} - [\text{H}^+]_{\text{aq,eq}})^2 + 4 \cdot K_{sp}' \cdot \gamma_{IL\pm}^{-2} \cdot \left(1 + \frac{K_a[\text{Hbet}^+]}{\gamma_{\text{HCl}\pm} \cdot [\text{H}^+]_{\text{aq,eq}}} \right)^{-1} \cdot \left(1 + \frac{\gamma_{\text{HCl}\pm} \cdot [\text{H}^+]_{\text{aq,eq}}}{K_a[\text{HTf}_2\text{N}]} \right)^{-1}}}{2}$$

Eq. 17

Unfortunately, the activity coefficients of the ionic liquid species are unknown and this limits the applicability of the equation above to a low acidity region where we can assume $\gamma_{IL\pm} \approx 1$. Nevertheless, Eq. 17 with such an assumption was used to fit the experimental data in the region up to 0.2 M HCl. In order to consider the expression above as a function of $[\text{H}^+]_{\text{aq,eq}}$ only, an empirical relation between $[\text{Cl}^-]_{\text{aq,eq}}$ and $[\text{H}^+]_{\text{aq,eq}}$ was used (see the Supplementary Information for details).

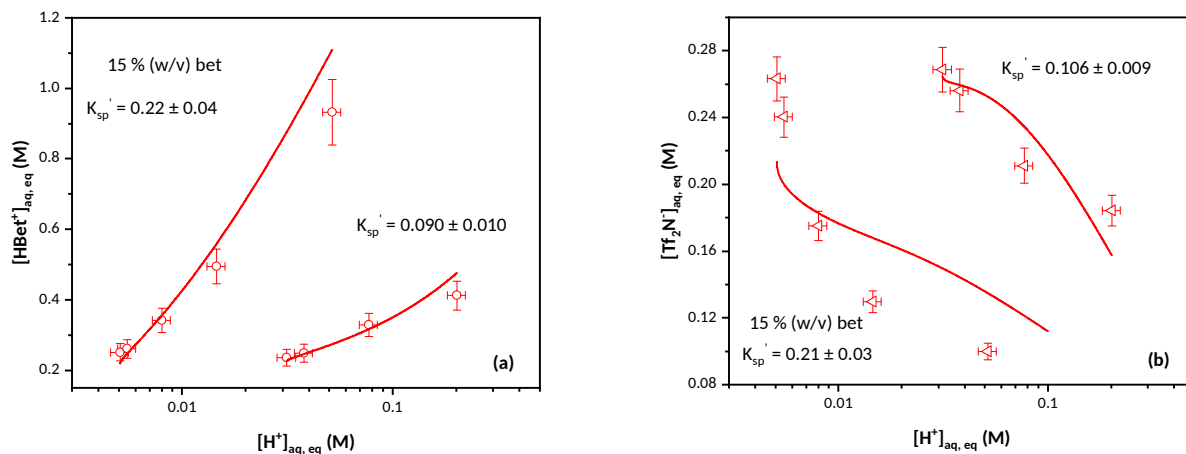


Figure 8. The concentration of protonated betaine as a function of the concentration of protons **(a)** and the concentration of bistriflimide as a function of the concentration of protons **(b)**. Both figures panels show data in the presence and absence of bet. The red lines are fits based on Eq. 17, which allows the conditional solubility product constant (K_{sp}') of $[Hbet][Tf_2N]$ to be determined as shown.

It can be seen that conditional solubility product value is increased by a factor of approximately 2 in the presence of 15 % bet in the aqueous phase.

The value of K_{sp}' in DCI can also be evaluated according to Eq. 18 (the simplified form of Eq. 13) using the experimental results of the equilibrium concentration of betaine- and fluorine-bearing species measured by the qNMR technique.

$$K_{sp}' = [Bet_{NMR}][F_{NMR}] \quad \text{Eq. 18}$$

By plotting the equilibrium $[Bet_{NMR}]$ values as a function of the inverse of the equilibrium $[F_{NMR}]$ based on Eq. 18, one can obtain a slope that is equal to the K_{sp}' of $[Hbet][Tf_2N]$ (Figure 9). The K_{sp}' was measured to be 0.099 ± 0.002 and this value is in agreement with the fitted parameter from Eq. 16. Due to the complexity of the biphasic system containing 15 % (w/v) bet, the slope-based K_{sp}' could not be calculated for this system.

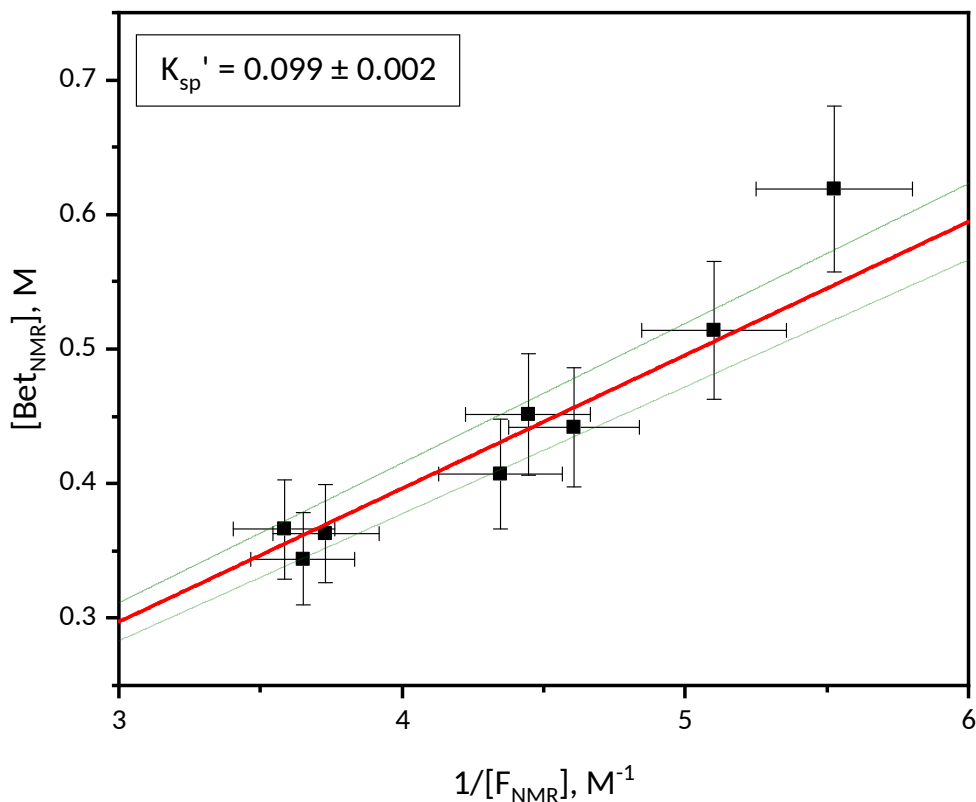


Figure 9. $[\text{Bet}_{\text{NMR}}]$ as a function of inverse $[F_{\text{NMR}}]$. The red line is a linear fit and the green lines represent the 95 % confidence interval.

4. Conclusion

The mutual solubility of $[\text{Hbet}][\text{Tf}_2\text{N}]$ and water in the presence of hydrochloric acid and betaine has been studied. It was found that the presence of acid increased the aqueous solubility of the IL cation while its effect on the IL anion was the opposite. This phenomenon was attributed to cation exchange between the protons and the Hbet^+ species along with favorable transfer of bistriflimide species into the organic phase in its protonated form ($[\text{HTf}_2\text{N}]$). Also, the transfer of $[\text{Hbet}^+]$ species into the aqueous phase is

most likely associated with the transfer of water molecules in the same direction. In the system containing both hydrochloric acid and 15 % (w/v) betaine, the transfer of water from the pre-equilibrated IL into the aqueous phase was generally higher than that in the system with only acid. The presence of betaine, betainium species and chloride ion is likely to reduce the availability of free water in the aqueous phase and to increase the transfer of water from the organic phase to the aqueous phase.

Zwitterionic betaine was found to be partially distributed between the two phases and its extracted species is most likely associated with water molecules in the organic phase. The addition of 15 % (w/v) betaine into the acidic aqueous phase leads to increased solubility of [Hbet][Tf₂N] ionic liquid.

In this work, a mathematical model to determine the conditional solubility product constant (K_{sp}') of [Hbet][Tf₂N] ionic liquid in DCI was developed. The obtained K_{sp}' values are approximately two times higher in the presence of 15 % betaine than without it.

Finally, this work provided evidence that unwanted loss of ionic liquid into the aqueous phase due to mutual solubility of the two phases can be avoided by controlling the acidity. Quantification of the anion constituent of the ionic liquid (in addition to its cation) should also be considered in projects employing this ionic liquid because it gives a more comprehensive understanding of the ions' behavior in the process.

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Conflict of interest:

Authors declare there is no conflict of interest regarding this publication.

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Effect of Aqueous Hydrochloric Acid and Zwitterionic Betaine on the Mutual Solubility between a Protic Betainium-based Ionic Liquid and Water

Merinda F. Volia,^{a, b} Evgeny E. Tereshatov,^{a*} Valérie Mazan,^c Charles M. Folden III^{a, d}
and Maria Boltoeva^c

^aCyclotron Institute, Texas A&M University, College Station, Texas 77843, USA

^bDepartment of Nuclear Engineering, Texas A&M University, College Station, Texas
77843, USA

^cUniversité de Strasbourg, CNRS, IPHC UMR 7178, F-67000 Strasbourg, France

^dDepartment of Chemistry, Texas A&M University, College Station, Texas 77843, USA

* Corresponding Author:

E-mail: etereshatov@tamu.edu

Address: Cyclotron Institute, Texas A&M University, TAMU 3366, College Station,
Texas 77843-3366, USA

Supplementary Information

1. Concentrations of individual species from the system of equations

Table S1 and S2 show the concentration of individual species evaluated by the system of equations (Eq. 5 in the main text). These data are presented graphically in the main text (see Figures 2-4).

Table S1. The concentration of individual species evaluated by the system of equations (Eq. 5 in the main text).

DCI_{init} (M)	$[H^+]$ (M)	$[HTf_2N]$ (M)	$[Tf_2N^-]$ (M)	$[Hbet^+]$ (M)	$[bet]$ (M)	$Y_{HCl\pm}$
0	0.048 ± 0.005	0.0147 ± 0.0007	0.259 ± 0.013	0.251 ± 0.025	0.093 ± 0.009	0.834
0.012	0.0314 ± 0.0006	0.0103 ± 0.0005	0.269 ± 0.013	0.236 ± 0.024	0.130 ± 0.013	0.858
0.051	0.0378 ± 0.0008	0.0117 ± 0.0006	0.256 ± 0.013	0.248 ± 0.025	0.115 ± 0.011	0.848
0.226	0.0770 ± 0.0015	0.0189 ± 0.0009	0.211 ± 0.011	0.329 ± 0.033	0.078 ± 0.008	0.812
0.497	0.202 ± 0.004	0.0407 ± 0.0020	0.184 ± 0.009	0.410 ± 0.040	0.0394 ± 0.0039	0.767
1.132	0.658 ± 0.013	0.091 ± 0.005	0.126 ± 0.006	0.430 ± 0.040	0.0126 ± 0.0013	0.769
3.191	2.220 ± 0.040	0.152 ± 0.008	$(4.37 \pm 0.22) \cdot 10^{-2}$	0.510 ± 0.050	$(3.10 \pm 0.31) \cdot 10^{-3}$	1.100
5.976	4.300 ± 0.090	0.168 ± 0.008	$(1.3 \pm 0.6) \cdot 10^{-3}$	0.620 ± 0.060	$(9.7 \pm 1.0) \cdot 10^{-4}$	2.186
8.036	5.659 ± 0.113	0.185 ± 0.009	$(6.19 \pm 0.31) \cdot 10^{-3}$	0.710 ± 0.070	$(5.1 \pm 0.5) \cdot 10^{-4}$	3.696

Table S2. The concentration of individual species evaluated by the system of equations (Eq. 5 in the main text).

DCI_{init} (M)	[H⁺] (M)	[HTf₂N] (M)	[Tf₂N⁻] (M)	[Hbet⁺] (M)	[bet] (M)	Y_{HCl}±
0	$(6.3 \pm 0.6) \cdot 10^{-3}$	$(2.11 \pm 0.11) \cdot 10^{-3}$	0.258 ± 0.013	0.288 ± 0.029	0.750 ± 0.080	0.923
0.009	$(5.07 \pm 0.10) \cdot 10^{-3}$	$(1.77 \pm 0.09) \cdot 10^{-3}$	0.263 ± 0.013	0.251 ± 0.025	0.790 ± 0.080	0.928
0.041	$(5.48 \pm 0.11) \cdot 10^{-3}$	$(1.74 \pm 0.09) \cdot 10^{-3}$	0.240 ± 0.012	0.261 ± 0.026	0.760 ± 0.080	0.926
0.198	$(8.02 \pm 0.16) \cdot 10^{-3}$	$(1.83 \pm 0.09) \cdot 10^{-3}$	0.175 ± 0.009	0.341 ± 0.034	0.690 ± 0.070	0.914
0.436	0.0146 ± 0.0003	$(2.40 \pm 0.12) \cdot 10^{-3}$	0.130 ± 0.006	0.490 ± 0.050	0.560 ± 0.060	0.891
0.998	0.0515 ± 0.0010	$(6.10 \pm 0.31) \cdot 10^{-3}$	0.100 ± 0.005	0.930 ± 0.090	0.323 ± 0.032	0.829
2.786	1.033 ± 0.021	$(5.41 \pm 0.27) \cdot 10^{-2}$	$(4.49 \pm 0.22) \cdot 10^{-2}$	1.420 ± 0.140	$(2.49 \pm 0.25) \cdot 10^{-2}$	0.818
5.150	2.960 ± 0.060	$(8.2 \pm 0.4) \cdot 10^{-2}$	$(1.4 \pm 0.7) \cdot 10^{-3}$	1.460 ± 0.150	$(5.3 \pm 0.5) \cdot 10^{-3}$	1.380
6.883	4.290 ± 0.090	$(1.1 \pm 0.5) \cdot 10^{-2}$	$(7.9 \pm 0.4) \cdot 10^{-3}$	1.490 ± 0.150	$(2.35 \pm 0.24) \cdot 10^{-3}$	2.182

2. Activity coefficient

The mean ionic activity coefficient of HCl ($\gamma_{HCl\pm}$) is shown in Figure S1 as a function of initial acid concentration. The plot was made based on literature data [1, 2].

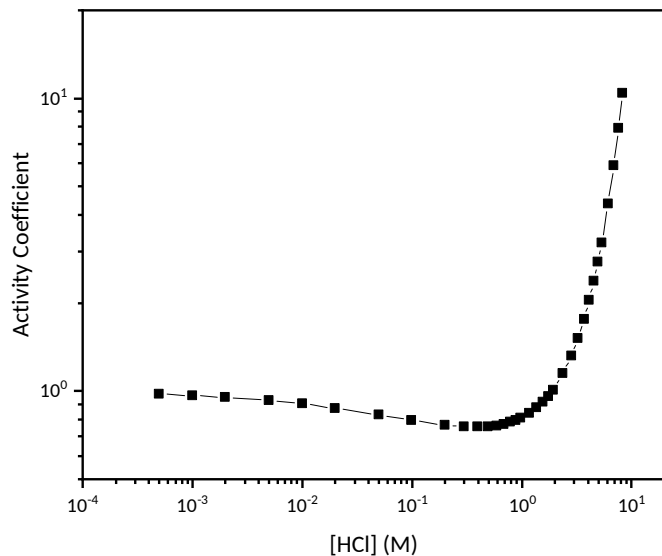


Figure S1. Mean ionic activity coefficient of HCl as the function of HCl concentration.

Table S3. Mean ionic activity coefficient of HCl.

HCl (M)	γ_{\pm}	HCl (M)	γ_{\pm}	HCl (M)	γ_{\pm}
0.000498	0.9752	0.591377	0.763	2.825111	1.316
0.000997	0.9656	0.6886294	0.772	3.264648	1.518
0.001993	0.9521	0.7855178	0.783	3.695738	1.762
0.004983	0.9285	0.8820464	0.795	4.118617	2.04
0.009966	0.9048	0.9782187	0.809	4.533048	2.38
0.019928	0.8755	1.1694586	0.84	4.939543	2.77

0.049791	0.8304	1.3591544	0.876	5.338412	3.22
0.099488	0.796	1.5474427	0.916	6.112676	4.37
0.198602	0.767	1.7342964	0.96	6.857565	5.9
0.297345	0.756	1.9196011	1.009	7.574278	7.94
0.395722	0.755	2.3767715	1.147	8.263997	10.44
0.493737	0.757				

3. Charge balance in the aqueous solution

The charge balance in the aqueous solution at equilibrium can be expressed as:

$$[H^+]_{aq,eq} + [Hbet^+]_{aq,eq} = [Tf_2N^-]_{aq,eq} + [Cl^-]_{aq,eq}.$$

Based on the equation above, the sum of equilibrium concentrations of the cations was plotted as a function of the sum of equilibrium concentrations of the anions (Figure S2). The plots show that the data are valid since the sum of cation concentrations is in agreement with the $y = x$ line, independent of Eq. 5 in the main text.

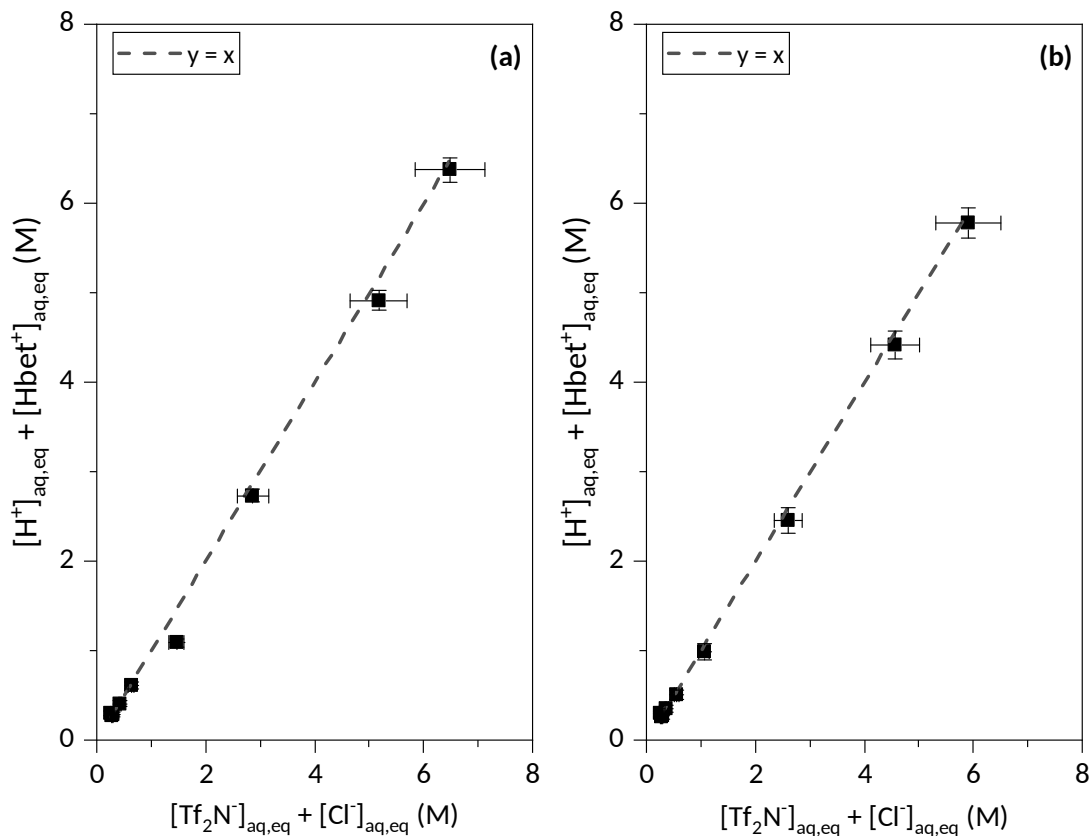


Figure S2. The plot of equilibrium concentrations of cations as a function of equilibrium concentrations of anions in the aqueous phase containing DCl **(a)** and aqueous phase containing DCl with 15 % (w/v) bet **(b)**. The dashed line shows the trend expected for perfect agreement between the cation and anion concentrations.

4. Chloride ion concentrations

Chloride ion concentrations measured by the Mohr methods are plotted as a function of initial DCl concentration (Figure S3). No transfer of chloride ions into the organic phase was observed based on this figure.

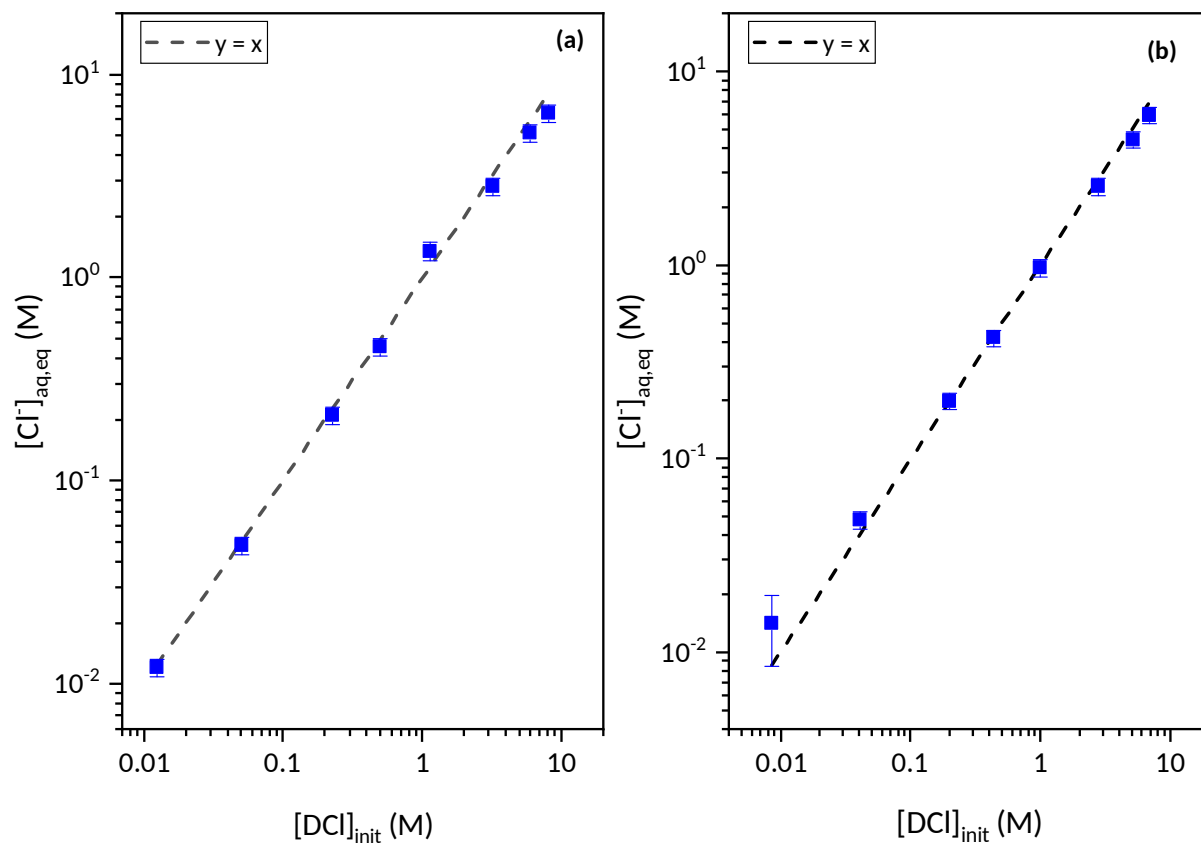


Figure S3. The equilibrium concentrations of $[\text{Cl}^-]$ after contacted with $[\text{Hbet}][\text{Tf}_2\text{N}]$ without the presence of bet (pure DCI) **(a)** and in the presence of 15 % (w/v) bet **(b)**. The dashed line shows the trend expected for perfect agreement between the initial and final concentrations.

5. Equilibrium concentrations of $[\text{H}^+]$ and $[\text{Cl}^-]$ ions at 3 – 8 M DCI

Plots of $[\text{H}^+]$ and $[\text{Cl}^-]$ ions in 3 – 8 M DCI show that the equilibrium concentrations of these ions are lower than the initial ones (Figure S4).

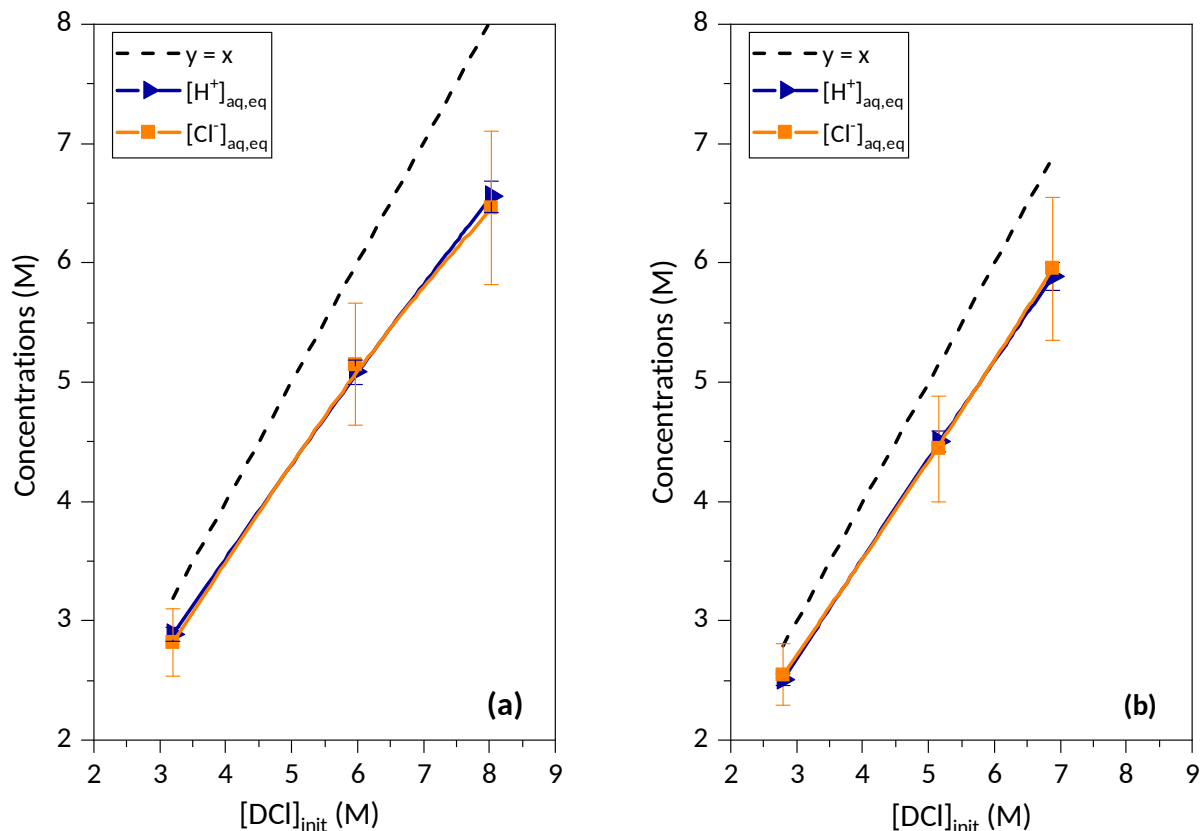


Figure S4. Plots of [H⁺] and [Cl⁻] equilibrium concentrations after contact with [Hbet][Tf₂N] without the presence of bet (pure DCI) **(a)** and in the presence of 15 % (w/v) bet **(b)**. The dashed line ($y = x$) indicates the reference value when the initial and equilibrium [H⁺] and [Cl⁻] are equal. The solid lines are drawn to guide the eye.

To verify this observation, in a separate experiments, [Hbet][Tf₂N] and [C₄mim][Tf₂N] ionic liquids (the latter was chosen for comparison) were washed with deionized water after being in contact with > 3 M HCl. The corresponding aqueous phases (after rinsing) were qualitatively tested for chloride content. In all cases, an addition of AgNO₃ led to a precipitate formation. Table S4 shows the measurement of the equilibrium

pH of the aqueous phases. The results show that the ILs were acidified after contact with concentrated acid (the uncertainty of the measurement is 0.05 pH unit). Thus, we observed the transfer of HCl into the organic phase (neglecting anion exchange between $[\text{Cl}^-]_{\text{aq}}$ and $[\text{Tf}_2\text{N}^-]_{\text{org}}$, which is in agreement with literature) [3]. It is likely that this acid is dissolved in water contained in the organic phase.

Table S4. The measurement of the equilibrium pH of the aqueous phases after the ionic liquid is washed with water. The ionic liquids were previously contacted with either water or 3 – 8 M HCl. The uncertainty of the pH measurements is 0.05 pH units.

$[\text{HCl}]_{\text{initial}} \text{ (M)}$	$[\text{Hbet}][\text{Tf}_2\text{N}]$	$[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$
	pH_{eq}	pH_{eq}
0	1.42	7.04
3	0.70	1.67
6	0.44	1.05
8	0.20	0.92

6. Extraction of species into [Hbet][Tf₂N]

Table S5. The concentrations of proton, bet, and HTf₂N species that were extracted into the organic phase from pure water and DCI.

DCI_{init} (M)	[H⁺]_{org,eq} (M)	[HTf₂N]_{org,eq} (M)	[bet]_{org,eq} (M)
0.000	0	0	$(1.9 \pm 1.0) \cdot 10^{-2}$
0.012	0.022 ± 0.039	-0.005 ± 0.020	$(2.5 \pm 1.3) \cdot 10^{-2}$
0.051	0.019 ± 0.039	0.006 ± 0.019	$(2.2 \pm 1.2) \cdot 10^{-2}$
0.226	0.060 ± 0.040	0.044 ± 0.018	$(1.3 \pm 0.7) \cdot 10^{-2}$
0.497	0.110 ± 0.050	0.049 ± 0.018	$(6.1 \pm 3.2) \cdot 10^{-3}$
1.132	0.100 ± 0.050	0.057 ± 0.017	$(2.0 \pm 1.1) \cdot 10^{-3}$
3.191	0.170 ± 0.050	0.078 ± 0.017	$(4.2 \pm 2.2) \cdot 10^{-4}$
5.976	0.280 ± 0.060	0.093 ± 0.016	$(1.1 \pm 0.6) \cdot 10^{-4}$
8.036	0.370 ± 0.070	0.083 ± 0.017	$(4.9 \pm 2.6) \cdot 10^{-5}$

Table S6. The concentrations of proton, bet, and HTf₂N species that were extracted into the organic phase from water and DCI containing 15 % (w/v) bet.

DCI_{init} (M)	[H⁺]_{org,eq} (M)	[HTf₂N]_{org,eq} (M)	[bet]_{org,eq} (M)
0	0	0	0.560 ± 0.080
0.009	0.000 ± 0.150	-0.005 ± 0.019	0.590 ± 0.080
0.041	-0.010 ± 0.150	0.018 ± 0.018	0.580 ± 0.080
0.198	0.000 ± 0.150	0.083 ± 0.016	0.520 ± 0.070
0.436	0.020 ± 0.150	0.128 ± 0.015	0.410 ± 0.060
0.998	0.220 ± 0.160	0.154 ± 0.014	0.200 ± 0.030
2.786	0.410 ± 0.180	0.161 ± 0.014	(1.3 ± 0.2) · 10 ⁻²
5.150	0.430 ± 0.180	0.164 ± 0.014	(2.8 ± 0.4) · 10 ⁻³
6.883	0.460 ± 0.180	0.146 ± 0.014	(1.2 ± 0.2) · 10 ⁻³

For the calculation of [bet]_{org,eq} in Table S5 and S6, the error on K_a[Hbet⁺] was estimated to be at the level of 5%.

7. Empirical equations for data fitting

In order to fit the data to understand the mechanism of ionic liquid solubility, the following empirical equations were used:

a) The system [Hbet][Tf₂N] – DCl:

$$\log ([Cl^-]_{aq, eq}) = 1.804 \cdot (\log ([H^+]_{aq, eq}) + 1.503)^{0.472} - 1.900 \quad \text{Eq. S1}$$

b) The system [Hbet][Tf₂N] – DCl in the presence of 15 % (w/v) betaine:

$$\log ([Cl^-]_{aq, eq}) = 2.300 \cdot (\log ([H^+]_{aq, eq}) + 2.294)^{0.245} - 2.293 \quad \text{Eq. S2}$$

Equations S1 and S2 are valid in the range of the corresponding equilibrium proton concentrations in Tables S1 and S2, respectively, when $[DCl]_{init} > 0$.

References

- [1] B.P. Nikolsky, Chemist's Handbook, Chemical Equilibrium and Kinetic, Property of Solutions, Electrode Processes, Chemistry, Leningrad, 1965, pp. 1008 (in Russian).
- [2] G. Åkerlöf, J. Teare, A Note on the Density of Aqueous Solutions of Hydrochloric Acid, J Am Chem Soc, 60 (1938) 1226-1228.
- [3] D. Dupont, D. Depuydt, K. Binnemans, Overview of the Effect of Salts on Biphasic Ionic Liquid/Water Solvent Extraction Systems: Anion Exchange, Mutual Solubility, and Thermomorphic Properties, J Phys Chem B, 119 (2015) 6747-6757.