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Aqueous N-H acid *bis*(trifluoromethylsulfonyl) imide Solution - [C₄mim][Tf₂N] Ionic Liquid Biphasic System: an Original Investigation by Diffusion Ordered Spectroscopy Nuclear Magnetic Resonance

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Abstract:

Transfers of solutes from an aqueous phase to an ionic liquid phase and vice versa has been well studied for years. On the other hand, influence of transferred solutes on the ionic liquid's structure is not yet evaluated. Therefore, we focus on the aqueous - ionic liquid biphasic system composed of two immiscible phase containing N-H acid *bis*(trifluoromethylsulfonyl) imide and [C₄mim][Tf₂N] ionic liquid. After mixing and separation of the two phases, a part of water, H₃O⁺, [Tf₂N]⁻ and H[Tf₂N] anions were transferred into [C₄mim][Tf₂N] ionic liquid phase. The presence of this solutes could modify the local structure of [C₄mim][Tf₂N] ionic liquid. So far, our goal is to evaluate this structural change using several tools. For this, one dimensional ¹H, ¹⁹F and Diffusion Ordered Spectroscopy Nuclear Magnetic Resonance were carried out on the [C₄mim][Tf₂N] phase. We observed that some of water molecules were free and formed local microstructure as water pocket inside the ionic liquid frame. The others were hydrogen bonded to [Tf₂N]⁻ anions or H[Tf₂N]. The N-H acid *bis*(trifluoromethylsulfonyl) imide has a salting in effect and the biphasic system turn in a single phase for [H[Tf₂N]]_{aq, init} = 3 M. The network of [C₄mim][Tf₂N] ionic liquid is gradually destroyed when the water brought by the acid H[Tf₂N] becomes the major species.

Keywords: Ionic liquid, NMR 1 and 2 dimensional, DOSY NMR, self-diffusion coefficient, HTf₂N.

1. Introduction

Ionic liquids (ILs) are good alternative to replace classical solvents in liquid-liquid extraction process because of their unique physicochemical properties like high chemical and thermal stability [1], non-flammability and very low vapour pressure [2]. A typical class of ILs used are 1-alkyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide (henceforth indicated as [C_nmim][Tf₂N], where n = 2, 4, 6, 8 and 10). They are the most studied ILs as solvents for metal extraction [3–5]. From aqueous nitric media, uranium, plutonium and fission products were extracted by [C_nmim][Tf₂N] ionic liquid [6–8]. A variety of ligands dissolved in [C_nmim][Tf₂N] as Tri-n-butylphosphate [9–12], malonamide [13], tri-alkylamines

[14] were used to extract actinides from aqueous nitric phase. The efficiency of ILs were demonstrated by a higher separation of uranium and actinides than with conventional organic solvent [9,15]. This idea was reinforced with the thallium extraction by $[C_n\text{mim}][\text{Tf}_2\text{N}]$ ionic liquid from aqueous hydrochloric acid[3]. To understand the extraction mechanism of metals, metallic ions, H_3O^+ , NO_3^- , Cl^- , $[C_n\text{mim}^+]$, $[\text{Tf}_2\text{N}^-]$ were titrated in aqueous phase and water was titrated in ionic liquid phase. We demonstrated the partial transfer of HNO_3 [16,17] and HTf_2N [18] in the ionic liquid phase with water except for HCl [18]. The transfer of water in the ionic liquid phase modifies their physicals properties. For example, viscosity of $[\text{C}_2\text{mim}][\text{Tf}_2\text{N}]$ and $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ decreases as the amount of water increases into them [19].

In our previous work we demonstrated that, HCl was not extracted [18], HNO_3 was slightly extracted [16,17] and $\text{H}[\text{Tf}_2\text{N}]$ [11] was extracted by the $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ ionic liquid. The transfer of solutes in the ionic liquid phase was accompanied by a transfer of water into it. Sieffert, Wipff [20] and Danten et al [21] demonstrated by molecular simulation, that water molecules are generally hydrogen-bonded to two $[\text{Tf}_2\text{N}^-]$ anions via their oxygen atoms in the $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ ionic liquid. A part of water is “quasi free” and the other one could form H-bonds with $[\text{Tf}_2\text{N}^-]$ anions [22]. In our previous work, we studied the biphasic system composed of $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ ionic liquid phase contacted with nitric and hydrochloric aqueous solutions with several initial concentration of acids. We used ^1H and ^{19}F Diffusion Ordered Spectroscopy Nuclear Magnetic Resonance (DOSY NMR) method to study transport properties of ionic liquid phase. The transfer of water and a tiny part of H_3O^+ and NO_3^- affected the diffusion of $[\text{C}_4\text{mim}^+]$ and $[\text{Tf}_2\text{N}^-]$ ions. The network of $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ ionic liquid begins to dismantle when the concentration of water and nitric acid reaches 40% in ionic liquid phase [23].

The organic phase of biphasic system, composed of $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ contacted with and N-H acid *bis*(trifluoromethylsulfonyl) imide solutions at different concentrations, was studied by ^1H , ^{19}F one dimensional NMR. Self-diffusion coefficient of $[\text{C}_4\text{mim}^+]$, $[\text{Tf}_2\text{N}^-]$, water and H_3O^+ ions were measured in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ phase by ^1H and ^{19}F DOSY NMR to understand the behavior of water and ionic species into the $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ phase.

2. Results and discussion

The ionic liquid 1-butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide (henceforth indicated as $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$) is investigated in the present work. Fig. 1 depicts chemical structure of the ionic liquid and the atom numbering of the cation.

Fig. 1. Chemical structure of ionic liquid cations and anion used in the present work.

2.1 Sample composition

Two types of liquid-liquid extraction experiments were performed by mixing neat $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ organic phase with aqueous solution containing:

- 0.50 $\text{H}_2\text{O}/0.50 \text{ D}_2\text{O}$ in v/v named HOD
- $\text{H}[\text{Tf}_2\text{N}]_{\text{aq, init}}$ acid in HOD at 0.502, 1.001, 1.502, 2.002, 2.500 and 3.003 M

In aqueous phase, only primary isotopic exchange processes are taken in account [24] (before contact with ionic liquid phase), the equilibria can be described by following reactions:

The dissociation of $\text{H}[\text{Tf}_2\text{N}]$ acid is taken in account:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Tf}_2\text{N}^-]}{[\text{HTf}_2\text{N}]}$$

Acid-dissociation constant K_a is equal to $0.70 \pm 0.04 \text{ mol dm}^{-3}$ [25] or 0.02 mol dm^{-3} [26]. The acid $\text{H}[\text{Tf}_2\text{N}]$ is slightly dissociated. Considering the value of $K_a = 0.7$, the degree of acid dissociation is 0.58, 0.41, 0.32, 0.26, 0.22, 0.19 for concentrations of $\text{H}[\text{Tf}_2\text{N}]_{\text{aq, init}} = 0.502, 1.001, 1.502, 2.002, 2.500$ and 3.003 M respectively. Thus H_2O , D_2O , HOD , H_2DO^+ , $\text{H}[\text{Tf}_2\text{N}]$, $[\text{Tf}_2\text{N}^-]$ and H_3O^+ exist in aqueous phase and the equilibria are reached very quickly [27]. The use of H_2O only, yields to a broad signal of water, which could overlap others, signals and disturb the NMR measurements. In previous work [18], it has been demonstrated that $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ ionic liquid extract $\text{H}[\text{Tf}_2\text{N}]$ and water. The two immiscible phases, acidic aqueous and ionic liquid are contacted and separated. The two phase mixed to a single one for $\text{H}[\text{Tf}_2\text{N}]_{\text{aq, init}} \geq 3 \text{ M}$ [16]. From these known results, table 1 describes compositions of aqueous phases and mole fraction of all entities presented in the ILs phase after liquid-liquid extraction.

Table 1 samples compositions of aqueous and ILs phases

Composition of aqueous phases		Composition of [C ₄ mim][Tf ₂ N] phases				
H[Tf ₂ N] _{aq, init} M [18]	[H ⁺ or D ⁺] _{aq, éq} M [18]	[H ⁺ or D ⁺] _{org, éq} M	Mole fraction of HOD	Mole fraction of H ⁺ or D ⁺	Mole fraction of [C ₄ mim ⁺]	Mole fraction of [Tf ₂ N ⁻]
0	pH = 6.01	/	0.13	0.00	0.43	0.43
0.502	0.492	0.053	0.16	0.01	0.41	0.42
1.001	0.926	0.148	0.23	0.02	0.37	0.39
1.502	1.337	0.293	0.33	0.03	0.31	0.34
2.002	1.709	0.496	0.46	0.04	0.23	0.27
2.500	1.968	0.894	0.57	0.06	0.15	0.21
3.003 monophasic sample	1.506	1.443	0.80	0.05	0.05	0.10

Up to $[H[Tf_2N]]_{aq, init} = 1.001$ M, [C₄mim⁺] cation and [Tf₂N⁻] anion are in the major quantity, followed by HOD and then H⁺ or D⁺. For $[H[Tf_2N]]_{aq, init} = 1.502$ M, amount of water, [C₄mim⁺] cation and [Tf₂N⁻] anion are of the same order of magnitude and H⁺ or D⁺ are in minor quantity. From $[H[Tf_2N]]_{aq, init} = 2.002$ M, water becomes the major species in ionic liquid phase and quantity of [Tf₂N⁻] anion is slightly higher than [C₄mim⁺] cation. In the case of monophasic sample for $[H[Tf_2N]]_{aq, init} = 3.003$ M, amount of HOD is sixteen times more important than [C₄mim⁺] cation and H⁺ or D⁺ and eight more than [Tf₂N⁻] anion. The quantity of [Tf₂N⁻] anion is twice as important as that [C₄mim⁺] cation and H⁺ or D⁺. Anion [Tf₂N⁻], by the two groups – CF₃, is hydrophobic and prefer to be in the IL phase [28]. The N-H acid *bis*(trifluoromethylsulfonyl) imide has got a salting in effect and thus can dissolve the hydrophobic ionic liquid [C₄mim][Tf₂N]. The solubility of the ionic liquid [C₄mim][Tf₂N] is 15 mM [17] in pure water and reaches 1.71 M in an solution of H[Tf₂N] 3 M.

2.2 ¹H and ¹⁹F 1D NMR measurements

¹H and ¹⁹F 1D NMR spectra of ionic liquid phases contacted with H[Tf₂N] solution, were recorded. The internal residual peak of [D₆]DMSO at 2.50 ppm is used as the reference of chemicals shifts. Figure 2 shows the ¹H 1D spectra of sample at each initial concentration of H[Tf₂N] in aqueous phase.

Fig.2. ^1H 1D spectra of the HOD/H[Tf₂N][C₄mim][Tf₂N] biphasic system.

Table SI 1 gives signals of cation [C₄mim⁺]. For each sample, the chemical shift of [C₄mim⁺] protons stayed constant. The ^1H NMR signal of water which is transferred into the ionic liquid phase is located at ≈ 4.00 ppm [29,30]. It's slightly shielded in comparison to the usual chemical shift of water at 4.79 ppm [31].

As seen in our previous work [23], an additional peak appears at 2.38 ppm for the sample [C₄mim][Tf₂N] ionic liquid saturated with HOD. A signal of proton appears at 4.56, 5.11, 5.33, 5.63, and 5.66 ppm as the initial concentration of H[Tf₂N]_{aq, init} = 1.001, 1.502, 2.002, 2.500 and 3.003 M in aqueous phases. The fact that the ^1H chemical shift of this proton moves towards the down-field proves that this proton is more and more deshielded. This proton is attributed to the bonded HOD fraction. HOD concentration in ionic liquid phase increase with the introduction of H[Tf₂N] into aqueous phase [18]. For exchanges between water free and linked through the ionic liquid network, a new reaction is added:

Furthermore, the amount of H₃O⁺ present in the ionic liquid phase is too small to detect their NMR signal. Thus, exchange between H₃O⁺ and D₂O eq (2) could not be seen by NMR time scale. It becomes faster and faster as mole fraction of HOD increase in the ionic liquid phase [32,33].

Fig.3. displays the ^{19}F 1D spectra of sample at each initial concentration of H[Tf₂N] in aqueous phase.

Fig. 3. ^{19}F 1D spectra of the HOD/H[Tf₂N]/[C₄mim][Tf₂N] biphasic system.

^{19}F 1D NMR spectra on the same ionic liquid phases were recorded, the reference was CF₃COONa dissolved in DMSO and its chemical shift was set at -74.00 ppm [34]. The chemical shift of -CF₃ from [Tf₂N]⁻ anion of the ionic liquid is slightly affected by the presence of water. The fluorine signal is on singlet for each sample. The amount of water increases drastically in the organic phase but disturbs very slightly the environment of -CF₃ group of [Tf₂N]⁻ anion.

2.3 Transport properties of ionic species and ionic interactions

Diffusion NMR measurements were carried out on ionic liquid phase contacted with HOD [23] and with H[Tf₂N] aqueous solution. Table 2 reports self-diffusion coefficients of [C₄mim⁺] cations D_+ , [Tf₂N]⁻ anions D_- and values of ratio $R = D_+/D_-$. All the self-diffusion coefficients D_+ and D_- in ILs phases from biphasic samples are higher than [C₄mim][Tf₂N] pure and dried ($D_+ = 3.00 \cdot 10^{-11}$ and $D_- = 2.10 \cdot 10^{-11} \text{ m}^2\text{s}^{-1}$) [35]. As seen in Table 2, D_+ is always superior to D_- for biphasic samples and their self-diffusion coefficients increase as the concentration of H[Tf₂N]_{aq,init} in aqueous phase increases. Increase in water content in the ionic liquid phase, the viscosity of the organic phase decreases, which increases the self-diffusion coefficients of each component. In the case of monophasic sample for H[Tf₂N]_{aq,init} = 3.003 M $D_+ \approx D_-$. R value with pure and dried [C₄mim][Tf₂N] is 1.43 [35]. With biphasic samples, R decreases from 1.43 to 1.13 and reaches ≈ 1 with the monophasic sample. Supplementary data displays ^1H and ^{19}F DOSY NMR spectra for each sample.

Table 2 reports self-diffusion coefficients of HOD D_{HOD} , bond water $D_{\text{bond water}}$ and other species $D_{\text{other Tf}_2\text{N-species}}$ measured in ionic liquid phase contacted with aqueous phase of H[Tf₂N]. Self-diffusion of HOD stays constant. For bond water, it begins to decrease and increase for the

monophasic sample to reach the same value of the water's self-diffusion coefficient. Several species are detected by ^{19}F NMR DOSY and their self-diffusion coefficients were measured until $\text{H}[\text{Tf}_2\text{N}]_{\text{aq,init}} = 1.001 \text{ M}$. Table 2

Self-diffusion coefficient of $[\text{C}_4\text{mim}^+]$, of $[\text{Tf}_2\text{N}^-]$, R values, HOD, bond water, other species of ^{19}F detected in ILs phases.

Composition of aqueous phases	The self-diffusions of $[\text{C}_4\text{mim}^+]$, of $[\text{Tf}_2\text{N}^-]$, R values, D_{HOD} , $D_{\text{Bond water}}$ and $D_{\text{other } ^{19}\text{F species}}$ observed in the organic phase					
$\text{H}[\text{Tf}_2\text{N}]_{\text{aq, init}} \text{ M}$ [18]	D_+ (m^2s^{-1})	D_- (m^2s^{-1})	R	D_{HOD} (m^2s^{-1})	$D_{\text{bond water}}$ (m^2s^{-1})	$D_{\text{other Tf}_2\text{N- species}}$ (m^2s^{-1})
0	$3.75 \cdot 10^{-11}$	$2.63 \cdot 10^{-11}$	1.43	$4.97 \cdot 10^{-10}$	$3.72 \cdot 10^{-10}$	* $2.05 \cdot 10^{-9}$ * $8.4 \cdot 10^{-10}$ $3.11 \cdot 10^{-10}$
0.502	$3.90 \cdot 10^{-11}$	$3.03 \cdot 10^{-11}$	1.29	$4.84 \cdot 10^{-10}$	* $3.11 \cdot 10^{-10}$	* $1.4 \cdot 10^{-10}$
1.001	$4.24 \cdot 10^{-11}$	$3.38 \cdot 10^{-11}$	1.25	$4.80 \cdot 10^{-10}$	$2.39 \cdot 10^{-10}$	$2.68 \cdot 10^{-9}$ $1.70 \cdot 10^{-9}$
1.502	$4.54 \cdot 10^{-11}$	$3.83 \cdot 10^{-11}$	1.19	$4.92 \cdot 10^{-10}$	$2.10 \cdot 10^{-10}$	not observed
2.002	$5.84 \cdot 10^{-11}$	$4.96 \cdot 10^{-11}$	1.18	$4.80 \cdot 10^{-10}$	$2.30 \cdot 10^{-10}$	
2.500	$7.14 \cdot 10^{-11}$	$6.30 \cdot 10^{-11}$	1.13	$4.86 \cdot 10^{-10}$	$2.78 \cdot 10^{-10}$	
3.003	$1.08 \cdot 10^{-10}$	$1.12 \cdot 10^{-10}$	0.96	$4.89 \cdot 10^{-10}$	$4.60 \cdot 10^{-10}$	
Monophasic sample						

* indicate that the measure of self-diffusion is difficult because the signal is tiny and close to the background.

Fig. 4 displays the R ratio as a function of $\text{H}[\text{Tf}_2\text{N}]_{\text{aq, init}}$. As shown in figure 4, a slope break appears for a concentration of 1.502 M in $\text{H}[\text{Tf}_2\text{N}]$ acid. At this concentration of acid, the molar fractions of HOD, cation and anion of the ionic liquid are equivalent. So two areas are defined, where molar fraction in HOD is lower than that of cation and anion and the second area where it is higher. The last point is for the monophasic sample.

Fig. 4. R values as a function of H[Tf₂N]_{aq, init} M

As long as the H[Tf₂N]_{aq, init} is less than 1.502 M, partial ion pairing between cation [C₄mim⁺] and anion [Tf₂N⁻] is slightly affected by the presence of species HOD and H[Tf₂N] transferred into ionic liquid phase. The structure of imidazolium based ionic liquid is well known [36–38], coulombic forces between the cation and anion are predominant but the hydrogen bond and Van der Waals interactions build the frame of the ionic liquid as a supramolecular structure [39,40]. By adding species as HOD, H₃O⁺, [Tf₂N⁻] and H[Tf₂N], in first time this species are inclusions in the supramolecular network of ionic liquid [C₄mim][Tf₂N] and the IL network is not yet affected.

For H[Tf₂N]_{aq, init} greater than 1.502 M, the water's mole fraction is greater than that of [C₄mim⁺] and [Tf₂N⁻] mole fraction in IL. Cations and anions move at almost the same speed. Thus, supramolecular structure is more and more dismantled while anion and cation form contact ion pairs surrounding of water. Contact ion pairs could be described as (C₄mim⁺, Tf₂N⁻)_i, H₂O_x.

Consider measurements of fluorinated species self-diffusion coefficients, at 0.502 M of H[Tf₂N]_{aq, init} is not obvious to conclude as regard the *D_{other Tf₂N}-species* because signals are tiny and close to the background. At 1.001 M of H[Tf₂N]_{aq, init}, two species move more approximately ten faster than bond water, it might be H[Tf₂N] or free [Tf₂N⁻]. For a concentration greater than 1.5 M in H[Tf₂N]_{aq, init}, there is no more signal detected for other [Tf₂N⁻] species. Water inside the organic phase, dilutes [C₄mim⁺] and [Tf₂N⁻] ions and a fortiori the other [Tf₂N⁻] species. So their self-diffusion coefficient could not be measured.

However, the transfer of amount of H[Tf₂N] in organic phase equation (5), brings water and H₃O⁺ into the ionic liquid phase. The dissociation of H[Tf₂N] in ionic liquid phase could be occurs as describe by equation (6).

As long as the $H[Tf_2N]_{aq, init} < 1.502 \text{ M}$, others species of $[Tf_2N^-]$ or $H[Tf_2N]$ moved quickly than the main species. The exchange described by equation (6) is enough slow to measure self-coefficients diffusions of $[Tf_2N^-]$ and $H[Tf_2N]$. $H[Tf_2N]_{aq, init} > 1.502 \text{ M}$, molar fraction of water is more and more important in the IL phase, to rise the speed of exchange described with equation (6). Figure 5 could be described the exchange between $H[Tf_2N]$ and $[Tf_2N^-]$ anion in ionic liquid phase [41].

Fig. 5. Proton exchange between anion bis(trifluoromethanesulfonyl)imide and N-H bis(trifluoromethanesulfonyl)imide

In pure $[C_4mim][Tf_2N]$ ionic liquid, both *trans* and *cis* $[Tf_2N^-]$ exist as described in figure 1. The standard Gibbs free energy difference between *trans* and *cis* conformation is reported to be as small as 0.2 kJ/mol [42] or 3.5 kJ/mol [43]. When $[Tf_2N^-]$ solvates protons in organic phase, the *cis* conformation is predominant [41]. The same trend was observed with the solvation of lithium ion by $[Tf_2N^-]$ in $[C_4mim][Tf_2N]$ ionic liquid [42].

Whatever the molar fraction of water, self-diffusion of HOD stays constants. HOD moves in its own microstructure inside the supramolecular network and even after two phase mixed to a single one for $H[Tf_2N]_{aq, init} \geq 3 \text{ M}$. H from bond water is more and more deshielded as $H[Tf_2N]_{aq, init}$ and HOD molar fraction increase as seen in Fig 2. Bond water has its self-diffusion coefficient, which increased to reach the same value of its HOD in the monophasic system, so bond water is diluted in HOD.

Self-diffusion assigned to bond water is a combination between self-diffusion of free water and the one of $[Tf_2N^-]$ anion. Through the assumption of fast exchange between free and associated species in NMR time scale, self-diffusion coefficient of bonded water can thus be written by [44,45].

$$D_{obs} = f_{free}D_{free} + f_{bound}D_{bound} \quad (6)$$

In our case, D_{obs} is $D_{bond \text{ water}}$, D_{free} is D_{HOD} and D_{bound} is D_- .

$$D_{bond \text{ water}} = f_{free}D_{HOD} + (1-f_{free})D_- \quad (7)$$

$$f_{free} = \frac{D_{bond \text{ water}} - D_-}{D_{HOD} - D_-} \quad (8)$$

Fraction f_{free} of free water is calculated from self-diffusion coefficient measured in the ionic liquid phase according to (8). The values are 0.73, 0.62, 0.46, 0.38, 0.42, 0.51 and 0.92 for each sample at $[H[Tf_2N]]_{aq, init} = 0.00, 0.502, 1.001, 1.502, 2.002, 2.500$ and 3.003 M, respectively. Fig. 6 displays the free fraction of water as a function of $H[Tf_2N]_{aq, init}$. As shown in Fig. 4, the same trend is observed with a slope break at 1.5 M acid.

Fig. 6. Free water fraction as a function of $H[Tf_2N]_{aq, init}$ M

As long as the $H[Tf_2N]_{aq, init}$ is less than 1.502 M, bond water fraction increases with the total amount of water increasing in ionic liquid phase. This promotes the formation of hydrogen bonds and exchange with free water as described by equation (4) which is rationalized by the deshielding of proton from water linked (see Fig.2.). For $H[Tf_2N]_{aq, init}$ greater than 1.502 M, bond water fraction decreases as the mole fraction of HOD increases. HOD is the majority species that can bind with $H [Tf_2N]$ anion by hydrogen bonds [46].

The figure 7 describes a schematic view of $[C_4mim][Tf_2N]$ ionic liquid frame saturated with water [23]. Water molecule hydrogen bonding with $[Tf_2N^-]$ by their sulfonyl group is drawn in red.

Fig. 7. Schematic view the $[C_4mim][Tf_2N]$ ionic liquid frame saturated with water from our previous work

When, we have studied biphasic systems composed of $[C_4mim][Tf_2N]$ ionic liquid and HCl acids with a concentration at 7.14 M and HNO_3 with different concentrations [23], salting in effect is less important than with $H[Tf_2N]$ acid. This means that the amount of water and to a lesser extent the amount of ions H_3O^+ , NO_3^- or Cl^- transferred in the ionic liquid phase is less important than with $H[Tf_2N]$. As a result, the network of ionic liquid is less disturbed with biphasic systems composed of $[C_4mim][Tf_2N]$ and HCl or HNO_3 acids. The transfer of water, H_3O^+ , $[Tf_2N]^-$ and $H[Tf_2N]$ species through the salting in effect of N-H acid *bis*(trifluoromethylsulfonyl) imide involves important changes in the structure of $[C_4mim][Tf_2N]$ ionic liquid network. Figure 8 schematically describes the structure of $[C_4mim][Tf_2N]$ ionic liquid network after contact with $H[Tf_2N]$ solution at 1.502 M and figure 9 with a 3.003 M solution. Bond water is shown in red, free water in blue and H_3O^+ in green.

Fig. 8. Schematic view the $[C_4mim][Tf_2N]$ ionic liquid frame contacted with $[HTf_2N]_{aq,init} = 1.502\text{ M}$

Fig. 9. Schematic view the $[C_4mim][Tf_2N]$ ionic liquid contacted with $[HTf_2N]_{aq,init} = 3.003\text{ M}$, (monophasic sample)

These figures respect the different proportions of chemical species based on their molar fractions given in Table 1. In addition, $-CF_3$ group does not take part in the formation of hydrogen bonds. This is confirmed by the small variation in chemical shift of fluorine as shown in Fig. 3.

3. Conclusion

$H[Tf_2N]$ has a salting in effect with $[C_4mim][Tf_2N]$ ionic liquid. This effect allows the extraction of water, H_3O^+ , $[Tf_2N^-]$ and $H[Tf_2N]$ species by $[C_4mim][Tf_2N]$ ionic liquid. As long as the molar fraction of water in the ionic liquid phase remains less than or equal to that of $[C_4mim^+]$ or $[Tf_2N^-]$ the structure of the network is maintained. Free water moves at its own speed and bound water is an inclusion in the $[C_4mim][Tf_2N]$ network. As soon as the molar fraction of the water is greater than that of $[C_4mim^+]$ or $[Tf_2N^-]$, the network of $[C_4mim][Tf_2N]$ ionic liquid is gradually dislocated until a single phase is formed between $[C_4mim][Tf_2N]$ and the $3.003\text{ M } H[Tf_2N]_{aq,init}$ solution. The cations and anions of the ionic liquid could form ion pairs surrounded by water and move together.

4. Experimental

4.1 Materials

High purity grade (99.9%) ionic liquid 1-butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide (henceforth indicated as [C₄mim][Tf₂N]), was purchased from Solvionic (Toulouse, France).

Deuterium oxide (D₂O, Sigma Aldrich) and dimethyl sulfoxide-d₆ ([d₆]DMSO, Sigma Aldrich) were of 99 atom % purity of deuterium. The N-H acid *bis*(trifluoromethylsulfonyl) imide (H[Tf₂N], >99%) was purchased from Kanto Chemical Co, Inc. and sodium trifluoroacetate (CF₃COONa, 98%) was purchased from Alfa Aesar. Acidic solutions were prepared with deionized water (ELGA PURELAB DV25) with a specific resistance of 18.2 MΩ·cm.

4.2 Samples preparation

Biphasic samples were setting with neat [C₄mim][Tf₂N] [23] and N-H acid *bis*(trifluoromethylsulfonyl) imide (henceforth indicated as H[Tf₂N]) aqueous solution. The H[Tf₂N] acid is a very hygroscopic salt, so heavy water was quickly added in the flask containing the powder. Initial solution was accurately titrated. Then, dilute solutions were prepared with a mix of heavy water and water. Aqueous solutions contained H[Tf₂N] at 0, 0.50, 1.00, 1.50, 2.00, 2.50 and 3.00 M. 1.144g of [C₄mimTf₂N] corresponding at 0.8 mL was precisely weighted in an Eppendorf tube (2 ml). 0.8 ml of dilute H[Tf₂N] acid solutions were added. The tubes were mixed during one hour on a mechanical shaker (IKA vibrax VXR basic) at $t = 23 \pm 2^\circ\text{C}$, at atmospheric pressure. Then, the samples were centrifuged for 4 min at 7000 rpm (Micro Star 12, VWR), the phases were separated and ILs phases were collected for NMR analysis.

NMR measurements required a double sample tube in order to separate the IL sample and the lock solvent. The coaxial inner tube (1.4 mm I.D., 1.7 mm O.D.) was filled with a small volume of ionic liquid (0.1 mL) and it was carefully sealed [47,48]. Then, the capillary tube was inserted into outer tube (regular 5 mm NMR glass tube) along with deuterated solvent, namely with [D₆]DMSO/CF₃COONa. Residual internal peaks of [D₆]DMSO (2.50 ppm) was used as ¹H chemical shifts reference [31,49], while the ¹⁹F chemical shifts were referenced to the peak of CF₃COONa dissolved in [D₆]DMSO (-74.00 ppm) [34]. Quantity of CF₃COONa in [D₆]DMSO was approximately equal to the mole number of [Tf₂N]⁻ anions in the capillary insert.

4.3 NMR Measurements

NMR acquisition method was described in our previous work [23,35]. Briefly, the one-dimensional spectra of ¹H and ¹⁹F were recorded on a Bruker 300 MHz instrument with a 5 mm PABBO BB-1H/D Z-GRD probe. The chemical shift uncertainty measurement was ± 0.01 ppm.

DOSY NMR experiments were carried out on a Bruker 600 MHz spectrometer equipped with a high strength z gradient probe DOTY Scientific, developing a pulse field gradient of 500 G/cm. Self-diffusion coefficients, *D*, of each species were measured with pulsed field gradient NMR experiments. Pulse sequence used was a stimulated echo with bipolar gradients and a longitudinal eddy current delay (BPLED) [50–52].

^1H DOSY NMR method measured $[\text{C}_4\text{mim}^+]$ self-diffusion coefficients that named D_+ , and the one of water D_{HOD} . ^{19}F DOSY NMR method measured $[\text{Tf}_2\text{N}^-]$ self-diffusion coefficients that named D_- . Thus, self-diffusion coefficients of IL constituent anion and cation were determined individually. Experimental errors on D were estimated at 10%. R was defined by the ratio D_+ divided by D_- [35].

4.4 Other Analytical Measurements

Protons' aqueous concentration was determined by acid-base titration (SCHOTT instrument Titroline easy) using NaOH standard solutions (Carlo Erba). Uncertainty of measuring concentration of H^+ or D^+ in aqueous phase was 2%. Total water content in ionic liquid phase was determined by coulometric Karl-Fisher technique (Hydranal[®]-Coulomat E, Fluka) and uncertainty was equal to 5%.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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BIBLIOGRAPHIE

- [1] M. Villanueva, A. Coronas, J. García, J. Salgado, Thermal Stability of Ionic Liquids for Their Application as New Absorbents, *Ind. Eng. Chem. Res.* 52 (2013) 15718–15727. <https://doi.org/10.1021/ie401656e>.
- [2] D.M. Fox, J.W. Gilman, A.B. Morgan, J.R. Shields, P.H. Maupin, R.E. Lyon, H.C. De Long, P.C. Trulove, Flammability and Thermal Analysis Characterization of Imidazolium-Based Ionic Liquids, *Ind. Eng. Chem. Res.* 47 (2008) 6327–6332. <https://doi.org/10.1021/ie800665u>.
- [3] E.E. Tereshatov, M.Y. Boltoeva, V. Mazan, M.F. Volia, C.M. Folden, Thallium Transfer from Hydrochloric Acid Media into Pure Ionic Liquids, *J. Phys. Chem. B.* 120 (2016) 2311–2322. <https://doi.org/10.1021/acs.jpcc.5b08924>.

- [4] N. Papaiconomou, S. Génand-Pinaz, J.-M. Leveque, S. Guittonneau, Selective extraction of gold and platinum in water using ionic liquids. A simple two-step extraction process, *Dalton Trans.* 42 (2013) 1979–1982. <https://doi.org/10.1039/C2DT32631K>.
- [5] N. Papaiconomou, I. Billard, E. Chainet, Extraction of iridium(IV) from aqueous solutions using hydrophilic/hydrophobic ionic liquids, *RSC Adv.* 4 (2014) 48260–48266. <https://doi.org/10.1039/C4RA06991A>.
- [6] J. Cui, L. Zhang, Metallurgical recovery of metals from electronic waste: A review, *Journal of Hazardous Materials.* 158 (2008) 228–256. <https://doi.org/10.1016/j.jhazmat.2008.02.001>.
- [7] F. Xie, T.A. Zhang, D. Dreisinger, F. Doyle, A critical review on solvent extraction of rare earths from aqueous solutions, *Minerals Engineering.* 56 (2014) 10–28. <https://doi.org/10.1016/j.mineng.2013.10.021>.
- [8] J. Rydberg, M. Cox, C. Musikas, G.R. Choppin, *Solvent Extraction Principles and Practice*, 2nd ed, Marcel Dekker, New York, 2004.
- [9] I. Billard, A. Ouadi, C. Gaillard, Liquid–liquid extraction of actinides, lanthanides, and fission products by use of ionic liquids: from discovery to understanding, *Analytical and Bioanalytical Chemistry.* 400 (2011) 1555–1566. <https://doi.org/10.1007/s00216-010-4478-x>.
- [10] I. Billard, A. Ouadi, E. Jobin, J. Champion, C. Gaillard, S. Georg, Understanding the Extraction Mechanism in Ionic Liquids: UO₂ 2+/HNO₃/TBP/C4-mimTf₂N as a Case Study, *Solvent Extraction and Ion Exchange.* 29 (2011) 577–601. <https://doi.org/10.1080/07366299.2011.566494>.
- [11] D.C. Gaillard, M. Boltoeva, I. Billard, S. Georg, V. Mazan, A. Ouadi, D. Ternova, C. Hennig, Insights into the Mechanism of Extraction of Uranium (VI) from Nitric Acid Solution into an Ionic Liquid by using Tri-n-butyl phosphate, *ChemPhysChem.* 16 (2015) 2653–2662. <https://doi.org/10.1002/cphc.201500283>.
- [12] Z. Kolarik, Ionic Liquids: How Far Do they Extend the Potential of Solvent Extraction of f-Elements?, *Solvent Extraction and Ion Exchange.* 31 (2013) 24–60. <https://doi.org/10.1080/07366299.2012.700589>.
- [13] M. Bonnaffé-Moity, A. Ouadi, V. Mazan, S. Miroshnichenko, D. Ternova, S. Georg, M. Sypula, C. Gaillard, I. Billard, Comparison of uranyl extraction mechanisms in an ionic liquid by use of malonamide or malonamide-functionalized ionic liquid, *Dalton Trans.* 41 (2012) 7526–7536. <https://doi.org/10.1039/C2DT12421A>.
- [14] S.A. Ansari, P.K. Mohapatra, V. Mazan, I. Billard, Extraction of actinides by tertiary amines in room temperature ionic liquids: evidence for anion exchange as a major process at high acidity and impact of acid nature, *RSC Adv.* 5 (2015) 35821–35829. <https://doi.org/10.1039/C5RA04882F>.
- [15] V.K. Manchanda, P.N. Pathak, Amides and diamides as promising extractants in the back end of the nuclear fuel cycle: an overview, *Separation and Purification Technology.* 35 (2004) 85–103. <https://doi.org/https://doi.org/10.1016/j.seppur.2003.09.005>.
- [16] C. Gaillard, V. Mazan, S. Georg, O. Klimchuk, M. Sypula, I. Billard, R. Schurhammer, G. Wipff, Acid extraction to a hydrophobic ionic liquid: the role of added tributylphosphate investigated by experiments and simulations, *Phys. Chem. Chem. Phys.* 14 (2012) 5187–5199. <https://doi.org/10.1039/C2CP40129K>.
- [17] V. Mazan, I. Billard, N. Papaiconomou, Experimental connections between aqueous–aqueous and aqueous–ionic liquid biphasic systems, *RSC Adv.* 4 (2014) 13371–13384. <https://doi.org/10.1039/C4RA00645C>.

- [18] V. Mazan, M.Y. Boltoeva, E.E. Tereshatov, C.M. Folden III, Mutual solubility of water and hydrophobic ionic liquids in the presence of hydrochloric acid, *RSC Adv.* 6 (2016) 56260–56270. <https://doi.org/10.1039/C6RA06791C>.
- [19] J.A. Widegren, A. Laesecke, J.W. Magee, The effect of dissolved water on the viscosities of hydrophobic room-temperature ionic liquids, *Chem. Commun.* (2005) 1610–1612. <https://doi.org/10.1039/B417348A>.
- [20] N. Sieffert, G. Wipff, The [BMI][Tf2N] Ionic Liquid/Water Binary System: A Molecular Dynamics Study of Phase Separation and of the Liquid–Liquid Interface, *J. Phys. Chem. B.* 110 (2006) 13076–13085. <https://doi.org/10.1021/jp061849q>.
- [21] Y. Danten, M.I. Cabaço, M. Besnard, Interaction of water diluted in 1-butyl-3-methyl imidazolium ionic liquids by vibrational spectroscopy modeling, *Journal of Molecular Liquids.* 153 (2010) 57–66. <https://doi.org/https://doi.org/10.1016/j.molliq.2009.07.001>.
- [22] T. Köddermann, C. Wertz, A. Heintz, R. Ludwig, The Association of Water in Ionic Liquids: A Reliable Measure of Polarity, *Angewandte Chemie International Edition.* 45 (2006) 3697–3702. <https://doi.org/10.1002/anie.200504471>.
- [23] V. Mazan, M. Boltoeva, Aqueous acidic solution - ionic liquid biphasic system: An original investigation by diffusion ordered spectroscopy nuclear magnetic resonance, *Journal of Molecular Liquids.* 269 (2018) 684–693. <https://doi.org/10.1016/j.molliq.2018.08.086>.
- [24] V.G. Anicich, A.D. Sen, Deuterium exchange in the systems of H₂O⁺/H₂O and H₃O⁺/H₂O, *International Journal of Mass Spectrometry and Ion Processes.* 172 (1998) 1–14. [https://doi.org/https://doi.org/10.1016/S0168-1176\(97\)00257-7](https://doi.org/https://doi.org/10.1016/S0168-1176(97)00257-7).
- [25] S. Katsuta, Y. Watanabe, Y. Araki, Y. Kudo, Extraction of Gold(III) from Hydrochloric Acid into Various Ionic Liquids: Relationship between Extraction Efficiency and Aqueous Solubility of Ionic Liquids, *ACS Sustainable Chem. Eng.* 4 (2016) 564–571. <https://doi.org/10.1021/acssuschemeng.5b00976>.
- [26] J. Foropoulos, D.D. DesMarteau, Synthesis, properties, and reactions of bis((trifluoromethyl)sulfonyl) imide, (CF₃SO₂)₂NH, *Inorg. Chem.* 23 (1984) 3720–3723. <https://doi.org/10.1021/ic00191a011>.
- [27] J.C. Duplan, L. Mahi, J.L. Brunet, NMR determination of the equilibrium constant for the liquid H₂O–D₂O mixture, *Chemical Physics Letters.* 413 (2005) 400–403. <https://doi.org/https://doi.org/10.1016/j.cplett.2005.07.005>.
- [28] 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. <https://doi.org/10.1021/acs.jpcc.5b02980>.
- [29] E.J. Cabrita, S. Berger, P. Bräuer, J. Kärger, High-Resolution DOSY NMR with Spins in Different Chemical Surroundings: Influence of Particle Exchange, *Journal of Magnetic Resonance.* 157 (2002) 124–131. <https://doi.org/https://doi.org/10.1006/jmre.2002.2574>.
- [30] E.J. Cabrita, S. Berger, HR-DOSY as a new tool for the study of chemical exchange phenomena, *Magnetic Resonance in Chemistry.* 40 (2002) S122–S127. <https://doi.org/10.1002/mrc.1082>.
- [31] G.R. Fulmer, A.J.M. Miller, N.H. Sherden, H.E. Gottlieb, A. Nudelman, B.M. Stoltz, J.E. Bercaw, K.I. Goldberg, NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist, *Organometallics.* 29 (2010) 2176–2179. <https://doi.org/10.1021/om100106e>.

- [32] E. Krahn, C. Marie, K. Nash, Probing organic phase ligand exchange kinetics of 4f/5f solvent extraction systems with NMR spectroscopy, *Coordination Chemistry Reviews*. 316 (2016) 21–35. <https://doi.org/https://doi.org/10.1016/j.ccr.2016.01.008>.
- [33] C.S. Johnson, Effects of Chemical Exchange in Diffusion-Ordered 2D NMR Spectra, *Journal of Magnetic Resonance, Series A*. 102 (1993) 214–218. <https://doi.org/https://doi.org/10.1006/jmra.1993.1093>.
- [34] R. Milton Silverstein, F.X. Webster, D.J. Kiemle, *Identification Spectrometrique de Composés Organiques*, De Boeck supérieur, 2007.
- [35] V. Mazan, M. Boltoeva, Insight into the ionic interactions in neat ionic liquids by Diffusion Ordered Spectroscopy Nuclear Magnetic Resonance, *Journal of Molecular Liquids*. 240 (2017) 74–79. <https://doi.org/https://doi.org/10.1016/j.molliq.2017.05.021>.
- [36] O. Russina, A. Triolo, L. Gontrani, R. Caminiti, D. Xiao, L.G.H. Jr, R.A. Bartsch, E.L. Quitevis, N. Pleckhova, K.R. Seddon, Morphology and intermolecular dynamics of 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ionic liquids: structural and dynamic evidence of nanoscale segregation, *Journal of Physics: Condensed Matter*. 21 (2009) 424121. <https://doi.org/10.1088/0953-8984/21/42/424121>.
- [37] O. Russina, A. Triolo, L. Gontrani, R. Caminiti, Mesoscopic Structural Heterogeneities in Room-Temperature Ionic Liquids, *J. Phys. Chem. Lett.* 3 (2012) 27–33. <https://doi.org/10.1021/jz201349z>.
- [38] D. Xiao, L.G. Hines, S. Li, R.A. Bartsch, E.L. Quitevis, O. Russina, A. Triolo, Effect of Cation Symmetry and Alkyl Chain Length on the Structure and Intermolecular Dynamics of 1,3-Dialkylimidazolium Bis(trifluoromethanesulfonyl)amide Ionic Liquids, *J. Phys. Chem. B*. 113 (2009) 6426–6433. <https://doi.org/10.1021/jp8102595>.
- [39] H.K. Stassen, R. Ludwig, A. Wulf, J. Dupont, Imidazolium Salt Ion Pairs in Solution, *Chemistry – A European Journal*. 21 (2015) 8324–8335. <https://doi.org/10.1002/chem.201500239>.
- [40] J. Dupont, On the solid, liquid and solution structural organization of imidazolium ionic liquids, *Journal of the Brazilian Chemical Society*. 15 (2004) 341–350.
- [41] L. Yu, B.S. Pizio, T.D. Vaden, Conductivity and Spectroscopic Investigation of Bis(trifluoromethanesulfonyl)imide Solution in Ionic Liquid 1-Butyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide, *J. Phys. Chem. B*. 116 (2012) 6553–6560. <https://doi.org/10.1021/jp301883e>.
- [42] Y. Umebayashi, S. Mori, K. Fujii, S. Tsuzuki, S. Seki, K. Hayamizu, S. Ishiguro, Raman Spectroscopic Studies and Ab Initio Calculations on Conformational Isomerism of 1-Butyl-3-methylimidazolium Bis-(trifluoromethanesulfonyl)amide Solvated to a Lithium Ion in Ionic Liquids: Effects of the Second Solvation Sphere of the Lithium Ion, *J. Phys. Chem. B*. 114 (2010) 6513–6521. <https://doi.org/10.1021/jp100898h>.
- [43] K. Fujii, T. Fujimori, T. Takamuku, R. Kanzaki, Y. Umebayashi, S. Ishiguro, Conformational Equilibrium of Bis(trifluoromethanesulfonyl) Imide Anion of a Room-Temperature Ionic Liquid: Raman Spectroscopic Study and DFT Calculations, *J. Phys. Chem. B*. 110 (2006) 8179–8183. <https://doi.org/10.1021/jp0612477>.
- [44] A.-L. Rollet, P. Porion, M. Vaultier, I. Billard, M. Deschamps, C. Bessada, L. Jouvensal, Anomalous Diffusion of Water in [BMIM][TFSI] Room-Temperature Ionic Liquid, *J. Phys. Chem. B*. 111 (2007) 11888–11891. <https://doi.org/10.1021/jp075378z>.

- [45] L.H. Lucas, J. Yan, C.K. Larive, E.R. Zartler, M.J. Shapiro, Transferred Nuclear Overhauser Effect in Nuclear Magnetic Resonance Diffusion Measurements of Ligand–Protein Binding, *Anal. Chem.* 75 (2003) 627–634. <https://doi.org/10.1021/ac020563o>.
- [46] E.S. Stoyanov, K.-C. Kim, C.A. Reed, A Strong Acid that Does Not Protonate Water, *J. Phys. Chem. A* 108 (2004) 9310–9315. <https://doi.org/10.1021/jp047409l>.
- [47] E. Martínez-Viviente, P.S. Pregosin, Low Temperature ¹H-, ¹⁹F-, and ³¹P-PGSE Diffusion Measurements. Applications to Cationic Alcohol Complexes, *Helvetica Chimica Acta* 86 (2003) 2364–2378. <https://doi.org/10.1002/hlca.200390190>.
- [48] Y. Lingscheid, S. Arenz, R. Giernoth, Heteronuclear NOE Spectroscopy of Ionic Liquids, *ChemPhysChem* 13 (2012) 261–266. <https://doi.org/10.1002/cphc.201100622>.
- [49] H.E. Gottlieb, V. Kotlyar, A. Nudelman, NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities, *J. Org. Chem.* 62 (1997) 7512–7515. <https://doi.org/10.1021/jo971176v>.
- [50] L. Avram, Y. Cohen, Diffusion NMR of molecular cages and capsules, *Chem. Soc. Rev.* 44 (2015) 586–602. <https://doi.org/10.1039/C4CS00197D>.
- [51] D.H. Wu, A.D. Chen, C.S. Johnson, An Improved Diffusion-Ordered Spectroscopy Experiment Incorporating Bipolar-Gradient Pulses, *Journal of Magnetic Resonance, Series A* 115 (1995) 260–264. <https://doi.org/https://doi.org/10.1006/jmra.1995.1176>.
- [52] C.S. Johnson, Diffusion ordered nuclear magnetic resonance spectroscopy: principles and applications, *Progress in Nuclear Magnetic Resonance Spectroscopy* 34 (1999) 203–256. [https://doi.org/10.1016/S0079-6565\(99\)00003-5](https://doi.org/10.1016/S0079-6565(99)00003-5).