Electronic Supporting Information

New metal extractants and super-acidic ionic liquids derived from sulfamic acid

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1. Chemicals and materials

Chemicals for extraction and leaching experiments

$ZnCl_2$ (98.5%), $FeCl_3$ (98%), $Fe(NO_3)_3$ (99%), NiO (76%), $CuCl_2$ anh. (99%), $Co(NO_3)_2{\cdot}6H_2O$ (99%), $Ni(NO_3)_2{\cdot}6H_2O$ (99%), Nd_2O_3 (99.9%), and $LaCl_3{\cdot}7H_2O$ (99.99%) were purchased from Acros Organics (Geel, Belgium). $NiCl_2$ (98%), $DyCl_3{\cdot}6H_2O$ (99.9%), $Zn(NO_3)_2{\cdot}6H_2O$ (99%), CuO (99%), La_2O_3 (99.9%), [C_2mim][Cl] (>95%),and $CoCl_2$ (97%) were bought from Sigma-Aldrich (Diegem, Belgium). $NdCl_3{\cdot}6H_2O$ (99.9%), $Dy(NO_3)_3{\cdot}6H_2O$ (99.9%), and Co_3O_4 (99.5%) were purchased from Strem Chemicals Inc. (Newburyport, USA). The 1000 mg L^{-1} gallium(III) standard solution in HNO_3 (2−5 wt%) was obtained from Chem-Lab (Zedelgem, Belgium) and $La(NO_3)_3{\cdot}6H_2O$ (99.9%) from chemPUR (Karlsruhe, Germany). Ethanol (Analytical reagent grade), and HCl (37%) were obtained from Fisher Scientific Limited (Loughborough, UK). $Nd(NO_3)_3{\cdot}6H_2O$ (99.9%) was purchased from Alfa Aesar (Karlsruhe, Germany). $Cu(NO_3)_2{\cdot}3H_2O$ (> 99.9%) was obtained from Merck Eurolab (Leicestershire, UK). A silicone solution in isopropanol was purchased from SERVA Electrophoresis GmbH (Germany). All chemicals were used as received without further purification.

Chemicals for ionic liquid/extractant synthesis and acidity determination

Bistriflimic acid (80 wt% in H_2O) (99%) was purchased from IoLiTec (HeilBronn, Germany). Diethylamine (99%), H_2SO_4 (98 wt% in H_2O), and phenol (99%) were purchased from Acros Organics (Geel, Belgium). Chlorosulfonic acid (98%), acetone (99.8, extra dry), and diethyl ether (99.8%) were obtained from Sigma-Aldrich (Diegem, Belgium). Dichloromethane (99.8%) was obtained from Fisher Scientific Limited (Loughborough, UK). Di-*n*-octylamine was purchased from Alfa Aesar (Karlsruhe, Germany).

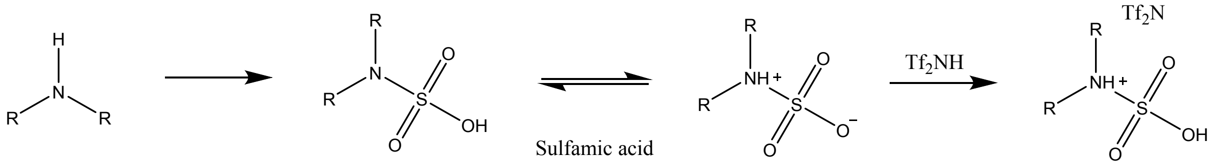
2. Equipment and characterization

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz for ^1H, 75 MHz for ^{13}C). The chemical shifts are noted in parts per million (ppm), referenced to tetramethylsilane for ^1H and ^{13}C. The coupling constants are given in Hertz. Solutions were made in D_2O, acetone-d_6 or $CDCl_3$. The spectra were analyzed with SpinWorks software. The Fourier Transform Infrared (FTIR) spectrum of the IL was recorded by a Bruker Vertex 70 spectrometer via the attenuated total reflectance (ATR) technique with a Bruker Platinum ATR accessory. The OPUS software package was used for analysis of the FTIR spectra. The viscosity of the ionic liquids was measured using an Anton-Paar rolling-ball viscometer Lovis 2000 M/ME. The density of the ionic liquids was determined using an Anton-Paar DMA 4500 M digital density meter. Melting points were determined on a Mettler-Toledo DSC 1 (STAR^e system) instrument at a heating rate of 10 °C min^{-1} under a helium atmosphere. Thermogravimetric analysis (TGA) was done on a TA Instruments T500 thermogravimeter (heating rate: 5 °C min^{-1} from room temperature to 400 °C, under a nitrogen atmosphere). A TMS-200 thermoshaker (Nemus Life) was used to shake samples during extraction experiments and a Heraeus Megafuge 1.0 centrifuge was used to accelerate phase separation. Total reflection X-ray fluorescence (TXRF) analysis was performed with a Bruker S2 Picofox TXRF spectrometer equipped with a molybdenum source. For the sample preparation, plastic microtubes were filled with a small amount of sample (100 mg), internal standard (Gallium solution) and ethanol/water (180 µL). The microtubes were then vigorously shaken on a vibrating plate (IKA MS 3 basic). Finally, a 4 µL drop of this solution was put on a quartz plate, previously treated with a silicone/isopropanol solution (Serva®) to avoid spreading of the sample droplet on the quartz plate. The quartz plates were then dried for 30 min at 60 °C prior to analysis. Each sample was measured for 8 min.

The acidity of the sulfamic acid-functionalized ionic liquids was tested qualitatively by dissolving 50 mg of phenol (pK_a = -6.5) and an equimolar amount of the acidic IL in deuterated chloroform (700 µL). Deuterated chloroform was used to avoid the levelling effect of water. The samples were then analyzed with ^1H and ^{13}C NMR to determine the percentage protonation of phenol. The effect of the acids H_2SO_4 and HSO_3Cl (with known pK_a's) was compared with $[(Et)_2NH\text{-}SO_3H][Tf_2N]$ and $[(Oct)_2NH\text{-}SO_3H][Tf_2N]$. By comparing the degree of protonation of phenol we were able to rank the acidity of the ILs compared to acids with known pK_a's (e. g. H_2SO_4, $HClO_4$, HSO_3Cl).

3. Overview of the synthetic strategy and the synthesized extractants and ionic liquids

The synthetic strategy was based on a 1-step or 2-step reaction (Scheme S 1). First the appropriate dialkylamine was reacted with chlorosulfonic acid to obtain the corresponding sulfamic acid (extractant). Then this sulfamic acid was reacted with the super acid HTf_2N to obtain the corresponding ionic liquid (IL). An overview of the synthesized ILs and extractants is given in Table S1.



Scheme S1. Synthetic strategy for the synthesis of dialkylammoniumsulfonic acid bis(trifluoromethylsulfonyl)imide ionic liquids.

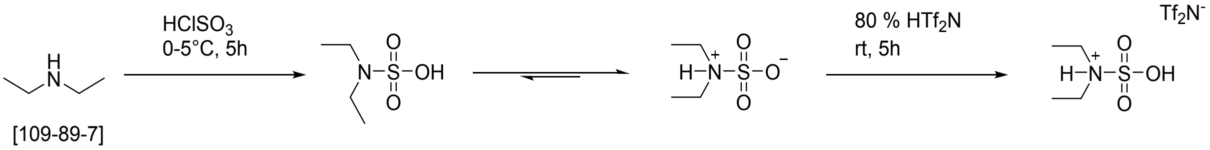
Table S1. Overview of the compounds synthesized in this work

Nr	IL abbreviation	Full name
1	$[(Et)_2NH\text{-}SO_3H][Tf_2N]$	Diethylammoniumsulfonic acid bistriflimide[(a)]
2	$[(Oct)_2NH\text{-}SO_3H][Tf_2N]$	Dioctylylammoniumsulfonic acid bistriflimide[(a)]
3	$(Et)_2NH\text{-}SO_3$	Diethylammoniumsulfamic acid
4	$(Oct)_2NH\text{-}SO_3$	Dioctylammoniumsulfamic acid

(a) Bistriflimide = bis(trifluoromethylsulfonyl)imide

Synthesis of ionic liquids and extractants

3.1 [(Et)$_2$NH-SO$_3$H][Tf$_2$N]



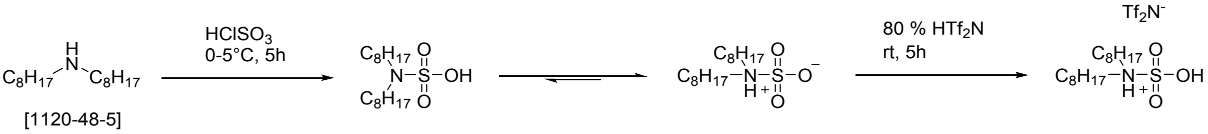
In a three-necked round bottom flask, equipped with stirring bar, diethylamine (20 g, 0.27 mol) was dissolved in 40 mL of DCM. The resulting mixture was stirred in an ice bath for 10 min. Chlorosulfonic acid (35.02 g, 0.30 mol) was slowly dropped into the solution under agitation, while keeping the temperature below 5 °C. The resulting reaction mixture was stirred for 5 h at 0 °C. The produced HCl gas, was properly trapped. The solvent was removed under reduced pressure, yielding a brown slurry. The slurry was stirred in 200 mL of diethyl ether overnight and a precipitate formed. The precipitate was filtered off, washed two times with diethyl ether and dried under vacuum. This yields 29.92 g (yield = 71%) of diethylsulfamic acid as a light brownish solid.

In a three-necked round bottom flask, equipped with stirring bar, diethylsulfamic acid (29.0 g, 0.19 mol) was dissolved in 40 mL of water. An aqueous solution of bis(trifluoromethylsulfonyl)imide acid (80 wt%) (66.53 g, 0.19 mol) was added dropwise at room temperature. The resulting mixture was stirred for 5 h. A white precipitate was formed, filtered off and dried under reduced pressure, yielding 41.64 g (yield = 51%) of [(Et)$_2$NH-SO$_3$H][Tf$_2$N] as a white solid.

Ionic liquid [(Et)$_2$NH-SO$_3$H][Tf$_2$N]

^{1}H NMR: (300 MHz, acetone-*d*$_6$, δ/ppm): 7.74 (s, 1H, NH), 5.62 (s, 1H, OH), 3.39 (m, 4H, 2 CH$_2$-N), 1.42 (t, 6H, J = 7.5 Hz, 2 CH$_3$). ^{13}C NMR (75 MHz, acetone-*d*$_6$, δ/ppm): 120.88 (CF$_3$, q, J = 320 Hz), 44.08 (CH$_2$), 11.53 (CH$_3$). ATR-FTIR: (ν/cm^{-1}): 2955, 2928, 257 (C-H stretch), 1450 (C-H bending), 1327 (asymmetric O=S=O stretch), 1183 (CF$_3$ stretch), 1137 (symmetric O=S=O stretch), 1050 (S-N stretch), 605 (O=S=O bending), 570 (CF$_3$ bending), 511 (CF$_3$ bending). Melting temperature: 58.9 °C, Purity: 98%, Water content: 3.2 wt%.

3.2 $[(Oct)_2NH\text{-}SO_3H][Tf_2N]$



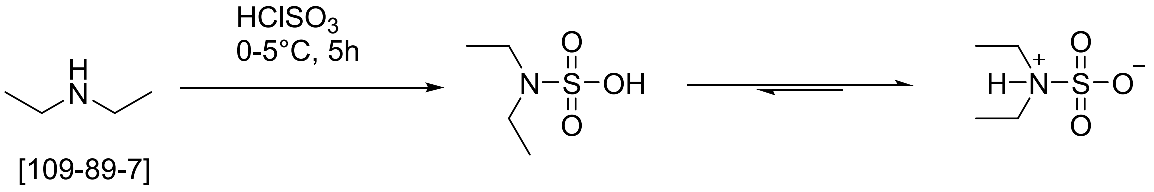
In a three-necked round bottom flask, equipped with stirring bar, dioctylamine (20 g, 0.08 mol) was dissolved in 40 mL of DCM. The resulting mixture was stirred in an ice bath for 10 min. Chlorosulfonic acid (10.61 g, 0.09 mol) was slowly dropped into the solution under agitation, while keeping the temperature below 5 °C. The resulting reaction mixture was stirred for 5 h at 0 °C. The produced HCl gas, was properly trapped. The solvent was removed under reduced pressure, yielding a brown slurry. The slurry was stirred in 200 mL of diethyl ether overnight and a white precipitate formed. The precipitate was filtered off, washed two times with diethyl ether and dried under vacuum. This yields 22.04 g (yield 83%) of dioctyllsulfamic acid as a white solid.

In a three-necked round bottom flask, equipped with stirring bar, dioctylsulfamic acid (22.0 g, 0.07 mol) was dissolved in 40 mL of water. An aqueous solution of bis(trifluoromethylsulfonyl)imide acid (80 wt%) (24.05 g, 0.07 mol) was added dropwise at room temperature. The resulting mixture was stirred for 5 h. A white precipitate was formed, filtered off and dried under reduced pressure, yielding 29.51 g (yield = 72%) of $[(Oct)_2NH\text{-}SO_3H][Tf_2N]$ as a white solid.

Ionic liquid $[(Oct)_2NH\text{-}SO_3H][Tf_2N]$

^{1}H NMR: (300 MHz, acetone-*d*$_6$, δ/ppm): 7.75 (s, 1H, NH), 4.0 (s, 1H, OH), 3.33 (m, 4H, 2 CH_2-N), 1.84 (m, 4H, 2 CH_2), 1.29 (m, 20H, 10 CH_2), 0.87 (t, 6H, J = 7.0 Hz, 2 CH_3). ^{13}C NMR (75 MHz, acetone-*d*$_6$, δ/ppm): 120.94 (CF_3, q, J = 319 Hz), 51.86 (CH_2), 49.49 (CH_2), 33.42 (CH_2), 27.51 (CH_2), 26.96 (CH_2), 25.88 (CH_2), 23.25 (CH_2), 14.35 (CH_3). ATR-FTIR: (v/cm^{-1}): 2957, 2924, 2856 (C-H stretch), 1435 (C-H bending), 1323 (asymmetric O=S=O stretch), 1188 (CF_3 stretch), 1136 (symmetric O=S=O stretch), 1059 (S-N stretch), 607 (O=S=O bending), 570 (CF_3 bending), 513 (CF_3 bending). Melting temperature: 63.3 °C. Purity: > 99%. Water content: 1.4 wt%.

3.3 $(Et)_2NH-SO_3$



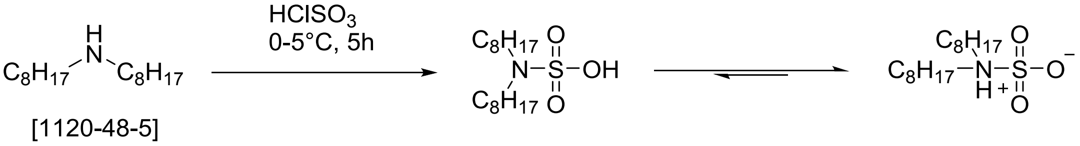
In a three-necked round bottom flask, equipped with stirring bar, diethylamine (20 g, 0.27 mol) was dissolved in 40 mL of DCM. The resulting mixture was stirred in an ice bath for 10 min. Chlorosulfonic acid (35.02 g, 0.30 mol) was slowly dropped into the solution under agitation, while keeping the temperature below 5 °C. The resulting reaction mixture was stirred for 5 h at 0 °C. The produced HCl gas, was properly trapped. The solvent was removed under reduced pressure, yielding a brown slurry. The slurry was stirred in 200 mL of diethyl ether overnight and a precipitate formed. The precipitate was filtered off, washed two times with diethyl ether and dried under vacuum. This yields 29.92 g (yield = 71%) of diethylsulfamic acid as a light brownish solid.

$(Et)_2NH-SO_3$

^1H NMR:(300 MHz, DMSO-*d*$_6$, δ/ppm): 8.47 (m, 1H, N-H), 2.92 (m, 4H, 2 CH_2-N), 1.19 (t, 6H, J = 7.0 Hz, 2 CH_3). ^{13}C NMR (75 MHz, DMSO-*d*$_6$, δ/ppm): 41.34 (CH_2), 10.79 (CH_3).

ATR-FTIR: (ν/cm^{-1}): 3172, 2992, 2870 (C-H stretch), 1450 (C-H bending), 1238 (asymmetric O=S=O stretch), 1043 (symmetric O=S=O stretch). No melting point could be determined (decomposes around 250 °C without melting). Purity: 96%. Water content: 2.8 wt%

3.4 $(Oct)_2NH\text{-}SO_3$



In a three-necked round bottom flask, equipped with stirring bar, dioctylamine (20 g, 0.08 mol) was dissolved in 40 mL of DCM. The resulting mixture was stirred in an ice bath for 10 min. Chlorosulfonic acid (10.61 g, 0.09 mol) was slowly dropped into the solution under agitation, while keeping the temperature below 5 °C. The resulting reaction mixture was stirred for 5 h at 0 °C. The produced HCl gas, was properly trapped. The solvent was removed under reduced pressure, yielding a brown slurry. The slurry was stirred in 200 mL of diethyl ether overnight and a white precipitate formed. The precipitate was filtered off, washed two times with diethyl ether and dried under vacuum. This yields 22.04 g (yield 83%) of dioctyllsulfamic acid as a white solid.

$(Oct)_2NH\text{-}SO_3$

^1H NMR: (300 MHz, $CDCl_3$, δ/ppm): 8.59 (m, 1H, NH), 3.10 (m, 4H, 2 CH_2-N), 1.85 (m, 4H, 2CH_2), 1.31 (m, 20H, 10 CH_2), 0.88 (t, 6H, J= 7.0 Hz, 2 CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 48.56 (CH_2), 31.70 (CH_2), 29.05 (CH_2), 26.91 (CH_2), 26.52 (CH_2), 25.98 (CH_2), 22.59 (CH_2), 14.04 (CH_3). ATR-FTIR: (v/cm^{-1}): 3170, 2921, 2854 (C-H stretch), 1454 (C-H bending), 1232 (asymmetric O=S=O stretch), 1046 (symmetric O=S=O stretch). No melting point could be determined (decomposes around 250 °C without melting). Purity: 99%. Water content: 1.1 wt%

4. Characterization and properties of the ionic liquids

Table S2 and Table S3 give an overview of the decomposition resistance of the pure ionic liquid or extractant in water mixtures upon heating over prolonged amounts of time (24 h). The decomposition was quantified using ^{1}H NMR but no signs of degradation could be observed in these conditions, thus confirming the stability of these alkylsulfamic acids and the corresponding ILs.

Table S2. Decomposition (%) of $[(Et)_2NH\text{-}OSO_3H][Tf_2N]$ in the absence and in the presence of water (NMR) at different temperatures over a 24 h interval.

	20 °C	**50 °C**	**80 °C**
Pure IL	< 1%	< 1%	< 1 %
IL/H_2O (1:1 wt/wt)	< 1%	< 1%	< 1%

Table S3. Decomposition (%) monitored by ^{1}H NMR of $[(Et)_2NH\text{-}OSO_3]$ in the absence and in the presence of water at different temperatures over a 24 h interval.

	20 °C	**50 °C**	**80 °C**
Pure IL	< 1%	< 1%	< 1 %
IL/H_2O (1:1 wt/wt)	< 1%	< 1%	< 1%

5. Experiments

A 1:1 wt/wt mixture of sulfamic acid IL and [C_2mim][Tf_2N] was used to investigate the dissolution of the highly inert lamp phosphor $BaMgAl_{10}O_{17}$ (BAM). Figure S1 shows the dissolution of the lamp phosphor as function of time for different temperatures. There is a noticeable increase in the dissolution speed with higher temperatures. Viscosity measurements showed that the leaching system had a viscosity of 19 cP at 90 °C.

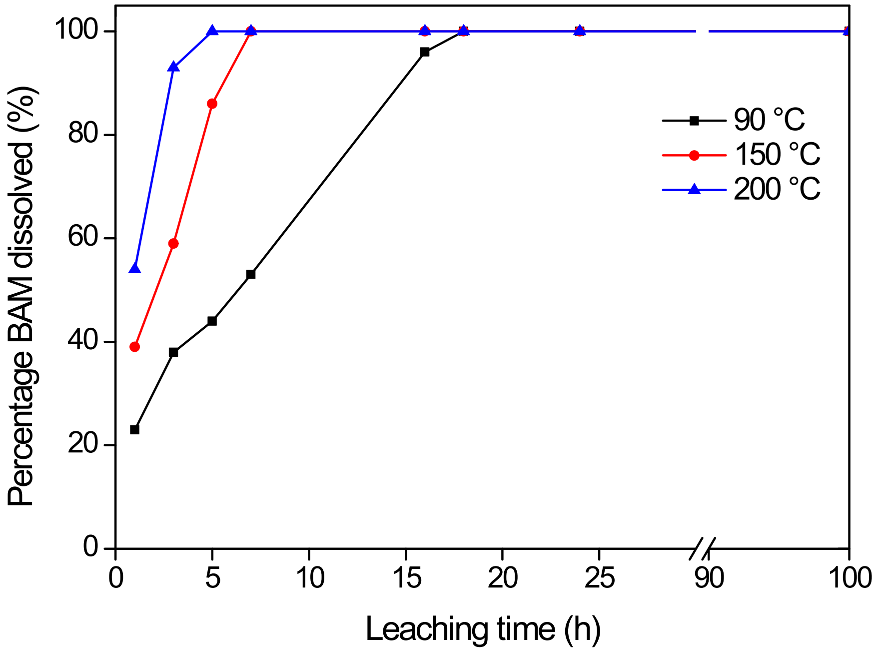


Figure S1. Dissolution of the lamp phosphor BAM as function of the temperature. The powder was stirred in a 1:1 wt/wt mixture of sulfamic acid IL and [C_2mim][Tf_2N]. A solid liquid ratio of 1/200 was used.

The influence of the IL diluent (Figure S2) on the leaching efficiency of the phosphor BAM was tested as well. BAM is not dissolved in [C_4mim][Tf_2N], which proves the ionic liquid diluent needs to have coordinating anions. For the ionic liquids with coordinating anions, the poorest results were found for [P_{66614}][Cl] (Cyphos® IL 101). Using Cyphos® IL 101 resulted in the formation of a white precipitate in the leaching mixture. The dissolution of BAM with the IL diluent [N_{8881}][Cl] (Aliquat® 336) was also less efficient than [C_2mim][Cl], due to the higher viscosity, the increased steric hindrance, and the lower mobility (longer alkyl chains) compared to [C_2mim][Cl]. These arguments are supported by the improved results found for a mixture of Aliquat® 128/Aliquat® 336 compared to pure Aliquat® 336. The viscosity of the mix of Aliquat® 128/Aliquat® 336 is lower than for pure Aliquat® 336. Using [Hbet][Tf_2N] or a mix of Aliquat® 128/Aliquat® 336 as the second ionic liquid still gave slightly poorer results compared to [C_2mim][Cl]. Furthermore, thanks to its lower molecular weight, much less [C_2mim][Cl] needs to be added to obtain 3 equivalents of diluents, compared to [Hbet][Tf_2N] or a mix of Aliquat® 128/Aliquat® 336.

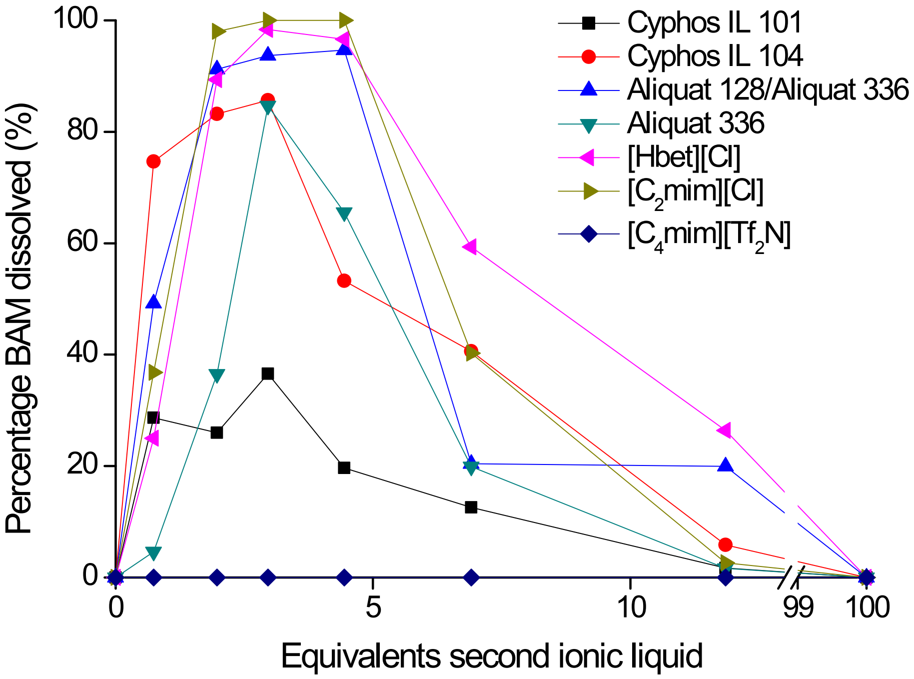


Figure S2. Dissolution of 10 mg of BAM as function of the ratio of ILs, using 500 mg of [$(Et)_2NH\text{-}SO_3H$][Tf_2N]. The samples were stirred for 24h at 150 °C.