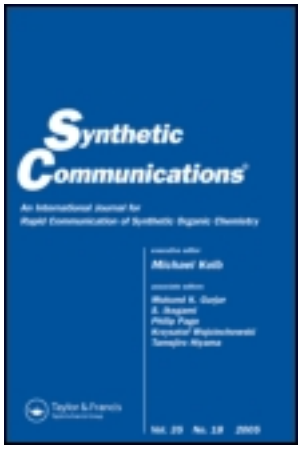
This article was downloaded by: [University North Carolina - Chapel Hill]
On: 23 June 2013, At: 02:26
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Synthesis and Characterization of Ammonium-, Pyridinium-, and Pyrrolidinium-Based Sulfonamido Functionalized Ionic Liquids

Shunmugavel Saravanamurugan [a], Rasmus Fehrmann [a] & Anders Riisager [a]

[a] Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark, Lyngby, Denmark

Accepted author version posted online: 11 Nov 2011.Published online: 18 Jul 2012.

To cite this article: Shunmugavel Saravanamurugan , Rasmus Fehrmann & Anders Riisager (2012): Synthesis and Characterization of Ammonium-, Pyridinium-, and Pyrrolidinium-Based Sulfonamido Functionalized Ionic Liquids, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 42:22, 3383-3394

To link to this article: http://dx.doi.org/10.1080/00397911.2011.582597

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Synthetic Communications®, 42: 3383–3394, 2012
Copyright © Taylor & Francis Group, LLC
ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2011.582597

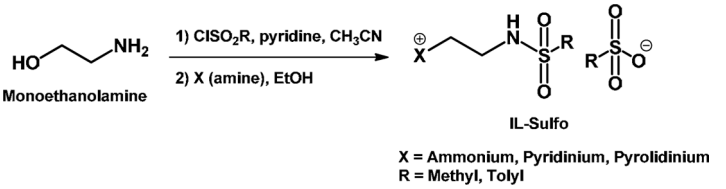
Downloaded by [University North Carolina - Chapel Hill] at 02:26 23 June 2013

SYNTHESIS AND CHARACTERIZATION OF AMMONIUM-, PYRIDINIUM-, AND PYRROLIDINIUM-BASED SULFONAMIDO FUNCTIONALIZED IONIC LIQUIDS

Shunmugavel Saravanamurugan, Rasmus Fehrmann, and Anders Riisager

Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark, Lyngby, Denmark

GRAPHICAL ABSTRACT



Abstract *New homologous ammonium-, pyridinium-, and pyrrolidinium-based sulfonamido functionalized ionic liquids have been synthesized in two steps using monoethanolamine, methanesulfonyl chloride, and tosyl chloride as precursors with ethanol as solvent. Attempts to synthesize dual amino functionalized ionic liquid containing both a primary and a secondary amine group in the same ionic liquid are also reported. All functionalized ionic liquids were characterized by ^{1}H and ^{13}C NMR. Melting point and thermal stability of the functionalized ionic liquids were measured by differential scanning calorimetry and thermogravimetric analysis.*

Keywords Amine; ionic liquid; methanesulfonyl; sulfonamido; tosyl

INTRODUCTION

New technologies where ionic liquids are used as catalysts, solvents, absorbents, electrolytes, and active materials in membranes have rapidly emerged within the past decade.[1–4] Some of the main advantages of applying ionic liquids in such applications are their practically nonvolatile nature, relatively high thermal stability, adjustable physical and chemical properties, recyclability, and good phase separation with lipophilic reagents.[5–8]

Received March 8, 2011.
Address correspondence to Anders Riisager, Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Building 207, Technical University of Denmark, DK 2800 Kgs. Lyngby, Denmark. E-mail: ar@kemi.dtu.dk

The first ionic liquid, ethanolammonium nitrate (melting point of 52–55 °C), was discovered in 1888.[9] Later, in 1914 Walden prepared the first room-temperature ionic liquid.[10] However, the first reported work using an ionic liquid as catalyst and solvent was published in 1985 for Friedel–Craft reactions with 1-methyl-3-ethylimidazolium chloride and aluminum chloride.[11] Since this pioneer study, the use of ionic liquids has progressively increased not only in the field of catalysis but also in other applications. For example, it has been found that classical ionic liquids such as imidazolium-based ionic liquids (often referred to as first-generation ionic liquids) have the ability to dissolve crystalline cellulose,[12] to act as absorbents and selectively take up gases (CO_2, SO_2, C_2H_4 etc.) by physisorption,[13] and to provide reusable reaction media for organic transformations.[14,15]

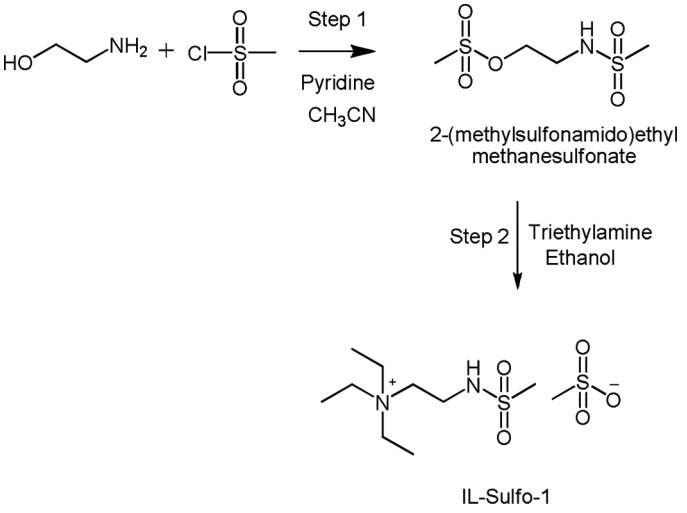
Owing to the lack of chemical functionality in the classical ionic liquids, recent efforts have aimed at developing new concepts by introduction of functional groups into the ionic liquids. In this juncture, Davis and coworkers reported in 2002 the first amine-functionalized imidazolium-based ionic liquids (task specific) for CO_2 capture, which can react with CO_2 at ambient temperature and pressure.[16] Subsequently, sulfonic acid tethered imidazolium-based ionic liquids have also been reported by the same group and applied for Fischer esterification and pinacol rearrangement reactions.[17] Here the liquids had excellent catalytic activity and potential to be recycled at least five times without loss of activity. Since this pioneer work, several other reports on the synthesis and application of new acid- and base-functionalized ionic liquids have followed.[18–20]

In this article, we report the synthesis and characterization of a new series of homologous sulfonamido functionalized ionic liquids containing ammonium, pyridinium, and pyrrolidinium cations. The strategy was to introduce an electron-withdrawing group, sulfonamido group, in the ionic liquid in proximity to a primary amine group in order to lower its basicity. Synthesis of bifunctionalized ionic liquids comprising both a primary and a secondary amine group was also attempted with the introduced synthetic methodology.

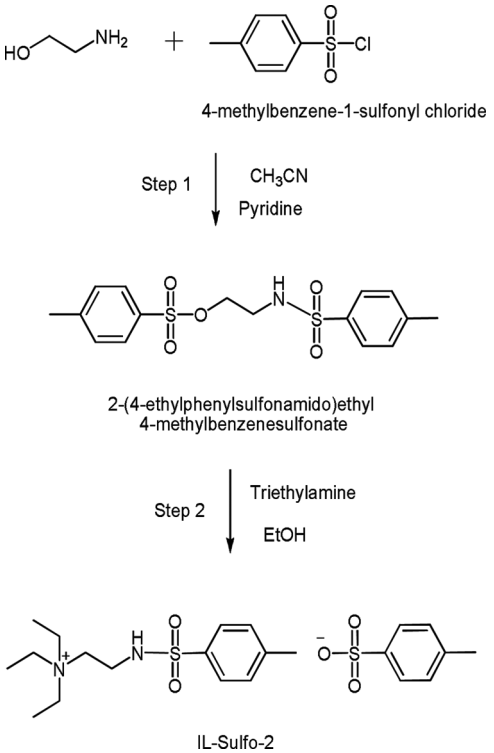
RESULTS AND DISCUSSION

Initially, we set out to synthesize amine functionalized ammonium-based ionic liquids in two steps as shown in Schemes 1 and 2. In the first step, monoethanolamine was reacted with methanesulfonyl chloride in acetonitrile (Scheme 1). Since the reaction was highly exothermic, the methanesulfonyl chloride was added dropwise at 0 °C. The reaction mixture turned from colorless to yellow, indicative of reaction. To ensure that a free NH group was formed in the intermediate product, a slight excess of pyridine was added to capture the liberated hydrogen chloride. After the addition of methanesulfonyl chloride, the reaction temperature was brought to room temperature and the mixture was stirred overnight. Finally, the targeted product, 2-(methylsulfonamido)ethyl methylsulfonate (MSAEMS), was isolated by column chromatography (46% yield). The identity of the product was confirmed by NMR analysis in $CDCl_3$ and dimethylsulfoxide (DMSO-d_6) solvents, where the NH signal appeared as triplets at 5.35 and 7.35 ppm, respectively, in the ^{1}H NMR spectra (in D_2O solvent the signal was not visible because of proton exchange). The isolated MSAEMS was subsequently used as a precursor to make the

Downloaded by [University North Carolina - Chapel Hill] at 02:26 23 June 2013



Scheme 1. Synthesis of IL-Sulfo-1.



Scheme 2. Synthesis of IL-Sulfo-2.

Downloaded by [University North Carolina - Chapel Hill] at 02:26 23 June 2013

sulfonamido functionalized ammonium-, pyridinium-, and pyrrolidinium-based ionic liquids in a second step.

In the second step, MSAEMS and triethylamine were allowed to react in ethanol while the reaction progress was monitored by ^{1}H NMR on aliquots withdrawn from the reaction mixture by following the disappearance of the O-CH_2 signal of MSAEMS at $\delta = 4.35$ ppm. The reaction was allowed to react until the signal was undetectable (typically 24 h). The resulting ionic liquid, *N,N,N*-triethyl-2-(methylsulfonamido)ethaneaminium methanesulfonate (IL-Sulfo-1) was purified by extraction with a mixture of toluene and dichloromethane and recovered as a colorless viscous liquid. The isolated yield of IL-Sulfo-1 was more than 95%.

A tosyl group was introduced into the ammonium-based ionic liquid by an analogous procedure (Scheme 2). In the first reaction step, the isolated yield of the corresponding product, 2-(4-methylphenylsulfonamido)ethyl-4-methylbenzenesulfonate (MPSAEMBS), was 35% and thus less than with MSAEMS. All aliphatic and aromatic protons, including the NH proton, were confirmed by ^{1}H NMR analysis. MPSAEMBS was further reacted with triethylamine to get the ionic liquid, *N,N,N*-triethyl-2-(methylphenylsulfonamido)ethaneaminium 4-methylbenzenesulfonate (IL-Sulfo-2). Excess reactants were removed by extraction with *n*-hexane under reflux, and the product was recovered as a solid. The isolated yield of the ionic liquid (IL-Sulfo-2) was here more than 98% and the identity was confirmed by ^{1}H and ^{13}C NMR.

By adopting the mentioned procedure, 1-(2-(methylsulfonamido)ethyl)pyridinium methanesulfonate (IL-Sulfo-1a), 1-methyl-1-(2-(methylsulfonamido)ethyl)-pyrrolidinium methanesulfonate (IL-Sulfo-1b), *N,N*-diethyl-2-hydroxy-*N*-(2-(methylsulfonamido)ethyl)ethaneaminium methanesulfonate (IL-Sulfo-1c), 1-(2-(4-methylphenylsulfonamido)ethyl)pyridinium 4-methylbenzenesulfonate (IL-Sulfo-2a), and 1-methyl-1-(2-(methylphenylsulfonamido)ethyl)pyrrolidinium methylbenzeneesulfonate (IL-Sulfo-2b) ionic liquids were also synthesized. Also here, the identity of the ionic liquids was confirmed by ^{1}H and ^{13}C NMR analysis and the yields were more than 95%. Additionally, high purity of the synthesized sulfonamido ionic liquids was also confirmed by ^{1}H NMR analysis. Hence, by comparing the integral area of the methyl singlets from the ionic liquid and unidentified peaks, all the ionic liquids were found to posses extraneous peaks corresponding to less than 3% of the area of the methyl singlets. The structures of all the synthesized sulfonamido functionalized ionic liquids are depicted in Fig. 1.

Attempts were made to synthesize a dual amino functionalized ionic liquid. The synthetic strategy was to introduce both a primary amine group and a substituted secondary amine group, a sulfonamide group, in the same ionic liquid. The bifunctionalized ionic liquid was synthesized in three steps following the strategy outlined in Scheme 3. As a source for the primary amine group, 3-(diethylamino)propylamine (DEAPA) was chosen. To facilitate reaction only with the tertiary amine of DEAPA, the primary amine group was initially protected as a carbamate. This was done as the first step by reacting DEAPA with an equimolar amount of the protecting reagent, di-*tert*-butyl dicarbonate (t-BOC) by dropwise addition of the reagent to the amine at room temperature (caution: exothermic reaction). The identity of the resulting amine protected compound, *tert*-butyl-(3-(diethylamino)propyl)carbamate,

Downloaded by [University North Carolina - Chapel Hill] at 02:26 23 June 2013

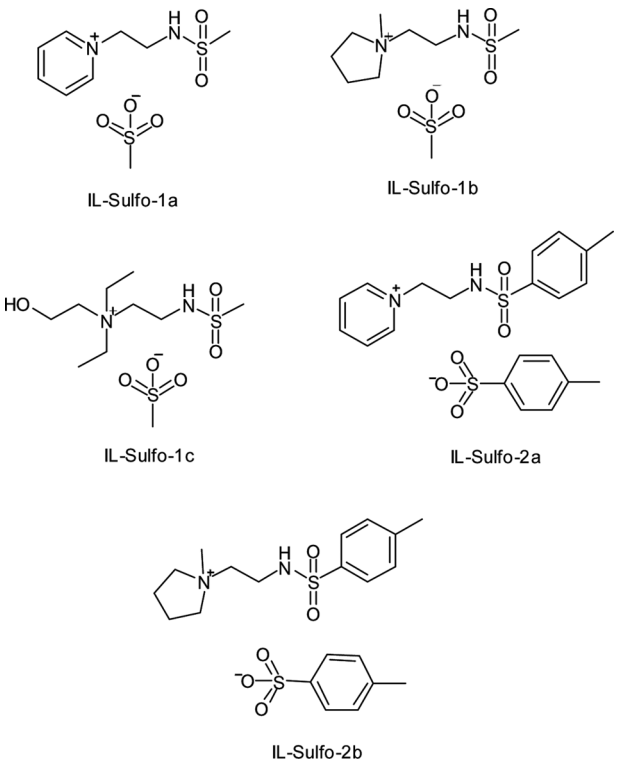
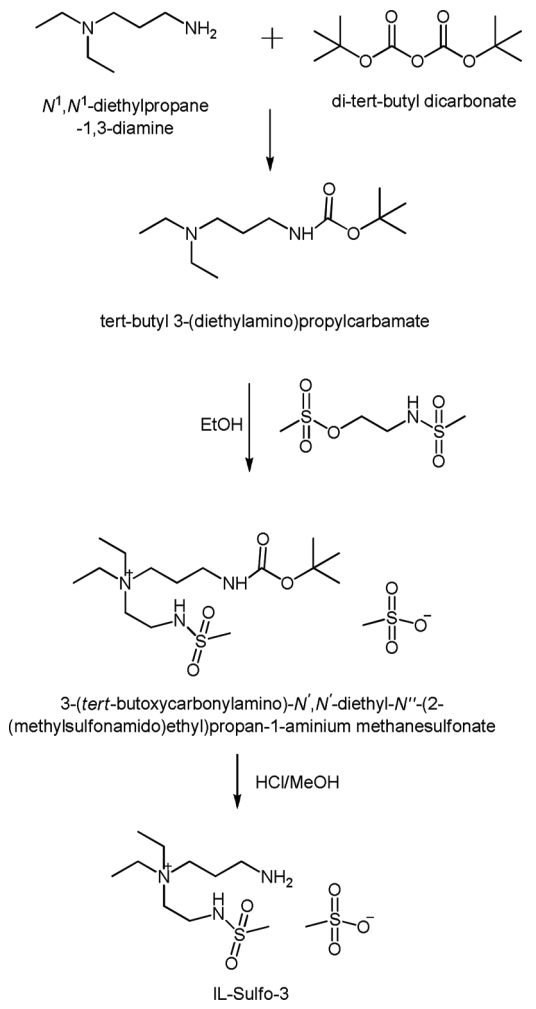


Figure 1. Structure of sulfonamido functionalized ionic liquids.

was confirmed by both ^{1}H and ^{13}C NMR. In a second reaction step, the carbamate-protected compound was further reacted with an equimolar amount of MSAEMS to get the sulfonamido functionalized ionic liquid, 3-((*tert*-butoxycarbonyl)amino)-*N*′, *N*′-diethyl-*N*″-(2-(methylsulfonamido)ethyl) propaneammonium methanesulfonate. The presence of the sulfonamide group in the product was also here confirmed by NMR analysis. Finally, in a third reaction step the carbamate protection group was removed by adding a few drops of hydrochloric acid to a methanolic solution of the protected amine ionic liquid. In the final product, the presence of both a primary and a secondary amine group was confirmed using ^{1}H NMR analysis by the disappearance of the signals from the t-BOC group (in D_2O) and appearance of the NH and NH_2 signals (in DMSO-d_6), respectively.

The thermal stability of the synthesized sulfonamide ionic liquids was determined by thermal gravimetric (TG) analysis (TGA/DSC 1 apparatus, Mettler Toledo). The ionic liquid (4 to 16 mg) was placed in a sample holder and heated from 40 to 600 °C (10 °C/min) under a nitrogen atmosphere. The measured thermographs (Fig. 2) revealed that all of the new functionalized ionic liquids remained stable up to at least 250 °C. Melting points of the ionic liquids were determined on 4 to 10 mg samples by differential scanning calorimetry using a TA-2620-DSC equipped with cryostat cooling (2 to 10 °C/min heating and cooling rates).

Downloaded by [University North Carolina - Chapel Hill] at 02:26 23 June 2013



Scheme 3. Synthesis of IL-Sulfo-3.

CONCLUSION

A homologous series of new sulfonamido functionalized ionic liquids with ammonium, pyridinium, and pyrrolidinium cations have been synthesized and characterized by NMR, differential scanning calorimetry (DSC), and TG analyses. The synthetic strategy also enabled synthesis of an ionic liquid comprising both a primary and a secondary amine group. TGA results revealed that all of the ionic liquids were thermally stable below 250 °C.

MATERIALS

Monoethanolamine (>99%, Fluka), pyridine (>99.8%, Fluka), acetonitrile (>99.9%, Sigma-Aldrich), methanesulfonyl chloride (>98%, Fluka), ethyl acetate

Downloaded by [University North Carolina - Chapel Hill] at 02:26 23 June 2013

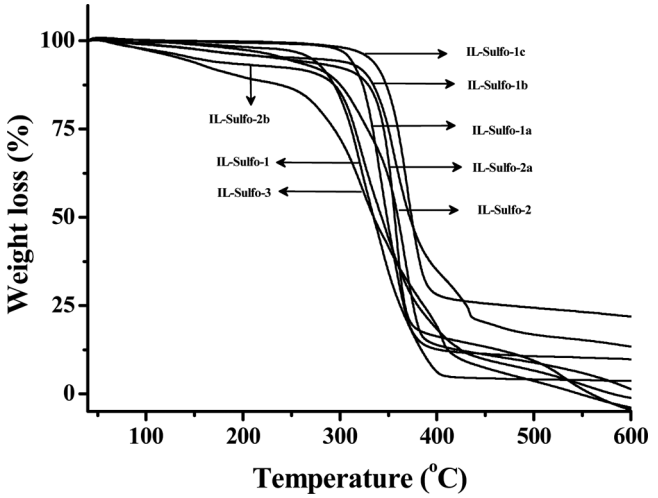


Figure 2. TGA thermographs of sulfonamido functionalized ionic liquids.

(>99.7%, Sigma-Aldrich), dichloromethane (>99.8%, Sigma-Aldrich), toluene (>99.9%, Sigma-Aldrich), toluene-4-sulfonyl chloride (>97%, Fluka), triethylamine (99.9%, Sigma-Aldrich), 1-methylpyrrolidine (>99%, Fluka), 2-diethylaminoethanol (>99%, Fluka), *n*-hexane (>96.5%, Sigma-Aldrich), and 3-(diethylamino)propylamine (>99 + %, Aldrich) were used as received.

EXPERIMENTAL

Synthesis of *N,N,N*-Triethyl-2-(methylsulfonamido)ethaneaminium Methanesulfonate (IL-Sulfo-1)

Step 1. Monoethanolamine (3.0 g, 49.1 mmol), pyridine (7.91 g, 100 mmol), and acetonitrile (65 ml) were mixed in a 250-ml, round-bottomed flask. Methanesulfonyl chloride (11.25 g, 98.2 mmol) was added dropwise to the reaction mixture at 0 °C. After the addition, the solution was brought to room temperature and allowed to stir overnight. Finally, the solvent was removed under reduced pressure, and the major product, 2-(methylsulfonamido)ethyl methylsulfonate (MSAEMS), was isolated by column chromatography using ethyl acetate/dichloromethane eluent. Yield = 46%.

^{1}H NMR (300 MHz, D_2O) $\delta = 3.02$ (s, 3H; H_3C-S-N), 3.18 (s, 3H; H_3C-S-O), 3.4–3.48 (t, 2H; CH_2-N), 4.3-4.4 (t, 2H; CH_2-O); ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 3.0$ (s, 3H; H_3C-S-N), 3.1 (s, 3H; H_3C-S-O), 3.4–3.5 (q, 2H; CH_2-N), 4.3–4.4 (t, 2H; CH_2-O), 5.3–5.42 (t, 1H; NH); ^{1}H NMR (300 MHz, DMSO-d_6) $\delta = 2.90$ (s, 3H; H_3C-S-N), 3.18 (s, 3H; H_3C-S-O), 3.2–3.3 (q, 2H; CH_2-N), 4.15–4.22 (t, 2H; CH_2-O), 7.3–7.4 (t, 1H; NH); ^{13}C NMR (75.5 MHz, D_2O) $\delta = 36.8$ (H_3C-S-N), 39.7 (H_2C-N), 41.9 (H_3C-S-O), 70.3 (H_2C-O); ^{13}C NMR (75.5 MHz, $CDCl_3$) $\delta = 37.7$ (H_3C-S-N), 40.9 (H_2C-N), 42.5 (H_3C-S-O), 69.2 (H_2C-O); ^{13}C NMR (75.5 MHz, DMSO-d_6) $\delta = 37.4$ (H_3C-S-N), 42.2 (H_2C-N), 49.9 (H_3C-S-O), 69.95 (H_2C-O).

Downloaded by [University North Carolina - Chapel Hill] at 02:26 23 June 2013

Step 2. MSAEMS (2.5 g, 11.5 mmol), triethylamine (3.2 g, 31.6 mmol), and 50 ml of ethanol were placed in a 100-ml, round-bottomed flask and refluxed at 110 °C. The solution was then cooled to room temperature, and the solvent removed under reduced pressure to get the ionic liquid, IL-Sulfo-1. The ionic liquid was purified by extraction with toluene–dichloromethane mixture and recovered as a colorless viscous liquid after removal of the solvent. Yield = 95%. Mp < −50 °C.

^{1}H NMR (300 MHz, D_2O) δ = 1.1–1.2 (t, 9H; $3CH_3$), 2.65 (s, 3H; H_3C-S-N), 2.98 (s, 3H; H_3C-S-O), 3.18–3.3 (m, 8H; 3(CH_2)-N and H_2C-N), 3.4–3.5 (t, 2H; H_2C-N); ^{13}C NMR (75.5 MHz, D_2O) δ = 6.83 (CH_3), 36.0 (H_2C-N), 38.7 (H_3C-S-N), 39.1 (H_3C-S-O), 53.4 [3(CH_2)-N], 55.3 (H_2C-N).

Synthesis of *N,N,N*-Triethyl-2-(methylphenylsulfonamido)-ethaneaminium 4-Methylbenzenesulfonate (IL-Sulfo-2)

Step 1. Monoethanolamine (5.0 g, 81.9 mmol), pyridine (12.97 g, 164 mmol), and acetonitrile (65 ml) were mixed in a 250-ml, round-bottomed flask. Toluene-4--sulfonyl chloride (31.2 g, 163.8 mmol) was dissolved in acetonitrile (20 ml) and added dropwise to the solution at 0 °C. Afterward, the solution was brought to room temperature and allowed to stir overnight at room temperature. The solvent was then removed under reduced pressure, and the major product, 2(4-methyl-phenylsulfonamido)ethyl-4-methylbenzenesulfonate (MPSAEMBS), was isolated by column chromatography using ethylacetate/dichloromethane eluent. Yield = 35%.

^{1}H NMR (300 MHz, DMSO-d_6) δ = 2.35 (s, 3H; H_3C-Ar-S-N), 2.4 (s, 3H; H_3C-Ar-S-O), 2.9–3.0 (q, 2H, H_2C-N), 3.9–4.0 (t, 2H, H_2C-O), 7.3–7.4 (d, 2H; Ar-CH), 7.4–7.5 (d, 2H; Ar-CH), 7.6–7.65 (d, 2H; CH), 7.7–7.8 (d, 2H; CH), 7.9–7.95 (t, 1H; NH); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ = 21.6 (H_3C-Ar-S-N), 21.7 (H_3C-Ar-S-O), 42.1 (H_2C-N), 69.8 (H_2C-O), 127.2 (Ar-CH), 128.3 (Ar-CH), 130.3 (Ar-CH), 130.8 (Ar-CH), 132.7 (C-S-N), 138 (Ar-C-CH_3), 143.5 (Ar-C-CH_3), 145.7 (C-S-O).

Step 2. MPSAEMBS (0.51 g, 1.38 mmol), triethylamine (0.75 g, 7.4 mmol), and 5.0 g of ethanol were placed in a 15-ml Ace pressure tube and refluxed at 100 °C for 24 h. The solution was then cooled to room temperature, and the solvent removed under reduced pressure to get the ionic liquid, IL-Sulfo-2. Unconverted reactants were removed by extraction with *n*-hexane under reflux, and the product recovered as a white solid. Yield = 98%. Mp = 133 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ = 1.1–1.2 (t, 9H; $3CH_3$), 2.28 (s, 3H; H_3C-Ar-S-N), 2.4 (s, 3H, H_3C-Ar-S-O), 3.05–3.17 (q, 2H, H_2C-N), 3.2–3.25 [(m, 8H; 4(H_2C)-N)], 7.1 (d, 2H; Ar-CH), 7.2–7.3 (q, 4H; Ar-CH), 7.7 (d, 2H; Ar-CH), 8.0–8.1 (t, 1H; NH); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ = 7.73 ($3CH_3$), 21.49 (H_3C-Ar-S-N), 21.68 (H_3C-Ar-S-O), 36.48 (H_2C-N), 53.1 [3(CH_2)-N], 55.5 (H_2C-N), 126.2 (Ar-CH), 127.3 (Ar-CH), 128.8 (Ar-CH), 130.5 (Ar-CH), 137.6 (Ar-C-S-N), 138.5 (Ar-CH), 143.8 (Ar-CH), 146.2 (Ar-C-S-O).

Synthesis of 1-(2-(Methylsulfonamido)ethyl)pyridinium Methanesulfonate (IL-Sulfo-1a)

MSAEMS (1.0 g, 4.6 mmol), pyridine (1.82 g, 23.0 mmol), and 5.0 g of ethanol were placed in a 15-ml Ace pressure tube and refluxed at 100 °C for 24 h. The

Downloaded by [University North Carolina - Chapel Hill] at 02:26 23 June 2013

solution was then cooled to room temperature, and the solvent removed under reduced pressure to get the ionic liquid, IL-Sulfo-1a. Unconverted reactants were removed by extraction with *n*-hexane and toluene–dichloromethane mixture, and the product recovered as a pale yellow solid. Yield = 97%. Mp = 83 °C.

^{1}H NMR (300 MHz, D_2O) δ = 2.8 (s, 3H; H_3C-S-N), 2.9 (s, 3H; H_3C-S-O), 3.5–3.6 (t, 2H; H_2C-N), 4.5–4.6 (t, 2H; H_2C-N-Ar), 8.0 (t, 2H, Ar-CH-N), 8.5 (t, 1H, Ar-CH), 8.8 (d, 2H, Ar-CH); ^{13}C NMR (75.5 MHz, D_2O) δ = 38.7 (H_3C-S-N), 39.2 (H_3C-S-O), 43.1 (H_2C-N), 61.6 (H_2C-N-Ar), 128.4 (Ar-CH), 145.1 (Ar-CH-N), 146.4 (Ar-CH).

Synthesis of 1-Methyl-1-(2-(methylsulfonamido)ethyl)pyrrolidinium Methanesulfonate (IL-Sulfo-1b)

MSAEMS (0.5 g, 2.3 mmol), 1-methylpyrrolidine (1.0 g, 11.74 mmol), and 5.0 g of ethanol were placed in a 15-ml Ace pressure tube and refluxed at 100 °C for 24 h. The solution was then cooled to room temperature, and the solvent removed under reduced pressure to get the ionic liquid, IL-Sulfo-1b. Unconverted reactants were removed by extraction with *n*-hexane and toluene–dichloromethane mixture and recovered as a colorless viscous liquid. Yield = 99%. Mp < −50 °C.

^{1}H NMR (300 MHz, D_2O) δ = 2.02–2.12 (t, 4H; $2CH_2$), 2.63 (s, 3H; H_3C-S-N), 2.99 (s, 3H; H_3C-S-O), 3.0 (s, 3H;CH_3), 3.4–3.6 (m, 8H; CH_2-N-CH_2,N-CH_2-CH_2-N); ^{13}C NMR (75.5 MHz, D_2O) δ = 21.33 ($2H_2C$), 37.85 (H_2C-N), 39.05 (H_3C-S-N), 39.14 (H_3C-S-O), 48.34 (H_3C-N), 62.92 (H_2C-N), 65.48 ($2H_2C$-N).

Synthesis of *N,N*-Diethyl-2-hydroxy-*N*-(2-(methylsulfonamido)-ethyl)ethaneaminium Methanesulfonate (IL-Sulfo-1c)

MSAEMS (0.5 g, 2.3 mmol), 2-diethylaminoethanol (1.34 g, 11.4 mmol), and 5.0 g of ethanol were placed in a 15-ml Ace pressure tube and refluxed at 100 °C for 24 h. The solution was then cooled to room temperature, and the solvent removed under reduced pressure to get the ionic liquid (IL-Sulfo-1c). Unconverted reactants were removed by extraction with *n*-hexane and toluene–dichloromethane mixture, and the product recovered as a colorless viscous liquid. Yield = 99%. Mp < −50 °C.

^{1}H NMR (300 MHz, D_2O) δ = 1.1–1.22 (t, 6H; $2CH_3$), 2.62 (s, 3H; H_3C-S-N), 2.97 (s, 3H; H_3C-S-O), 3.25–3.45 [m, 10H; -CH_2-N-$(CH_2)_2$-CH_2,-CH_2-N], 3.85 (t, 2H;CH_2-OH); ^{13}C NMR (75.5 MHz, D_2O) δ = 7.19 ($2H_3C$), 36.20 (H_2C-N), 39.03 (H_3C-S-NH), 39.28 (H_3C-S-O), 49.27 (H_2C-N), 55.07 [2(H_2C)-N], 56.84 (H_2C-N), 59.04 (H_2C-OH).

Synthesis of 1-(2-(4-Methylphenylsulfonamido)ethyl)pyridinium 4-Methylbenzenesulfonate (IL-Sulfo-2a)

MPSAEMBS (0.51 g, 1.38 mmol), pyridine (0.54 g, 6.8 mmol), and 5.0 g of ethanol were placed in a 15-ml Ace pressure tube and refluxed at 100 °C for 24 h. The solution was then cooled to room temperature, and the solvent removed under reduced pressure to get the ionic liquid, IL-Sulfo-2a. Unconverted reactants were

Downloaded by [University North Carolina - Chapel Hill] at 02:26 23 June 2013

removed by extracting with *n*-hexane under reflux, and the product recovered as a solid. Yield = 90%. Mp = 180 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ = 2.27 (s, 3H; H_3C-Ar-S-N), 2.4 (s, 3H; H_3C-Ar-S-O), 3.3–3.4 (q, 2H, H_2C-N), 4.6–4.7 (t, 2H, H_2C-N-Ar), 7.1 (d, 2H; Ar-CH), 7.4 (d, 2H; Ar-CH), 7.45 (d, 2H; Ar-CH), 7.5 (d, 2H; Ar-CH), 7.92 (t, 1H; NH), 8.2 (t, 2H; Ar-CH), 8.6 (t, 1H; Ar-CH), 9.0 (d, 2H; Ar-CH-N); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ = 21.49 (H_3C-Ar-S-N), 21.50 (H_3C-Ar-S-O), 42.35 (H_2C-N-S), 60.15 (H2C-N-Ar), 126.2 (Ar-CH), 127.12 (Ar-CH), 128.56 (Ar-CH), 128.83 (Ar-CH), 130.5 (Ar-CH), 137.2 (Ar-C-S), 138.2 (Ar-CH), 144.0 (Ar-CH), 145.97 (Ar-CH-N), 146.0 (Ar-C-S), 146.2 (Ar-CH), 146.3 (Ar-CH).

Synthesis of 1-Methyl-1-(2-(methylphenylsulfonamido)ethyl)-pyrrolidinium 4-Methylbenzenesulfonate (IL-Sulfo-2b)

MPSAEMBS (0.31 g, 0.84 mmol), 1-methylpyrrolidine (0.36 g, 4.2 mmol), and 5.0 g of ethanol were placed in a 15-ml Ace pressure tube and refluxed at 100 °C for 24 h. The solution was then cooled to room temperature, and the solvent removed under reduced pressure to get IL-Sulfo-3b. Unconverted reactants were removed by extracting with n-hexane under reflux, and the product recovered as a solid. Yield = 92%. Mp = 129 °C.

^{1}H NMR (300 MHz, D_2O) δ = 1.9–2.1 (t, 4H; 2CH_2), 2.2 (s, 3H; H_3C-Ar-S-N), 2.24 (s, 3H; H_3C-Ar-S-O), 2.95 (s, 3H; H_3C-N), 3.18–3.21 (t, 2H; H_2C-N), 3.22–3.34 [m, 6H; CH_2-N-(CH_2)-CH_2], 7.2 (d, 2H; Ar-CH), 7.3 (d, 2H; Ar-CH), 7.5 (d, 2H; Ar-CH), 7.6 (d, 2H; Ar-CH); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ = 21.36 (H_3C-Ar-S-N), 21.46 (2H_2C), 21.66 (H_3C-Ar-S-O), 38.16 (H_2C-N), 48.08 (H_3C-N), 62.56 (H_2C-N), 64.74 [2(H_2C)-N], 126.17 (Ar-CH), 127.36 (Ar-CH), 128.88 (Ar-CH), 130.51 (Ar-CH), 137.38 (Ar-C-S-N), 138.62 (Ar-CH), 143.82 (Ar-CH), 146.03 (Ar-C-S-O).

Synthesis of Dual-Amino Functionalized Ionic Liquid, 3-Amino-*N,N*-diethyl-*N*-(2-(Methylsulfonamido)ethyl)propaneammonium Methanesulfonate (IL-Sulfo-3)

Step 1: Protection of amino group. Di-*tert*-butyl dicarbonate (8.38 g, 38.4 mmol) was added drop wise to neat 3-(diethylamino)propylamine (DEAPA) (5.0 g, 38.4 mmol) at room temperature (caution: exothermic reaction). The reaction mixture was allowed to stir overnight. The major by-product, *tert*-butanol, was then removed at reduced pressure to give *tert*-butyl(3-(diethylamino)propyl)carbamate. Yield = 98%.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.5–1.0 (t, 6H; CH_3), 1.35 (s, 9H; 3(CH_3)-O), 1.2–2.0 (p, 2H; CH_2), 2.3–2.4 [m, 6H; 3(CH_2)-N], 3.15 (q, 2H; H_2C-N); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 11.89 (CH_3), 26.8 (CH_2), 28.6 (3CH_3), 61.6 (H_2C-N), 40.3 (H_2C-N), 46.9 (H_2C-N), 51.8 (H_2C-N), 78.7 (C-O) 156.3 (C=O).

Step 2: Addition of sulfonamido group. MSAEMS (1.0 g, 4.6 mmol) and *tert*-butyl(3-(diethylamino)propyl)carbamate (1.27 g, 5.5 mmol) and 50 ml of ethanol were placed in a 100-ml round-bottomed flask and refluxed at 110 °C for 48 h. The solution was then cooled to room temperature, and the solvent removed under

Downloaded by [University North Carolina - Chapel Hill] at 02:26 23 June 2013

reduced pressure to get the ionic liquid, 3-((*tert*-butoxycarbonyl)amino)-*N,N*-diethyl-*N*-(2-(methylsulfonamido)ethyl)propaneammonium methanesulfonate. The ionic liquid was purified by extraction with toluene–dichloromethane mixture and recovered as a brownish yellow viscous liquid. Yield = 90%.

^{1}H NMR (300 MHz, D_2O) $\delta = 1.05$–1.20 (t, 6H; $2CH_3$), 1.22–1.3 (s, 9H; $3CH_3$), 1.7–1.81 (m, 2H; CH_2), 2.61 (s, 3H; H_3C-S-N), 2.9 (s, 3H, H_3C-S-O), 3.0–3.1 (t, 2H; H_2C-N), 3.1–3.2 (m, 2H, H_2C-N), 3.2–3.35 [m, 6H, $3(CH_2)$-N], 3.37–3.41 (t, 2H, CH_2); ^{13}C NMR (75.5 MHz, D_2O) $\delta = 6.90$ ($2H_3C$-N), 22.01 (CH_2), 27.92 [$3(H_3C)$-O], 36.11 (H_2C-N), 36.81 (H_2C-N), 38.78 (H_3C-S-N), 39.14 (H_3C-S-O), 54.16 [$2(H_2C)$-N], 55.5 (H_2C-N), 55.7 (H_2C-N), 81.2 (C-O), 158 (C=O).

Step 3: Deprotection of amino group. The amino-protected ionic liquid was dissolved in methanol. A few drops of hydrochloric acid (27%) were added to the methanolic solution at room temperature, and the mixture was then allowed to stir overnight. The unconverted, protected ionic liquid was extracted with dichloromethane and obtained as a brownish yellow viscous liquid after removal of the volatile solvent under reduced pressure. Yield = 91%. Mp $< -50\,^\circ$C.

^{1}H NMR (300 MHz, D_2O) $\delta = 1.1$–1.12 (t, 6H; CH_3), 1.9–2.1 (m, 2H; CH_2), 2.62 (s, 3H; H_3C-S-N), 2.8–3.0 (t, 2H; H_2C-N), 3.0 (s, 3H, H_3C-S-O), 3.2–3.38 [m, 8H; $4(CH_2)$-N], 3.4–3.45 (t, 2H, CH_2-N); ^{13}C NMR (75.5 MHz, D_2O) $\delta = 7.06$ ($2CH_3$), 20 (CH_2), 36.15 (H_2C-N), 36.47 (H_2C-N), 38.81 (H_3C-S-N), 39.19 (H_3C-S-O), 54.45 [$(CH_2)_2$-N], 54.46 (H_2C-N), 56.15 (H_2C-N).

ACKNOWLEDGMENT

This work was financially supported by the Danish Strategic Research Agency, Dong Energy A/S, and Vattenfall A/S.

REFERENCES

1. Olivier-Bourbigou, H.; Magna, L.; Morvan, D. Ionic liquids and catalysis: Recent progress from knowledge to applications. *Appl. Catal. A* **2010**, *373*, 1–56.
2. Huang, J. H.; Ruther, T. Why are ionic liquids attractive for CO_2 absorption? An overview. *Aus. J. Chem.* **2009**, *62*, 298–308.
3. Orita, A.; Kamijima, K.; Yoshida, M. Allyl-functionalized ionic liquids as electrolytes for electric double-layer capacitors. *J. Power Sources* **2010**, *195*, 7471–7479.
4. Branco, L. C.; Crespo, J. G.; Afonso, C. A. M. Ionic liquids as an efficient bulk membrane for the selective transport of organic compounds. *J. Phys. Org. Chem.* **2008**, *21*, 718–723.
5. Greaves, T. L.; Drummond, C. J. Protic ionic liquids: Properties and applications. *Chem. Rev.* **2008**, *108*, 206–237.
6. Parvulescu, V. I.; Hardacre, C. Catalysis in ionic liquids. *Chem. Rev.* **2007**, *107*, 2615–2665.
7. Huang, J.; Riisager, A.; Berg, R. W.; Fehrmann, R. Tuning ionic liquids for high gas solubility and reversible gas sorption. *J. Mol. Catal. A* **2008**, *279*, 170–176.
8. Freire, M. G.; Carvalho, P. J.; Gardas, R. L.; Marrucho, I. M.; Santos, L. M. N. B. F.; Coutinho, J. A. P. Mutual solubilities of water and the [C(n)mim][Tf_2N] hydrophobic ionic liquids. *J. Phys. Chem. B* **2008**, *112*, 1604–1610.

Downloaded by [University North Carolina - Chapel Hill] at 02:26 23 June 2013

9. Gabriel, S.; Weiner, J. Ueber einige abkommlinge des propylamins. *Ber.* **1888**, *21*, 2669–2679.
10. Walden, P. Uber die molekulargobe und elektrische leitfahigkeit einiger geschmolzener salze. *Bull. Acad. Imp. Sci.* **1914**, 1800.
11. Boon, J. A.; Levisky, J. A.; Pflug, J. L.; Wilkes, J. S. Friedel–Crafts reactions in ambient-temperature molten salts. *J. Org. Chem.* **1986**, *51*, 480–483.
12. Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. Dissolution of cellulose with ionic liquids. *J. Am. Chem. Soc.* **2002**, *124*, 4974–4975.
13. Jacquemin, J.; Husson, P.; Majer, V.; Gomes, M. F. C. Low-pressure solubilities and thermodynamics of solvation of eight gases in 1-butyl-3-methylimidazolium hexafluorophosphate. *Fluid Phase Equilib.* **2006**, *240*, 87–95.
14. Riisager, A.; Fehrmann, R.; Flicker, S.; Van Hal, R.; Haumann, M.; Wasserscheid, P. Very stable and highly regioselective supported ionic-liquid-phase (SILP) catalysis: Continuous flow fixed-bed hydroformylation of propene. *Angew. Chem. Int. Ed.* **2005**, *44*, 815–819.
15. Ståhlberg, T.; Sørensen, M. G.; Riisager, A. Direct conversion of glucose to 5-(hydroxymethyl)furfural in ionic liquids with lanthanide catalysts. *Green Chem.* **2010**, *12*, 321–325.
16. Bates, E. D.; Mayton, R. D.; Davis, J. H. CO_2 capture by a task-specific ionic liquid. *J. Am. Chem. Soc.* **2002**, *124*, 926–927
17. Cole, A. C.; Jensen, J. L.; Ntai, I.; Tran, K. L. T.; Weaver, K. J.; Forbes, D. C.; Davis, J. H. Novel Brønsted acidic ionic liquids and their use as dual solvent–catalyst. *J. Am. Chem. Soc.* **2002**, *124*, 5962–5963.
18. Winkel, A.; Reddy, P. V. G.; Wilhelm, R. Recent advances in the synthesis and application of chiral ionic liquids. *Synthesis* **2008**, 999–1016.
19. Du, Z.; Li, Z.; Deng, Y. Synthesis and characterisation of sulfonyl-functionalised ionic liquids. *Synth. Commun.* **2005**, *35*, 1343–1349.
20. Li, X.; Zhao, D.; Fei, Z.; Wang, L. Applications of functionalised ionic liquids. *Sci. China Ser. B: Chem.* **2006**, *49*, 385–401.

Downloaded by [University North Carolina - Chapel Hill] at 02:26 23 June 2013