

COMMUNICATION

Alkylsulfuric acid ionic liquids: a promising class of strongly acidic room-temperature ionic liquids

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Strongly acidic ($pK_a \approx -3.5$) room-temperature ionic liquids (ILs) with $-\text{OSO}_3\text{H}$ functionalized cations are introduced. The strong acidity, easy synthesis, and better physical properties of these $\text{R}-\text{OSO}_3\text{H}$ ILs make them excellent alternatives to the well-known sulfonic acid ($\text{R}-\text{SO}_3\text{H}$) ILs, especially in the domain of metal processing.

Brønsted-acid ionic liquids (ILs) are a very interesting class of solvents.¹ They are highly tunable, soluble in a wide range of organic solvents, and often also reusable. The fact that they are non-volatile (no toxic fumes) also makes them safer and more convenient to handle than traditional mineral acids.¹ Acidic ILs have been used as catalysts in organic synthesis, but also for the dissolution of metal oxides, and as acidic extractants in solvent extraction of metal ions.¹⁻¹² Currently, the two main classes of Brønsted-acid ILs are the carboxylic acid ($-\text{COOH}$) ILs and sulfonic acid ($\text{R}-\text{SO}_3\text{H}$) ILs.^{1,4,13} The acid group is located on the IL cation so that upon deprotonation zwitterions are formed, which can effectively coordinate to metal ions.^{1,5,10} Recently, we have synthesized the first examples of water-immiscible sulfonic acid ILs, which were liquid at room temperature.¹⁰ Sulfonic acid extractants are typically avoided in traditional solvent extraction due to their detergent properties, micelle formation and low solubility in the organic phase.¹⁴ These issues were solved by incorporating the sulfonic acid extractants in the structure of an IL.¹⁰ However, the high charge density of the sulfonic acid group still caused a high viscosity, a tendency to form gels, and the need to use long alkyl chains (hexyl, octyl) to make the sulfonic acid ILs water immiscible.¹⁰ The synthesis of these compounds was therefore relatively expensive since cyclic sultones and amines with long alkyl chains were required.^{1,10} As an answer to these problem, we present in this Communication a different class of strongly acidic room-temperature ILs which are simple to make and contain alkylsulfuric acid ($\text{R}-\text{OSO}_3\text{H}$) functionalized cations (Figure 1). The synthesis, stability and physical properties are discussed, as

well as their ability to dissolve and extract metal ions. The focus in this work is on metal processing in these ILs, but the increased acidity of $\text{R}-\text{OSO}_3\text{H}$ groups ($pK_a \approx -3.5$),¹⁵ compared to sulfonic acids ($\text{R}-\text{SO}_3\text{H}$) ILs ($pK_a \approx -2$),¹⁶ should also improve their efficiency as Brønsted-acid catalyst and could be the object of future research.^{15,17} The stronger acidity makes a difference for the protonation of organic species (e.g. carboxylic acids, aldehydes, ketones) in water-free solvents and therefore for the catalysis of certain reactions such as the Fischer esterification.^{1,3,6,13,15-22} The additional oxygen atom of the $\text{R}-\text{OSO}_3\text{H}$ group, compared to sulfonic acids ($\text{R}-\text{SO}_3\text{H}$), not only increases the acidity, but also decreases the charge density of the end group, thus lowering the viscosity and increasing the hydrophobicity. The direct consequence is that we were able to synthesize low-viscous, room-temperature ILs that are water-immiscible even with short alkyl chains (methyl, ethyl), instead of the hexyl or octyl chains required for similar sulfonic acid ILs.¹⁰ Furthermore, alkylsulfuric acids and alkylsulfates are known for their low toxicity and biodegradability, which is why they are used as detergents in many household cleaning products (e.g. sodium dodecyl sulfate, SDS).^{23,24} It is also possible to synthesize certain alkylsulfuric acid ILs starting from the widely available biomolecule and animal food additive *choline chloride*.^{15,17,25,26} These ILs thus fit in the trend towards more bio-based and biodegradable ILs.²⁵⁻³⁰

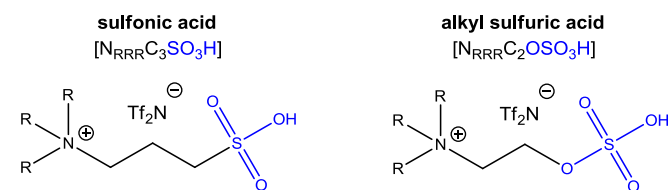
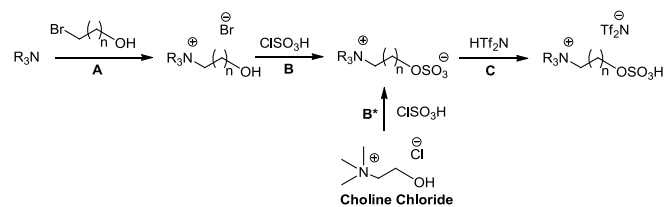


Figure 1. Comparison between the well-known sulfonic acid ILs (left) and the alkylsulfuric acid ILs (right), described in this work.



Scheme 1. General synthesis method for alkylsulfuric acid functionalized ammonium-based ILs. The same method applies for phosphonium-based ILs.

The detailed synthesis and characterization are described in the ESI, but a schematic overview is given here (Scheme 1). The general synthesis route started by alkylating a trialkylamine or trialkylphosphine with a linear ω -bromoalcohol (A), followed by the addition of chlorosulfonic acid to convert the alcohol to a sulfate group (B).³¹ The zwitterion was then reacted with bistriflimic acid (HTf₂N) to produce the desired IL (C). The strong acidity of the IL cation makes it mandatory to use IL anions derived from even stronger acids, in order to avoid cross-protonation. Bis(trifluoromethylsulfonyl)imide (bistriflimide, Tf₂N⁻) anions were chosen due to their tendency to form stable and low-viscous ILs.³² The synthesis route depicted in Scheme 1 is flexible and allows control over the length of the alkyl chains on the amine and the length of the carbon linker attached to the -OSO₃H group. Alternatively, the bio-compound *choline chloride*^{25,26} can be used as building block to make the trimethyl IL in a convenient two-step method (B*^{15,17}). An overview of the synthesized ILs and their physical properties is given in Table 1. The ILs are all liquid at room temperature and have relatively low viscosities even at 25 °C. Note that the glass transition temperatures and viscosities are lower than for the equivalent sulfonic acid ILs reported in our previous work.¹⁰ We attributed this to the fact that the extra oxygen atom has an electron-withdrawing effect, thus lowering the intermolecular forces. The lower charge density of the alkylsulfuric acid group also translates in a more hydrophobic character, compared to sulfonic acid ILs.¹⁰ The alkylsulfuric acid ILs cover a broad range of miscibility from water-miscible to miscible in hydrocarbons (Table 2), which is useful for a potential use as Brønsted-acid catalysts and even for non-aqueous (IL/hydrocarbon) solvent extraction systems.

Table 1. Physical properties of the ionic liquids described in this work.

Nr	Ionic liquid	T _g (°C) ^(a)	Viscosity (cP) 25 °C	Density 25 °C (g cm ⁻³)
1	[N ₁₁₁ C ₂ OSO ₃ H][Tf ₂ N]	-28	324	1.58
2	[N ₂₂₂ C ₂ OSO ₃ H][Tf ₂ N]	< -80	378	1.46
3	[N ₆₆₆ C ₂ OSO ₃ H][Tf ₂ N]	< -80	1950	1.30
4	[N ₈₈₈ C ₂ OSO ₃ H][Tf ₂ N]	< -80	1538	1.28
5	[P ₄₄₄ C ₂ OSO ₃ H][Tf ₂ N]	< -80	739	1.40
6	[P ₈₈₈ C ₂ OSO ₃ H][Tf ₂ N]	< -80	1332	1.23
7	[N ₁₁₁ C ₃ OSO ₃ H][Tf ₂ N]	< -80	1337	1.59
8	[N ₁₁₁ C ₄ OSO ₃ H][Tf ₂ N]	< -80	1258	1.54

^(a) Glass transition temperature (T_g): measured by DSC (lower limit: -80 °C)

Table 2. Miscibility of the alkylsulfuric acid ILs in different solvents.

ILs	1	2	3	4	5	6	7	8
Water	±	-	-	-	gel	gel	+	-
DMF	+	+	±	±	+	±	+	+
Acetonitrile	+	+	+	+	+	±	+	+
EG	+	+	-	-	-	-	+	+
Methanol	+	+	-	-	+	-	+	+
Ethanol	-	+	+	±	+	-	+	+
Acetone	+	+	+	+	+	+	+	+
Toluene	-	-	±	+	-	+	-	+
<i>n</i> -Heptane	-	-	-	-	-	-	-	+

^a Miscible (+), partially miscible (±) or immiscible (-)

The increased hydrophobicity of these ILs compared to sulfonic acid ILs, is also evident from the fact that the ILs with ethyl chains or longer (IL 2–6) are water-immiscible (Table 2), while the analogue sulfonic acid ILs [N_{RRR}C₃SO₃H][Tf₂N] required more expensive precursors with hexyl or octyl chains to be immiscible in water.¹⁰ IL 1 is particularly interesting since it can form thermomorphic aqueous biphasic systems (ABS) when salts (e.g. NaCl, Na₂SO₄) are added to induce phase separation.^{33–35} Such thermomorphic biphasic systems can mix reversibly with water above a certain temperature, called the cloud point temperature.^{8,34,36–39} Similar behavior has been observed for the analogue carboxyl-functionalized IL: betainium bistriflimide [Hbet][Tf₂N] and this phenomenon is of great interest for solvent extraction as it effectively removes the phase boundary.^{8,37,38,40} An overview of the influence of the salt concentration on the cloud point temperature of this ABS system is given in ESI (Table S2). The best results were found for 1.0 M NaCl or 0.5 M Na₂SO₄, with excellent phase separation at room temperature and relatively low cloud point temperatures around 48 °C. Figure 2 shows the mixing and demixing of IL 1 with water (1:1 wt/wt), containing 1.5 M of NaCl. The fact that IL 1 shows this interesting behavior is a lucky coincidence since this is the IL that can be prepared from choline chloride (Scheme 1).

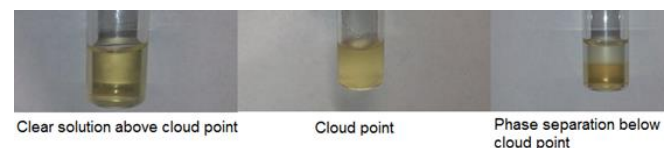


Figure 2. Thermomorphic mixing/demixing of the [N₁₁₁C₂OSO₃H][Tf₂N]:H₂O system (1:1 wt/wt) with NaCl (1.5 M). The cloud point of this system is 48 °C.

Alkylsulfates can decompose in water to form the corresponding alcohol and sulfuric acid, but it is generally accepted that they have a relatively good kinetic resistance against hydrolysis.^{27,33,41,42} To test the stability of the ILs, thermogravimetric analysis (TGA) was first carried out using a nitrogen atmosphere, which showed a degradation temperature of approximately 330 °C (ESI, Figure S1). Then, the stability of the ILs was tested with an air atmosphere (20–150 °C) and mixed with water (1:1 wt/wt) (20–80 °C) over a 24 h interval, using NMR to monitor the degradation, but no signs of degradation were observed (ESI, Table S3).

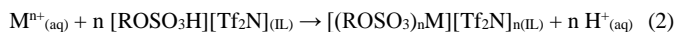
From previous work, it is known that acidic ILs such as carboxylic acid ILs are able to efficiently dissolve metal oxides since only water and metal cations are formed, which can be solvated by the IL zwitterions created during the deprotonation.^{2,5,9,43} Metal salts (e.g. NaCl) are poorly soluble in these ILs due to the inefficient anion solvation.⁹ These ILs thus offer the possibility to selectively dissolve metal oxides.⁹ For alkylsulfuric acid ILs, the dissolution reaction of metal oxides (e.g. CuO) could be as follows (eq 1):



The dissolution of a range of metal oxides was tested in IL–H₂O systems (20 wt% H₂O) at 80 °C (24 h) using [N₁₁₁C₂OSO₃H][Tf₂N]. This ionic liquid could efficiently dissolve metal oxides including CaO, CuO, NiO, La₂O₃, Nd₂O₃, Co₃O₄ and Fe₂O₃, which is not surprising considering its strong acidity and high affinity for metal ions. The alkylsulfuric acid IL allows the dissolution of the same metal oxides as the analogue sulfonic acid IL [N₁₁₁C₃SO₃H][Tf₂N] (pK_a ≈ -2),¹⁰ prepared in previous work. This is expected due to the leveling effect of water. However, differences are observed when comparing the dissolution of metal oxides with the carboxylic acid IL [N₁₁₁C₁COOH][Tf₂N] (= [Hbet][Tf₂N]) (pK_a ≈ 2).^{5,9,43} This ionic liquid cannot efficiently dissolve inert oxides such as Fe₂O₃ or Co₃O₄, but it has nevertheless shown a lot of promise for the treatment and recycling of metal-rich products and waste residues, due to its acidity, metal affinity and thermomorphic behavior.^{2,9} The more strongly acidic alkylsulfuric acid ILs could be useful to speed up these leaching processes or allow the treatment of more inert residues such as bauxite residue or iron oxide slags.⁴⁴ The alkylsulfuric acid ILs are very strong acids and do not produce noxious fumes like most mineral acids (e.g. HCl, HNO₃).^{1,16} This makes them particularly attractive as potentially green leaching agents. [N₁₁₁C₂OSO₃H][Tf₂N] is preferred compared to the analogues with longer alkyl chains due to its easy synthesis and lower viscosity. An overview and comparison of metal oxide dissolution by these ILs is given in the ESI (Table S4).

The water-immiscible alkylsulfuric acid ILs can also be used as organic phase to extract metal ions from aqueous solutions. These are interesting extractants, as their very strong acidity makes it possible to efficiently extract metal ions even from highly acidic solutions (pH < 0). This is not possible with weaker acids such as carboxylic acid or phosphoric acid extractants.⁴⁵ Unfortunately, alkylsulfuric acid or alkylsulfate extractants are difficult to use in traditional solvent extraction due to their detergent properties.^{14,46,47} These polar extractants do not dissolve in the organic phase unless long alkyl chains are used, which in their turn cause micelle formation. Therefore, very little is known about solvent extraction with alkylsulfuric acid or alkylsulfate extractants. ILs thus offer a unique opportunity to study these “inaccessible” extractants, since no detergent behavior is observed and stable biphasic systems were obtained. Furthermore, the use of a pure ionic liquid phase with extractants incorporated in their structure, drastically increases the extractant concentration compared to organic solvents that typically have a low solubility for such acidic extractants.^{48,49} The advantage of incorporating alkylsulfuric acid groups on the cation instead of using ILs with alkylsulfate anions is that acidic cations form

zwitterions upon deprotonation, which can coordinate the metal ions.^{11,38} This means that acidic protons are exchanged by metal ions (eq 2), instead of transferring organic cations to the aqueous phase as is commonly the case for ionic liquids with extracting anions (e.g. alkylsulfate anions).^{45,50,51}



The extraction efficiency was tested by contacting the ILs [N₁₁₁C₂OSO₃H][Tf₂N] and [N₈₈₈C₂OSO₃H][Tf₂N] with aqueous solutions (1:1 ratio wt/wt), containing metal chlorides (1 mmol L⁻¹, pH 2.7). NaCl (1.5 M) was added to the [N₁₁₁C₂OSO₃H][Tf₂N] system to obtain a biphasic system. After extraction, the metal concentrations were measured by total reflection X-ray fluorescence (TXRF) to determine the percentage extraction %E (eq 3):

$$\%E = \frac{n_{\text{IL}}}{n_{\text{IL}} + n_{\text{aq}}} \times 100 \quad (3)$$

Here, *n*_{IL} and *n*_{aq} are the number of moles of the metal ion in the IL phase and aqueous phase, respectively. The results are shown in Figure 3. The extraction efficiencies are intermediate between carboxyl-functionalized ILs such as [Hbet][Tf₂N] (poor extraction for most metal ions),³⁸ and sulfonic acid ILs which fully extract most studied metal ions from chloride solutions (> 80%).¹⁰ This trend is logical based on the charge density of the functional group: R-COO⁻ < R-OSO₃⁻ < R-SO₃⁻. The intermediate extraction efficiency of the alkylsulfuric acid ILs is useful as it allows separation of metal ions. It is also very interesting to observe that the inversed extraction trend for rare-earth ions (La > Nd > Dy > Y), previously observed for sulfonic acid ILs, also occurs for these alkylsulfuric acid ILs. This confirms the hypothesis that bulky functional groups lead to a reversal of the normal (charge density based) extraction series for the rare-earth ions (La < Nd < Dy < Y), which is observed for carboxylic acid extractants.^{10,38,52,53}

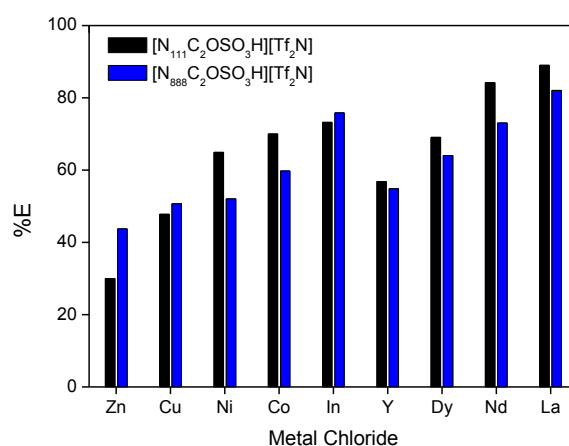


Figure 3. Percentage extraction (%E) from a metal chloride solution (1 mmol L⁻¹, pH 2.7) using the IL [N₁₁₁C₂OSO₃H][Tf₂N] and [N₈₈₈C₂OSO₃H][Tf₂N] as org. phase. Zn(II), Cu(II), Ni(II), Co(II), In(III), Y(III), Dy(III), Nd(III) and La(III) were tested.

In conclusion, this Communication discusses a promising class of very acidic ILs with alkylsulfuric acid functionalized cations. These

ILs can be synthesized cheaply and offer improved physical properties compared to sulfonic acid ILs, which are used as Brønsted-acid catalysts in organic synthesis. The stronger acidity of alkylsulfuric acid ILs and their miscibility in various organic solvents makes them excellent alternatives for sulfonic acid ILs. This Communication also focusses on the possibility of metal processing in these ILs, including the dissolution of metal oxides and the extraction of metal ions from aqueous solutions. These strongly acidic extractants can efficiently extract metal ions even from very acidic solutions (pH < 0), which is not possible with commonly used carboxylic acid or phosphoric acid extractants. Furthermore, incorporating alkylsulfuric acid groups into the structure of the IL finally allowed the study of this type of extractants, since in traditional solvent extraction alkylsulfuric acid extractants are difficult to use due to their strong detergent properties. These versatile alkylsulfuric acid ILs thus open up a range of interesting applications and it is our hope that this Communication will stimulate further research interest for these ILs.

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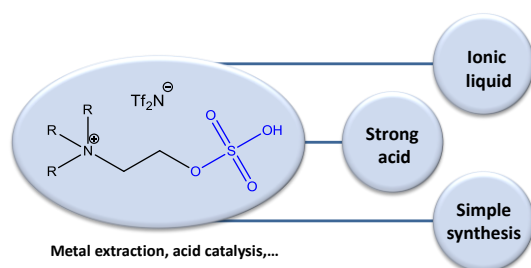
Notes and references

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

1. A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes and J. H. Davis, *J. Am. Chem. Soc.*, 2002, **124**, 5962-5963.
2. D. Dupont and K. Binnemans, *Green Chem.*, 2015, **17**, 2150-2163.
3. D. Fang, X.-L. Zhou, Z.-W. Ye and Z.-L. Liu, *Ind. Eng. Chem. Res.*, 2006, **45**, 7982-7984.
4. Z. Fei, D. Zhao, T. J. Geldbach, R. Scopelliti and P. J. Dyson, *Chem-Eur. J.*, 2004, **10**, 4886-4893.
5. P. Nockemann, B. Thijs, S. Pittois, J. Thoen, C. Glorieux, K. Van Hecke, L. Van Meervelt, B. Kirchner and K. Binnemans, *J. Phys. Chem. B*, 2006, **110**, 20978-20992.
6. D.-J. Tao, J. Wu, Z.-Z. Wang, Z.-H. Lu, Z. Yang and X.-S. Chen, *RSC Adv.*, 2014, **4**, 1-7.
7. Q. Wu, H. Chen, M. Han, D. Wang and J. Wang, *Ind. Eng. Chem. Res.*, 2007, **46**, 7955-7960.
8. T. Vander Hoogerstraete, B. Onghena and K. Binnemans, *J. Phys. Chem. Lett.*, 2013, **4**, 1659-1663.
9. D. Dupont and K. Binnemans, *Green Chem.*, 2015, **17**, 856-868.
10. D. Dupont, S. Raïguel and K. Binnemans, *Chem. Commun.*, 2015, **51**, 9006-9009.
11. K. Sasaki, K. Takao, T. Suzuki, T. Mori, T. Arai and Y. Ikeda, *Dalton Trans.*, 2014, **43**, 5648-5651.
12. J. W. Freiderich, J. J. Stankovich, H. Luo, S. Dai and B. A. Moyer, *Eur. J. Inorg. Chem.*, 2015, **2015**, 4354-4361.
13. C. Yue, D. Fang, L. Liu and T.-F. Yi, *J. Mol. Liq.*, 2011, **163**, 99-121.
14. G. Y. Markovits and G. R. Choppin, in *Ion Exch. Solvent Extr.*, eds. J. A. Marinsky and Y. Marcus, Marcel Dekker, New York, USA, 1973, vol. 3, pp. 51-81.
15. H. Peng, S. Sun, Y. Hu, R. Xing and D. Fang, *Heteroat. Chem.*, 2015, **26**, 215-223.
16. J. P. Guthrie, *Can. J. Chem.*, 1978, **56**, 2342.
17. S. P. Satsia, P. N. Kalaria and D. K. Raval, *J. Mol. Catal. A: Chem.*, 2014, **391**, 41-47.
18. J. Gui, X. Cong, D. Liu, X. Zhang, Z. Hu and Z. Sun, *Catal. Commun.*, 2004, **5**, 473-477.
19. P. N. Muskarwar, S. Senthil Kumar and P. R. Bhagat, *J. Mol. Catal. A: Chem.*, 2013, **380**, 112-117.
20. J. Shen, H. Wang, H. Liu, Y. Sun and Z. Liu, *J. Mol. Catal. A: Chem.*, 2008, **280**, 24-28.
21. Q. Zhang, S. Zhang and Y. Deng, *Green Chem.*, 2011, **13**, 2619-2637.
22. D. Zhao, J. Wang and E. Zhou, *Green Chem.*, 2007, **9**, 1219-1222.
23. A. Wibbertmann, I. Mangelsdorf, K. Gamon and R. Sedlak, *Ecotoxicol. Environ. Saf.*, 2011, **74**, 1089-1106.
24. K. Weisenberger, D. Mayer and S. R. Sandler, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, Germany, 2000.
25. Y. Fukaya, Y. Iizuka, K. Sekikawa and H. Ohno, *Green Chem.*, 2007, **9**, 1155-1157.
26. K. D. Weaver, H. J. Kim, J. Sun, D. R. MacFarlane and G. D. Elliott, *Green Chem.*, 2010, **12**, 507-513.
27. M. T. Garcia, N. Gathergood and P. J. Scammells, *Green Chem.*, 2005, **7**, 9-14.
28. H. Ohno and K. Fukumoto, *Acc. Chem. Res.*, 2007, **40**, 1122-1129.
29. G.-h. Tao, L. He, W.-s. Liu, L. Xu, W. Xiong, T. Wang and Y. Kou, *Green Chem.*, 2006, **8**, 639-646.
30. G.-h. Tao, L. He, N. Sun and Y. Kou, *Chem. Commun.*, 2005, 3562-3564.
31. R. J. W. Cremlyn, *Chlorosulfonic Acid*, Royal Society of Chemistry, Cambridge, UK, 2002.
32. J. D. Holbrey, R. D. Rogers, R. A. Mantz, P. C. Trulove, V. A. Cocalia, A. E. Visser, J. L. Anderson, J. L. Anthony, J. F. Brennecke, E. J. Maginn, T. Welton and R. A. Mantz, in *Ionic Liquids in Synthesis*, Wiley-VCH, Darmstadt, Germany, 2008, pp. 57-174.
33. F. J. Deive, A. Rodríguez, I. M. Marrucho and L. P. N. Rebelo, *J. Chem. Thermodyn.*, 2011, **43**, 1565-1572.
34. M. G. Freire, A. F. M. Claudio, J. M. M. Araujo, J. A. P. Coutinho, I. M. Marrucho, J. N. C. Lopes and L. P. N. Rebelo, *Chem. Soc. Rev.*, 2012, **41**, 4966-4995.
35. S. Shahriari, C. M. S. S. Neves, M. G. Freire and J. A. P. Coutinho, *J. Phys. Chem. B*, 2012, **116**, 7252-7258.
36. S. P. M. Ventura, C. M. S. S. Neves, M. G. Freire, I. M. Marrucho, J. Oliveira and J. A. P. Coutinho, *J. Phys. Chem. B*, 2009, **113**, 9304-9310.
37. D. Depuydt, L. Liu, C. Glorieux, W. Dehaen and K. Binnemans, *Chem. Commun.*, 2015, **51**, 14183-14186.
38. B. Onghena and K. Binnemans, *Ind. Eng. Chem. Res.*, 2015, **54**, 1887-1898.
39. Y. Kohno, S. Saita, Y. Men, J. Yuan and H. Ohno, *Polym. Chem.*, 2015, **6**, 2163-2178.
40. T. Vander Hoogerstraete, B. Onghena and K. Binnemans, *Int. J. Mol. Sci.*, 2013, **14**, 21353-21377.
41. R. Wolfenden and Y. Yuan, *P. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 83-86.
42. T.-Y. Wu, S.-G. Su, S.-T. Gung, M.-W. Lin, Y.-C. Lin, C.-A. Lai and I. W. Sun, *Electrochim. Acta*, 2010, **55**, 4475-4482.
43. P. Nockemann, B. Thijs, T. N. Parac-Vogt, K. Van Hecke, L. Van Meervelt, B. Tinant, I. Hartenbach, T. Schleid, V. T. Ngan, M. T. Nguyen and K. Binnemans, *Inorg. Chem.*, 2008, **47**, 9987-9999.
44. K. Binnemans, P. T. Jones, B. Blanpain, T. Van Gerven and Y. Pontikes, *J. Clean. Prod.*, 2015, **99**, 17-38.
45. A. C. Du Preez and S. J. Preston, *Solvent Extr. Ion Exch.*, 1992, **10**, 207-230.
46. E. O. Otu and A. D. Westland, *Solvent Extr. Ion Exch.*, 1991, **9**, 875-883.
47. T. Sekine and Y. Hasegawa, *Solvent extraction chemistry: fundamentals and applications*, Marcel Dekker, New York, USA, 1977.
48. A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. J. H. Davis and R. D. Rogers, *Chem. Commun.*, 2001, 135-136.
49. H. Zhao, S. Xia and P. Ma, *J. Chem. Technol. Biotechnol.*, 2005, **80**, 1089-1096.
50. N. Kozonoi and Y. Ikeda, *Monatsh. Chem.*, 2007, **138**, 1145-1151.
51. N. Papaiconomou, J.-M. Lee, J. Salminen, M. von Stosch and J. M. Prausnitz, *Ind. Eng. Chem. Res.*, 2008, **47**, 5080-5086.
52. J. S. Preston and A. C. Du Preez, *Solvent Extraction Processes for the Separation of Rare Earths Metals*, In Proceedings of International Solvent Extraction Conference Japan, 1990.
53. K. Larsson and K. Binnemans, *Hydrometallurgy*, 2015, **156**, 206-214.

Graphical abstract



Alkylsulfuric acid ILs are simple to make and offer a more strongly acidic alternative to sulfonic acid ILs for applications in catalysis, metal extraction and dissolution of metal oxides.