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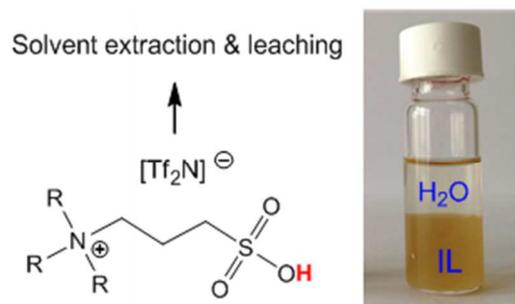
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Graphical abstract



Sulfonic acid functionalized ionic liquids can dissolve metal oxides and extract metal ions very efficiently.

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Sulfonic acid functionalized ionic liquids for dissolution of metal oxides and solvent extraction of metal ions

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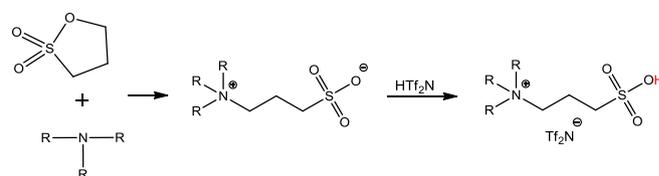
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New sulfonic acid functionalized ionic liquids (SAFILs) with bis(trifluoromethylsulfonyl)imide anions were synthesized. These ionic liquids are strong Brønsted acids and can solubilize metal oxides. Water-immiscible SAFILs were used as organic phase in solvent extraction studies.

Inorganic and organic acids are important in many chemical processes including organic synthesis, catalysis, processing of (bio)materials, dissolution of metal ores and as extractants in solvent extraction. Unfortunately, many (strong) acids produce noxious and corrosive fumes. Acid-functionalized ionic liquids are promising new materials as they combine the advantage of a liquid (large contact area), with the advantages of solid-state acids (negligible vapor pressure and reusability).^{1,2} Another advantage is their versatility: an infinite number of ionic liquids (ILs) can be designed based on different cations, anions and functional groups.³ The two main classes of Brønsted-acidic ILs are the carboxyl functionalized ILs and the sulfonic acid functionalized ILs (SAFILs).^{2,4-16} Carboxyl functionalized ILs such as betainium bis(trifluoromethylsulfonyl)imide [Hbet][Tf₂N], have been used successfully for the dissolution of metal oxides and the separation of metals by solvent extraction.^{4,5,17-23} So far, SAFILs have not been used for solvent extraction since no biphasic SAFIL–H₂O systems have been reported. The currently known SAFILs are hydrophilic (water miscible) due to the polar sulfonic acid functionalized cation and the choice of anion (Cl⁻, Br⁻, NO₃⁻, HSO₄⁻, BF₄⁻, PF₆⁻, CH₃CO₂⁻, CF₃SO₃⁻, CH₃SO₃⁻, *p*-CH₃C₆H₄SO₃⁻, etc).^{1,2,7-16,24,25} Because of their high melting points and viscosities, these SAFILs have been used mainly in diluted form as homogeneous catalyst in organic synthesis and for the hydrolysis of carbohydrates.^{2,7-16} Their zwitterions have also been of interest as liquid crystals and as electrolytes in lithium ion batteries.²⁶⁻³⁰ SAFILs with the right physical properties can open the way to new applications using the SAFILs in their pure form.

In this Communication, we introduce a series of new quaternary ammonium- and phosphonium-based SAFILs with bis(trifluoromethylsulfonyl)imide (Tf₂N⁻) anions. The very stable Tf₂N⁻ anion is the conjugated base of the super acid HTf₂N and has a low coordinating ability which explains the superior physical properties of Tf₂N-containing ILs, including a relatively low viscosity, low melting point and high thermal stability.^{26,31} These SAFILs can therefore be used undiluted. The combination of long alkyl chains and Tf₂N⁻ anions also allows synthesizing hydrophobic (water-immiscible) SAFILs. The new hydrophobic SAFILs were used as organic phase in solvent extraction systems for metal ions, while hydrophilic SAFILs were used for dissolution of metal oxides.

The SAFILs were prepared by reacting a trialkylamine or trialkylphosphine with 1,3-propanesultone to form sulfonate zwitterions (Scheme 1).^{2,10,32,33} Then, a stoichiometric amount of the acid HTf₂N was added to the zwitterion to obtain the ionic liquid in quantitative yield. Detailed synthesis procedures and characterization data are provided in the Electronic Supplementary Information. The physical properties of the ILs are summarized in Table 1. All the compounds are room-temperature ILs. When cooling the ILs in a DSC instrument, a glass transition was observed (no crystallization).



Scheme 1. Synthetic strategy for trialkylammoniumpropanesulfonic acid bis(trifluoromethylsulfonyl)imide ILs, abbreviated as [N_{RRR}C₃SO₃H][Tf₂N]. The same scheme applies for the phosphonium analogues [P_{RRR}C₃SO₃H][Tf₂N]. R = methyl (1), ethyl (2), propyl (3), butyl (4), hexyl (6), octyl (8) or phenyl (Ph).

Table 1. Physical properties of the SAFILs described in this work.

Nr	Ionic liquid	T _g (°C) ^(a)	Viscosity (cP) 30 °C / 80 °C	T _{deg} (°C) ^(b)
1	[PPh ₃ C ₃ SO ₃ H][Tf ₂ N]	-39	≥ 10000 / 482	319
2	[N ₁₁₁ C ₃ SO ₃ H][Tf ₂ N]	-48	3230 / 180	275
3	[N ₂₂₂ C ₃ SO ₃ H][Tf ₂ N]	-57	1463 / 79	275
4	[N ₃₃₃ C ₃ SO ₃ H][Tf ₂ N]	-37	≥ 10000 / 229	275
5	[N ₄₄₄ C ₃ SO ₃ H][Tf ₂ N]	-40	≥ 10000 / 310	275
6	[P ₄₄₄ C ₃ SO ₃ H][Tf ₂ N]	-50	1888/119	307
7	[N ₆₆₆ C ₃ SO ₃ H][Tf ₂ N]	-61	1347/111	270
8	[P ₆₆₆ C ₃ SO ₃ H][Tf ₂ N]	-64	621/62	300
9	[N ₈₈₈ C ₃ SO ₃ H][Tf ₂ N]	-61	1703/125	265
10	[P ₈₈₈ C ₃ SO ₃ H][Tf ₂ N]	-56	1916/116	320

^(a) Glass transition temperature (T_g): measured with DSC.

^(b) Degradation temperature (T_{deg}): measured by TGA (5 °C·min⁻¹, N₂)

The TGA curves are shown in Figure S1.

The phosphonium ILs have a better thermal stability and lower viscosity than their ammonium analogues, although the viscosity of these ILs remains relatively high.³⁴ Increasing the temperature or adding water (Figure S2), greatly reduces the viscosity for all ILs which makes them easier to handle. SAFILs are usually hydrophilic due to the polar sulfonic acid group on the cation. To counter this effect, long alkyl side chains can be used in combination with the hydrophobic anion Tf₂N⁻. The different SAFILs were contacted with water, acetone and toluene (1:1 wt/wt ratio) to test their miscibility (Table 2). SAFILs (**1**, **2**, **3**, **4**, **5**, **6**) were found to be hydrophilic (water-miscible) and are among the rare examples of water-miscible ILs with the Tf₂N⁻ anion. SAFILs (**7**, **8**, **9**, **10**) were found to be hydrophobic (water-immiscible). Without additives, the hydrophobic SAFILs form a gel when contacted with water. Gel formation can be suppressed by adding an alcohol as a modifier to the system. The best results were obtained adding ethanol (≈ 5 wt%) to SAFIL (**8**) or (**9**), and butanol (≈ 5 wt%) to SAFIL (**10**). The use of higher alcohols has been reported for solvent extraction systems with non-polar solvents like toluene.^{35–38} Stable biphasic systems with a low viscosity and fast phase separation could be obtained this way for the *water-immiscible* SAFILs (**8**, **9**, **10**) (Figure 1). An aqueous biphasic system with a sharp phase boundary was observed for the *water-miscible* SAFIL (**6**) [P₄₄₄C₃SO₃H][Tf₂N] after addition of sulfuric acid (1–2 M) to the aqueous phase (Figure 1). The acid suppresses the deprotonation of the sulfonic acid group of the IL and therefore decreases the polarity of the IL, thus inducing phase separation. This hypothesis is supported by the fact that the salting-out agent Na₂SO₄ did not cause phase separation.³⁹

Table 2. Density (g·cm⁻³) (25 °C) and miscibility of the SAFILs in water, acetone and toluene (1:1 ratio wt/wt).

IL	1	2	3	4	5	6	7	8	9	10
Density	1.50	1.57	1.55	1.42	1.35	1.36	1.32	1.26	1.17	1.20
Water	+	+	+	+	+	+	-	-	-	-
Acetone	+	+	+	+	+	+	+	+	+	+
Toluene	-	-	-	-	-	-	+	+	+	+

Miscible (+) or immiscible (-)

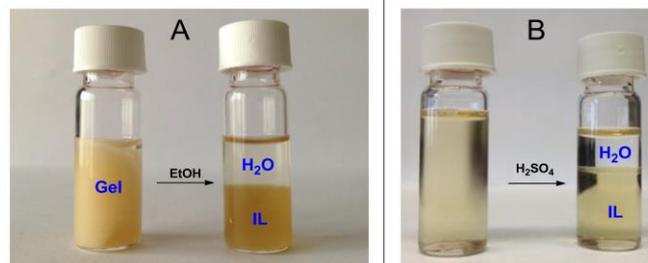
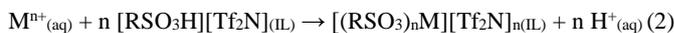


Figure 1. (A) The slightly colored, water-immiscible SAFIL (**9**) is shown as a [N₈₈₈C₃SO₃H][Tf₂N]-H₂O system (1:1 ratio wt/wt), before and after addition of ethanol (5 wt%) to suppress the gel formation. (B) The water-miscible SAFIL (**6**) is shown as a [P₄₄₄C₃SO₃H][Tf₂N]-H₂O system (1:1 ratio wt/wt) before and after adding sulfuric acid (2 M) to obtain an aqueous biphasic system.

The existence of biphasic SAFIL-H₂O systems opens the way to solvent extraction of metal ions. To the best of our knowledge, no reports exist on the use of sulfonic acid functionalized ILs for solvent extraction. Not much is known about solvent extraction with sulfonic acid extractants either, because their surfactant properties often cause micelle formation, which hampers phase separation.^{40,41} A few papers mention solvent extraction using ILs with sulfonate anions, e.g. 1-butyl-3-methylimidazolium nonafluorobutanesulfonate, but their extraction mechanism is based on cation exchange (eq 1), leading to loss of IL cations to the aqueous phase.^{42–44} On the other hand, the ILs described in this work have sulfonic acid functionalized cations, which can be deprotonated to form zwitterions. The SAFILs with long alkyl chains (hexyl, octyl) have water-immiscible zwitterions, which means that the acidic protons can be exchanged by metal ions, generally without transfer of IL cations or anions to the water phase (eq 2). This proton exchange mechanism is controlled by the pH. The same mechanism has been observed for ILs with carboxyl-functionalized cations such as [Hbet][Tf₂N].^{17,19}



The water-immiscible SAFIL [N₈₈₈C₃SO₃H][Tf₂N] was contacted with water (1:1 ratio wt/wt) containing various metal chloride salts (1 mmol·L⁻¹). Ethanol was added (5 wt%) to obtain a stable biphasic system with a sharp phase boundary (Figure 1). The metal concentrations were measured by TXRF to determine the distribution ratio *D* (eq 3) and percentage extraction %*E* (eq 4):

$$D = \frac{[M]_{IL}}{[M]_{aq}} \quad (3)$$

$$\%E = \frac{n_{IL}}{n_{IL} + n_{aq}} \quad (4)$$

Here [M]_{IL} and [M]_{aq} are the equilibrium concentrations and *n* the corresponding number of moles in the IL phase and aqueous phase, respectively. Figure 2 shows the extraction results without pH modification. The pH of the water phase is then in the range 0–0.2.

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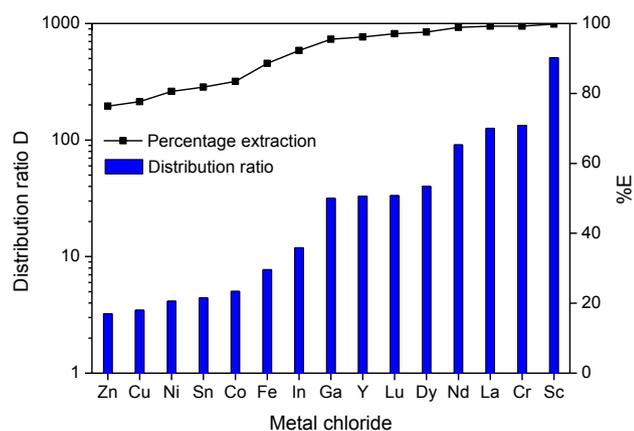


Figure 2. Distribution ratio (D) and percentage extraction ($\%E$) in $[\text{N}_{888}\text{C}_3\text{SO}_3\text{H}][\text{Tf}_2\text{N}]-\text{H}_2\text{O}$ for the metal chlorides ($1 \text{ mmol}\cdot\text{L}^{-1}$): Zn(II), Cu(II), Ni(II), Sn(II), Co(II), Fe(III), In(III), Ga(III), Y(III), Lu(III), Dy(III), Nd(III), La(III), Cr(III), Sc(III).

The SAFIL $[\text{N}_{888}\text{C}_3\text{SO}_3\text{H}][\text{Tf}_2\text{N}]$ is able to extract a wide range of metal ions (Figure 2), with a particularly high affinity for rare-earth ions especially compared to the affinity of carboxylic acid extractants and ILs at similar pH values.^{17,45} Notice that the lanthanide ions are extracted in the reverse order ($\text{La(III)} > \text{Nd(III)} > \text{Dy(III)} > \text{Lu(III)}$) than the one expected on the basis of their charge density. This could be due to sterical hindrance of the sulfonate groups and octyl side chains which causes smaller lanthanides to be less efficiently coordinated. This reversal of the lanthanide extraction sequence is unusual, but sterical hindrance of ligands is known to influence the extraction sequence of the lanthanides and to eventually fully reverse it.⁴⁵⁻⁴⁸ A typical example is the reversal when switching from linear thiocyanate ligands to more sterically demanding nitrate ligands in quaternary ammonium extraction systems.⁴⁷ Preston and du Preez attributed this behavior to the interplay of electrostatic and steric effects.⁴⁹ Since the extraction occurs via a proton exchange mechanism (eq 2), the extraction efficiencies and mutual separation of the metal ions can be modified by adjusting the pH of the aqueous phase (Figure 3).⁴⁵

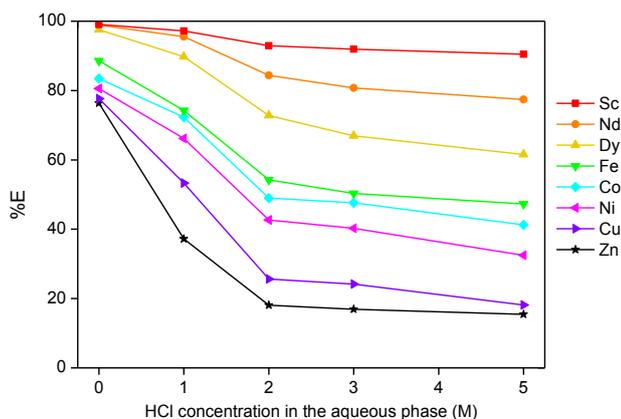


Figure 3. Influence of the initial acid concentration in the aqueous phase on the extraction (%) of Zn(II), Cu(II), Ni(II), Co(II), Fe(III), Dy(III), Nd(III), Sc(III) ions.

Finally, the dissolution of metal oxides in the strongly Brønsted acidic SAFILs ($\text{pK}_a \approx -2$) was tested.² The dissolution of metal oxides has been described in detail for carboxylic acid functionalized ILs, but has not been investigated for the more strongly acidic SAFILs.^{4,5,20,22} Metal salts (e.g. NaCl) are poorly soluble in conventional ILs due to the inefficient anion solvation.²⁰ Brønsted-acidic ILs can therefore selectively dissolve metal oxides because metal oxides form only metal cations and water when reacted with an acid (eq 5). This offers opportunities for the selective leaching of metal oxides from a mixture of minerals or salts or for the cleaning of oxidized metal surfaces.²⁰ Water can be added to accelerate the dissolution kinetics by lowering the viscosity and improving proton exchange, but the selectivity towards metal oxides is then reduced.^{4,5,20}



The dissolution of a range of metal oxides was tested in SAFIL– H_2O systems (1:1 ratio wt/wt) at 80°C for SAFILs (**2**, **3**, **9**). In these conditions, the IL solutions have a low viscosity ($< 25 \text{ cP}$) (Figure S2). It was found that these ILs could dissolve large (stoichiometric) amounts of ZnO, CuO, NiO, La_2O_3 , Nd_2O_3 , Y_2O_3 , MnO, CoO, Co_3O_4 , Fe_2O_3 and to a lesser extent also TiO_2 , Al_2O_3 , Cr_2O_3 , WO_3 . This is an improvement compared to the carboxyl functionalized IL $[\text{Hbet}][\text{Tf}_2\text{N}]$ which cannot efficiently dissolve the more inert oxides: CoO, Co_3O_4 , Fe_2O_3 , TiO_2 , Al_2O_3 , Cr_2O_3 , WO_3 .^{4,5} The strong acidity and high affinity of SAFILs for metal ions makes them very suitable for the dissolution of metal oxides (Figure 4). For the same reason, methanesulfonic acid has also been highlighted as a promising leaching agents since it can dissolve a wide range of metal salts, many of them in significantly higher concentrations than in hydrochloric or sulfuric acid.⁵⁰ The use of IL analogues is therefore certainly an interesting evolution since ILs have the additional advantage of a negligible vapor pressure and improved reusability.

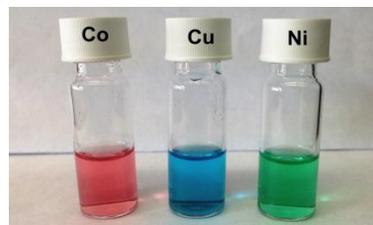


Figure 4. Dissolution of Co_3O_4 , CuO and NiO in $[\text{N}_{111}\text{C}_3\text{SO}_3\text{H}][\text{Tf}_2\text{N}]$ (50 mg/g).

In summary, we have synthesized a range of new sulfonic acid functionalized ionic liquids (SAFILs) with Tf_2N^- anions showing excellent physical properties. Solvent extraction of metal ions was demonstrated using the new hydrophobic (water-immiscible) SAFILs. The highly acidic SAFILs were also used for the dissolution of metal oxides. This work will hopefully stimulate further research on these promising ILs besides their current use as homogeneous catalysts.

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Notes and references

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Electronic Supplementary Information (ESI) available: List of used chemicals, equipment, synthesis procedures for the ILs and characterization data (NMR, CHN, TGA, DSC, viscosity). See DOI: 10.1039/c000000x/

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