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Synthesis and Physicochemical Properties of Bis(fluoroalkanesulfon)amide-Based Ionic Liquids

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A series of bis(fluoroalkanesulfon)amides were synthesized in good yield from the reaction of fluoroalkanesulfonamides and fluoroalkylsulfonyl fluorides. Ionic liquids based on these amide anions and an imidazolium cation demonstrated high densities and a wide temperature range for the liquid state.

Introduction

Ionic liquids have attracted significant attention in recent years.[1] Due to their favorable properties such as high ionic mobility, negligible vapor pressure, wide electrochemical window, good thermal stability, and high conductivity, numerous ionic liquids have been synthesized and used as solvents for electrochemistry, biochemistry, polymer chemistry, organic synthesis, and catalytic process as well as separation science.[1,2] Reactions conducted in ionic liquids often show improved reactivity and selectivity.[2] In addition, ionic liquids could be used as high-performance lubricants.[3] Thus, much attention has been paid to the application of ionic liquids in tribology. Ionic liquid crystals are new liquid-crystalline compounds,[4] which are considered to be novel materials not only displaying lamellar mesophases but also exhibiting nematic columnar phases. Studies on liquid-crystalline ionic liquids have shown that the choice of the anion has a strong influence on the mesophase behavior.[4] Piperidinium, piperazinium, and morpholinium cations combined with different types of anions exhibit rich mesomorphic behavior.[5] Indeed, besides liquid-crystalline behavior, the physicochemical properties of ionic liquids are much influenced by the type of anion. For example, ionic liquids containing the bis(trifluoromethanesulfon)amide anion are very hydrophobic. A high charge/discharge capacity and a wide operating temperature range could be obtained for lithium batteries by employing bis(fluoroalkanesulfon)amide-based ionic liquids as electrolytes.[6] Thus, it is inferred that bis(fluoroalkanesulfon)amides might be the suitable anion to endow ionic liquids with useful properties. However, only a few bis(fluoroalkanesulfon) amides have been reported so far.[7] To expand the research on amide-type ionic liquids, we explored the preparation of bis(fluoroalkanesulfon)amides and investigated the synthesis and physicochemical properties of these amide-based ionic liquids.

Results and Discussion

As shown in Table 1, treatment of fluoroalkanesulfonamide with the corresponding fluoroalkylsulfonyl fluoride gave the symmetrically substituted amide (entries 1–5). Triethylamine was used as the solvent as well as the catalyst and reagent for the reaction. Hydrodeiodination inevitably happened under these basic conditions,[8] affording the corresponding hydrogenolysis amide (entries 2–4). A longer reaction time was needed with elongation of the fluoroalkyl chain. The reaction of fluoroalkanesulfonamides with different chain length and fluoroalkylsulfonyl fluoride resulted in the formation of asymmetrically substituted amides (entries 6–8). Diamides **1i**–**1k** were readily obtained from the reaction of the disulfonyl fluorides with trifluoromethanesulfonamide (entries 9–11). Bis(fluoroalkanesulfon)amide salts **5** with short alkyl chain are slightly soluble in water, which leads to the loss of the salts while being washed with water during workup (entries 7–9). However, washing with water is necessary for complete removal of water-soluble fluorides and iodides. Otherwise, large amounts of HF and I_2 would be generated during the acidification stage, making further purification difficult. For those amides with high boiling point and high fluorine content, extraction with F113 ($CF_2ClCFCl_2$) became a relatively efficient procedure for the isolation of the final product (entries 4–5, 11).

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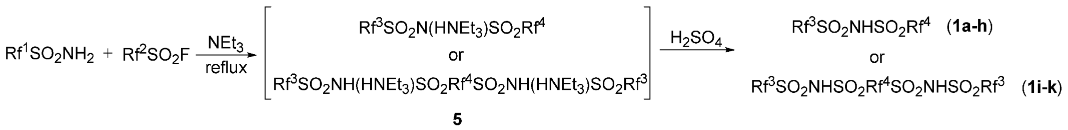
Table 1. Preparation of symmetric and asymmetric amides.



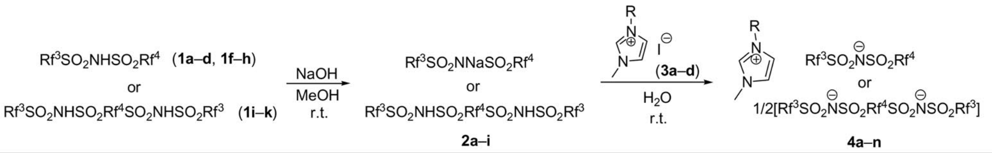
Entry	Rf^1[a]	Rf^2SO_2F	Time (h)	$Rf^3SO_2NHSO_2Rf^4$ or $Rf^3SO_2NHSO_2Rf^4SO_2NHSO_2Rf^3$	Yield (%)[b]
1	$Cl(CF_2)_2$	$Cl(CF_2)_2SO_2F$	12	$[Cl(CF_2)_2SO_2]_2NH$ (**1a**)	81
2	$I(CF_2)_2O(CF_2)_2$	$I(CF_2)_2O(CF_2)_2SO_2F$	29	$[H(CF_2)_2O(CF_2)_2SO_2]_2NH$ (**1b**)	86
3	$I(CF_2)_4O(CF_2)_2$	$I(CF_2)_4O(CF_2)_2SO_2F$	36	$[H(CF_2)_4O(CF_2)_2SO_2]_2NH$ (**1c**)	82
4[c]	$I(CF_2)_6O(CF_2)_2$	$I(CF_2)_6O(CF_2)_2SO_2F$	60	$[H(CF_2)_6O(CF_2)_2SO_2]_2NH$ (**1d**)	41
5[c]	$Cl(CF_2)_6O(CF_2)_2$	$Cl(CF_2)_6O(CF_2)_2SO_2F$	50	$[Cl(CF_2)_6O(CF_2)_2SO_2]_2NH$ (**1e**)	46
6	$CF_3(CF_2)_3$	$I(CF_2)_2O(CF_2)_2SO_2F$	42	$CF_3(CF_2)_3SO_2NHSO_2(CF_2)_2O(CF_2)_2H$ (**1f**)	88
7	$Cl(CF_2)_2$	$I(CF_2)_2O(CF_2)_2SO_2F$	29	$Cl(CF_2)_2SO_2NHSO_2(CF_2)_2O(CF_2)_2H$ (**1g**)	70
8	CF_3	$I(CF_2)_2O(CF_2)_2SO_2F$	37	$CF_3SO_2NHSO_2(CF_2)_2O(CF_2)_2H$ (**1h**)	69
9	CF_3	$FSO_2(CF_2)_2O(CF_2)_2SO_2F$	27	$CF_3SO_2NHSO_2(CF_2)_2O(CF_2)_2SO_2NHSO_2CF_3$ (**1i**)	64
10	CF_3	$FSO_2(CF_2)_2O(CF_2)_4O(CF_2)_2SO_2F$	43	$CF_3SO_2NHSO_2(CF_2)_2O(CF_2)_4O(CF_2)_2SO_2NHSO_2CF_3$ (**1j**)	94
11[c]	CF_3	$FSO_2(CF_2)_2O(CF_2)_8O(CF_2)_2\ SO_2F$	48	$CF_3SO_2NHSO_2(CF_2)_2O(CF_2)_8O(CF_2)_2SO_2NHSO_2CF_3$ (**1k**)	66

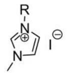
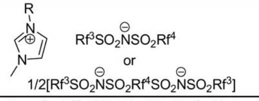
[a] $Rf^1SO_2NH_2$ were synthesized according to our previous work.[9] [b] Isolated yield. [c] Purified by column chromatography.

Reaction of these bis(fluoroalkanesulfon)amides with NaOH in methanol could convert them into the corresponding sodium salts (Table 2). Subsequent anion exchange reaction with imidazolium iodides afforded the room-temperature ionic liquids **4a**–**n** in good yields. It was found that the ionic liquids, even sodium salts **2a**–**i**, were soluble in a variety of organic solvents, thus making the purification simple and efficient. The good solubility might result from the coexistence of the long lipophilic fluoroalkyl chain and the hydrophilic amide group. However, the ionic liquids with short fluoroalkyl chain became slightly soluble in water, leading to their inevitable loss during workup. Therefore, the yield of **4a** and **4k** was relatively lower as compared with other ionic liquids (entries 1, 11).

Densities and thermal properties are given in Table 3. All of these ionic liquids exhibited higher density than the commonly used ones, which might be the result of the increase in fluorine content. For instance, with *N*,*N*-dimethylimidazolium as the cation, elongation of the fluoroalkyl chain would increase the density (entries 2, 6, and 7, entries 8 and 10, entries 11 and 13), which is much higher than that observed with bis(trifluoromethanesulfon)amide as the anion.[10] On the other hand, the variation of the density showed a trend similar to that in common ionic liquids (entries 2–5, entries 11 and 12, entries 13 and 14). For example, with $[H(CF_2)_2O(CF_2)_2SO_2]_2N^-$ as the anion, changing the alkyl group from methyl (in **4b**) to butyl (in **4e**) caused the density to decrease from 1.82 to 1.68 g/cm³ (entries 2–5). Another important feature of these ionic liquids is their low glass transition temperature and good thermal stability. *N*,*N*-dimethylimidazolium-based ionic liquids are usually solid at ambient temperature even when bis(trifluoromethanesulfon)amide is used as the anion. However, all of ionic liquids **4a**–**n** are liquid at room temperature, showing

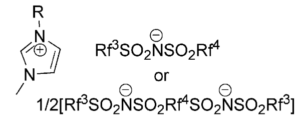
Table 2. Synthesis of ionic liquids.



Entry	$Rf^3SO_2NNaSO_2Rf^4$ or $Rf^3SO_2NNaSO_2Rf^4SO_2NNaSO_2Rf^3$	Yield (%)[a]		 $Rf^3SO_2\overset{\ominus}{N}SO_2Rf^4$ or $1/2[Rf^3SO_2\overset{\ominus}{N}SO_2Rf^4SO_2\overset{\ominus}{N}SO_2Rf^3]$	Yield (%)[a]
1	$[Cl(CF_2)_2SO_2]_2NNa$ (**2a**)	72	R = CH_3 (**3a**)	[mmim]$\{[Cl(CF_2)_2SO_2]_2N\}$ (**4a**)	58
2	$[H(CF_2)_2O(CF_2)_2SO_2]_2NNa$ (**2b**)	93	R = CH_3 (**3a**)	[mmim]$\{[H(CF_2)_2O(CF_2)_2SO_2]_2N\}$ (**4b**)	87
3	$[H(CF_2)_2O(CF_2)_2SO_2]_2NNa$ (**2b**)		R = C_2H_5 (**3b**)	[emim]$\{[H(CF_2)_2O(CF_2)_2SO_2]_2N\}$ (**4c**)	91
4	$[H(CF_2)_2O(CF_2)_2SO_2]_2NNa$ (**2b**)		R = n-C_3H_7 (**3c**)	[pmim]$\{[H(CF_2)_2O(CF_2)_2SO_2]_2N\}$ (**4d**)	87
5	$[H(CF_2)_2O(CF_2)_2SO_2]_2NNa$ (**2b**)		R = n-C_4H_9 (**3d**)	[bmim]$\{[H(CF_2)_2O(CF_2)_2SO_2]_2N\}$ (**4e**)	91
6	$[H(CF_2)_4O(CF_2)_2SO_2]_2NNa$ (**2c**)	73	R = CH_3 (**3a**)	[mmim]$\{[H(CF_2)_4O(CF_2)_2SO_2]_2N\}$ (**4f**)	95
7	$[H(CF_2)_6O(CF_2)_2SO_2]_2NNa$ (**2d**)	77	R = CH_3 (**3a**)	[mmim]$\{[H(CF_2)_6O(CF_2)_2SO_2]_2N\}$ (**4g**)	89
8	$CF_3(CF_2)_3SO_2NNaSO_2(CF_2)_2O(CF_2)_2H$ (**2e**)	75	R = CH_3 (**3a**)	[mmim]$[CF_3(CF_2)_3SO_2NSO_2(CF_2)_2O(CF_2)_2H]$ (**4h**)	95
9	$Cl(CF_2)_2SO_2NNaSO_2(CF_2)_2O(CF_2)_2H$ (**2f**)	87	R = CH_3 (**3a**)	[mmim]$[Cl(CF_2)_2SO_2NSO_2(CF_2)_2O(CF_2)_2H]$ (**4i**)	71
10	$CF_3SO_2NNaSO_2(CF_2)_2O(CF_2)_2H$ (**2g**)	75	R = CH_3 (**3a**)	[mmim]$[CF_3SO_2NSO_2(CF_2)_2O(CF_2)_2H]$ (**4j**)	76
11	$CF_3SO_2NNaSO_2(CF_2)_2O(CF_2)_2SO_2NNaSO_2CF_3$ (**2h**)	85	R = CH_3 (**3a**)	$[mmim]_2[CF_3SO_2NSO_2(CF_2)_2O(CF_2)_2SO_2NSO_2CF_3]$ (**4k**)	51
12	$CF_3SO_2NNaSO_2(CF_2)_2O(CF_2)_2SO_2NNaSO_2CF_3$ (**2h**)		R = n-C_4H_9 (**3d**)	$[bmim]_2[CF_3SO_2NSO_2(CF_2)_2O(CF_2)_2SO_2NSO_2CF_3]$ (**4l**)	72
13	$CF_3SO_2NNaSO_2(CF_2)_2O(CF_2)_4O(CF_2)_2SO_2NNaSO_2CF_3$ (**2i**)	94	R = CH_3 (**3a**)	$[mmim]_2[CF_3SO_2NSO_2(CF_2)_2O(CF_2)_4O(CF_2)_2SO_2NSO_2CF_3]$ (**4m**)	76
14	$CF_3SO_2NNaSO_2(CF_2)_2O(CF_2)_4O(CF_2)_2SO_2NNaSO_2CF_3$ (**2i**)		R = n-C_4H_9 (**3d**)	$[bmim]_2[CF_3SO_2NSO_2(CF_2)_2O(CF_2)_4O(CF_2)_2SO_2NSO_2CF_3]$ (**4n**)	85

[a] Isolated yield.

Table 3. The properties of bis(fluoroalkanesulfon)amide-based ionic liquids.

Entry		ρ $(\mathrm{g\,cm^{-3}})$[a]	T_g (°C)[b]	T_d (°C)[c]	μ $(\mathrm{mm^2\,s^{-1}})$[d]
1	**4a**	1.89	–103.4	398.9	160.3
2	**4b**	1.82	–97.6	414.0	164.1
3	**4c**	1.75	–99.4	393.0	127.1
4	**4d**	1.73	–97.3	398.0	133.2
5	**4e**	1.68	–97.6	393.0	158.4
6	**4f**	1.92	–86.4	393.1	236.2
7	**4g**	1.95	–83.2	407.9	465.1
8	**4h**	1.75	–94.1	402.0	217.9
9	**4i**	1.85	–101.0	406.1	175.0
10	**4j**	1.71	–81.9	422.7	70.0
11	**4k**	1.81	–80.6	444.9	712.5
12	**4l**	1.66	–86.5	447.5	667.0
13	**4m**	1.89	–113.8	446.0	1359.7
14	**4n**	1.71	–71.1	443.3	968.8

[a] Pycnometer, 25 °C. [b] Determined by DSC. DSC data were recorded in the range –150 to 200 °C with a heating rate of 10 °C/min. [c] Determined by TGA. T_d was T_{onset}. [d] Ubbelohde viscosity meter, 25 °C.

a rather low glass transition temperature below –80 °C. Moreover, they are all thermally stable to >390 °C, as determined by thermogravimetric analysis (TGA), demonstrating a wide temperature range for the liquid state. It can be inferred that the bis(fluoroalkanesulfon)amide anions contribute to this peculiar thermal behavior. Moreover, the viscosity of these ionic liquids was influenced by the anions and cations. Elongation of the fluoroalkyl chain in amides increased their viscosity (Table 3, entries 1, 2, 6, and 7, entries 8–10, entries 11 and 13, entries 12 and 14). Changing the alkyl group on the cation from methyl to ethyl, propyl, or butyl resulted in a decrease of the viscosity (entries 2–5, entries 11–12, and entries 13–14).

Conclusion

A series of bis(fluoroalkanesulfon)amides were synthesized in good yield from the reaction of fluoroalkanesulfonamides and fluoroalkylsulfonyl fluorides. The combination of bis(fluoroalkanesulfon)amide anions with imidazolium cations afforded a variety of novel ionic liquids, which demonstrated high densities from 1.66 to 1.95 g/cm^3 and a wide liquid range. Further investigations on the applications of these ionic liquids in lithium batteries are going on.

Experimental Section

General: Unless otherwise stated, NMR spectra were recorded in deuteriated acetone at 300 MHz (^{1}H NMR) and 282 MHz (^{19}F NMR). All chemical shifts were reported in ppm relative to TMS and $CFCl_3$ (positive for downfield shifts) as external standards. Analytical pure Et_3N and MeOH were used without any purification. Fluoroalkanesulfonamides were synthesized according to our previous publication.[9] $Cl(CF_2)_2SO_2F$, $FO_2S(CF_2)_2O(CF_2)_2SO_2F$, $FO_2S(CF_2)_2O(CF_2)_4O(CF_2)_2SO_2F$, $FO_2S(CF_2)_2O(CF_2)_8O(CF_2)_2SO_2F$, and imidazolium iodides **3a**–**d** were prepared according to the literature.[11] Other reagents used below were all purchased from commercial sources.

Typical Procedure for the Preparation of 1a–c, 1f–j: In a 1000 mL round-bottomed flask, $I(CF_2)_2O(CF_2)_2SO_2F$ (180 g, 95%, 0.401 mol) was added to a mixture of $I(CF_2)_2O(CF_2)_2SO_2NH_2$ (155 g, 0.365 mol) and Et_3N (300 mL) and heated at reflux for 29 h. After cooling, the resulting biphasic system was separated. The lower brown fluorous layer was diluted by CH_2Cl_2 (700 mL), washed with H_2O (6 × 400 mL), and dried with anhydrous Na_2SO_4. The solvent was evaporated, and the brown residue was dried in vacuo. After being acidified with concentrated H_2SO_4, the crude product was obtained by vacuum distillation. Vacuum redistillation afforded pure $[H(CF_2)_2O(CF_2)_2SO_2]_2NH$ (**1b**) (110 °C/60 Pa, 182 g, 0.315 mol, 86%) as a white solid. ^{1}H NMR: δ = 6.51 (tt, J = 52.1, 3.6 Hz, 2 H) ppm. ^{19}F NMR: δ = –138.7 (d, J = 52.1 Hz, 4 F), –117.0 (s, 4 F), –89.1 (s, 4 F), –81.1 (t, J = 12.4 Hz, 4 F) ppm. MS (ESI): m/z (%) = 575.8 (100) $[M - H]^-$. IR (KBr): $\tilde{\nu}$ = 3580, 1629, 1426, 1333, 1287, 1148, 977, 858, 749, 616, 526 cm^{-1}. $C_8H_3F_{16}NO_6S_2$ (577.22): calcd. C 16.65, H 0.52, N 2.43; found C 16.73, H 0.56, N 2.25.

Typical Procedure for the Preparation of 1d, 1e, and 1k: $Cl(CF_2)_6O(CF_2)_2SO_2F$ (5.87 g, 96%, 10.5 mmol) and $Cl(CF_2)_6O(CF_2)_2SO_2NH_2$ (5.39 g, 10.1 mmol) were mixed in Et_3N (10 mL). Then the mixture was heated at reflux for 50 h. After removing the upper Et_3N layer, the lower brown fluorous residue was washed with H_2O, dried in vacuum, acidified with concentrated H_2SO_4, and extracted by F113. The crude product was purified by column chromatography on silica gel by using dichloromethane/acetonitrile (4:1) as the eluent. Pure $[Cl(CF_2)_6O(CF_2)_2SO_2]_2NH$ (**1e**) was obtained as a white solid (4.87 g, 4.66 mmol, 46%). ^{19}F NMR: δ = –125.1 (m, 4 F), –121.7 (m, 4 F), –121.1 (m, 4 F), –120.0 (m, 4 F), –116.7 (s, 4 F), –82.7 (m, 4 F), –80.9 (m, 4 F), –68.5 (t, J = 12.3 Hz, 4 F) ppm. MS (ESI): m/z (%) = 1043.7 (100) $[M - H]^-$. IR (KBr): $\tilde{\nu}$ = 3650, 1369, 1342, 1207, 1147, 1099, 1047, 985, 887, 778, 706, 699, 683, 656, 624, 545, 516 cm^{-1}. $C_{16}HCl_2F_{32}NO_6S_2$ (1046.17): calcd. C 18.37, H 0.10, N 1.34; found C 17.99, H <0.3, N 1.57.

Typical Procedure for the Preparation of 2a–i: In a 25 mL round-bottomed flask, **1b** (2.33 g, 4.04 mmol) was dissolved in CH_3OH

(15 mL), and NaOH (0.165 g, 4.12 mmol) was added. The reaction mixture was then stirred at room temperature for several hours. After removing the solvent, the residue was extracted with ethyl ether (3 × 10 mL). The ether layer was evaporated, and the solution was dried in vacuum to give pure $[H(CF_2)_2O(CF_2)_2SO_2]_2NNa$ (**2b**) as a white solid (2.25 g, 3.75 mmol, 93%). ^1H NMR (D_2O): δ = 6.33 (tt, J = 52.1, 3.2 Hz, 2 H) ppm. ^{19}F NMR (D_2O): δ = –135.8 (dt, J = 52.1, 4.2 Hz, 4 F), –114.2 (s, 4 F), –85.9 (m, 4 F), –78.7 (t, J = 12.4 Hz, 4 F) ppm. MS (ESI): m/z (%) = 575.8 (100) [M – Na]$^-$. IR (KBr): $\tilde{\nu}$ = 1371, 1343, 1289, 1187, 1137, 1091, 994, 854, 771, 650, 624, 574, 527 cm^{-1}. $C_8H_2F_{16}NNaO_6S_2$ (599.20): calcd. C 16.04, H 0.34, N 2.34; found C 16.26, H 0.75, N 2.64.

Typical Procedure for the Preparation of 4a–n: Under vigorous stirring, a solution of **3a** (0.802 g, 3.58 mmol) in H_2O (10 mL) was added to a solution of **2e** (2.09 g, 3.47 mmol) in H_2O (10 mL), and the mixture was stirred at room temperature for 8 h. After removing the water layer, the lower phase was collected and washed with water (5 × 20 mL). The pure product **4h** was dried at 80 °C under reduced pressure to afford a light yellow liquid (2.22 g, 3.29 mmol, 95%). ^1H NMR: δ = 8.93 (s, 1 H), 7.67 (d, J = 1.5 Hz, 2 H), 6.52 (tt, J = 52.2, 3.6 Hz, 1 H), 4.04 (s, 6 H) ppm. ^{19}F NMR: δ = –139.9 (dt, J = 52.2, 4.0 Hz, 2 F), –127.2 (m, 2 F), –122.2 (m, 2 F), –118.1 (s, 2 F), –114.4 (t, J = 13.8 Hz, 2 F), –90.0 (m, 2 F), –82.3 (m, 2 F), –82.2 (m, 3 F) ppm. MS (ESI): m/z (%) = 97.1 (100) [M$^+$], 577.8 (100) [M$^-$]. IR (KBr): $\tilde{\nu}$ = 3166, 3132, 1578, 1425, 1355, 1286, 1177, 1078, 1031, 1009, 981, 874, 856, 748, 696, 649, 624, 591, 520 cm^{-1}. $C_{13}H_{10}F_{17}N_3O_5S_2$ (675.34): calcd. C 23.12, H 1.49, N 6.22; found C 22.87, H 1.50, N 6.20.

Supporting Information (see footnote on the first page of this article): NMR spectra for compounds **1a**–**k**, **2a**–**i**, and **4a**–**n**.

Acknowledgments

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