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Syntheses of Very Dense Halogenated Liquids

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Abstract: A family of halogenated liquids with densities ranging from 1.95 to 2.80 g cm^{-3} was readily synthesized by a one-pot procedure. These liquids exhibit characteristics of ionic liquids with melting/transition points lower than room temperature, long liquid ranges, and marked hydrolytic and thermal stabilities.

Ionic liquids have become a blossoming research topic in recent years.[1] So far, the majority of the efforts have been focused on using ionic liquids as solvents for organic reactions, catalysis, and other processes such as electrochemical, biochemical, as well as separation science.[2] On the other hand, there are very promising potential applications of ionic liquids as new materials, including new media for preparation of micro- or nanomaterials,[3] aerosol or gels,[4] gas absorbents,[5] CO_2 capture reagents,[6] lubricants,[7] and so on. In these cases, the properties of unique solubility, nonvolatility, and thermal stability of ionic liquids led to their successful use.

One of the interesting points is that the density of ionic liquids is higher than that of hydrocarbons,[2b] usually by more than 1.0 g cm^{-3}. The highest density reported for an ionic liquid was 2.40 g cm^{-3} for 34−66 mol % $[(CH_3)_3S]Br/AlBr_3]$,[8] but the moisture-sensitivity and toxicity of the anion limits its practical utilization where high-density fluids are needed. For example, floated inertial instruments such as certain types of accelerometers and gyroscopes require flotation fluids for operation.[9] Such fluids must have high densities to provide adequate flotation for structural components and also require relatively high viscosities for good damping properties. Flotation fluids such as polychlorotrifluoroethylene (CTFE), with a density of 1.90−1.95 g cm^{-3}, polybromotrifluoroethylene (BTFE) at 2.02−2.38 g cm^{-3}, and many other kinds of polyhalogenated fluids, such as polybrominated succinate (2.25−2.30 g cm^{-3}), 1,1,3,5,5-pentabromoperfluoropentane (~2.62 g cm^{-3}), and 1,1,3,5,7,7-hexabromoperfluoroheptane (~2.65 g cm^{-3}), have desirable properties. To date, at the cutting edge of damping/flotation fluids are the materials that contain a highly halogenated aryl group bonded via an ester linkage to a highly halogenated alkyl group.[9g−i] Those materials containing iodine with very high density (>2.70 g cm^{-3}) are most often solid at 25 °C.

Many of the halogenated compounds are volatile and highly toxic, which would be a major problem for use at ambient or elevated temperature. To circumvent this problem, nonvolatile ionic liquids may become the fluids of choice. In our preliminary work, the density of 1,3-di-(3,3,3-trifluoropropyl)imidazolium bis(trifluoromethylsulfonyl)amide was 1.85 g cm^{-3},[10] and methylimidazolium, pyridinium, and pyridazinium salts containing $SF_5(CF_2)_n(CH_2)_m-$ ($n = 2$ or 4, $m = 2$ or 4) exhibited densities of ~2 g cm^{-3}.[11] Owing to the diversity of structure and ease of quaternization, we chose imidazole analogues as the leading candidates to develop as highly dense ionic liquids, with the key protocol of introducing bromine or iodine into the cations.

All the halogenated ionic liquids were synthesized in a one-pot procedure, the intermediates of quaternization or bromination were not isolated before continuing with metathesis reactions. The product was pumped overnight at 60 °C at 0.1 mmHg to give sufficient purity for satisfactory spectral data (Scheme 1). For all final products, yields were 68−90%.

Generally, the order of increasing density for ionic liquids composed of a single cation is $[CH_3SO_3]^- \approx [BF_4]^- < [CF_3CO_2]^- < [CF_3SO_3]^- < PF_6^- < [(CF_3SO_2)_2N]^-$ (Tf_2N^-). Hexafluoroantimonate (V) (SbF_6^-)[12] was envisioned as an anion candidate which would contribute to higher density. Unfortunately, the dibrominated ionic liquid **(2b)** that contained SbF_6^- proved to be a solid at room temperature. Similarly, when the anion of **2b** was changed to PF_6^- (**2a**), the melting point increased a few degrees from 64.4 to 70.7 °C. However, with the bis(trifluoromethanesulfonyl)amide anion (NTf_2^-) (**2c**), it became liquid, with a glass transition temperature at −52 °C and a density of 1.95 g cm^{-3}, much higher than those

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SCHEME 1. Syntheses of Dense Halogenated Liquids

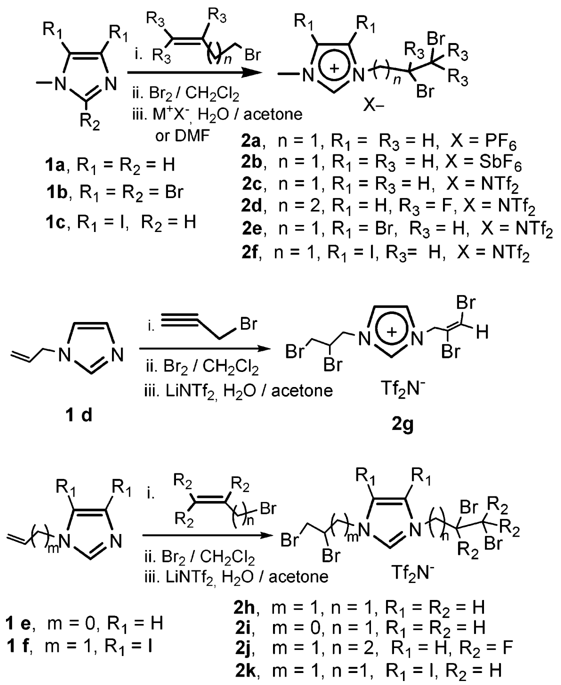

TABLE 1. Yields and Physical Properties for Halogenated Ionic Liquids

compd	yield (%)	Tg (Tm)[a]	Td[a]	density[b]	viscosity[c]
2a	81	(70.7)	263		
2b	76	(64.4)	289		
2c	90	−52	268	1.95	95.3
2d	75	−55	284	2.11	89.5
2e	85	−24	307	2.26	987.2
2f	70	−16	287	2.55	*d*
2g	71	−35	258	2.30	311.0
2h	86	−34	250	2.22	1071
2i	84	−24	246	2.25	1245
2j	69	−32	273	2.35	1106
2k	68	−2.9	282	2.80	*d*

[a] Determined by DSC, °C. [b] Pycnometer, 25 °C, g cm^{-3}. [c] Minivis II, cP, 60 °C. [d] Viscosity > 1500 cP.

of common nonhaloaluminate ionic liquids, illustrating the advantage of the anion which gives products with wide liquid ranges and high densities. The densities of ionic liquids are also affected by the cation, e.g., by the replacement of allyl bromide with 1,1,2-trifluoro-4-bromobutene as the electrophile,[13] the resultant ionic liquid **2d** with a density of 2.11 g cm^{-3} was much denser than **2c**.

These data clearly indicate that bromine on the cation of an ionic liquid has an obvious effect on its density. Building on this result, our continuing efforts were centered on preparing polyhalogenated room-temperature ionic liquids. One of the targets was a pentabrominated ionic liquid to be obtained by using 1-methyl-2,4,5-tribromoimidazole.[14] But surprisingly, after quaternization, some of the bromine is lost from the 2-position, and after metathesis and bromination, followed by washing with aqueous Na_2SO_3 solution, only a single tetrabrominated product, **2e**, was isolated, with a density of 2.26 g cm^{-3}.

Attempts to transform 1-allyl-3-propargylimidazolium bromides to a hexabrominated ionic liquid also failed. For compounds with an alkyne substituent, only the tetrabromo adduct (**2g**) was identified on the basis of ^1H and ^{13}C NMR spectra. Noteworthy, it also was an anti stereospecific bromine addition reaction similar to the bromination reaction of alkynes when an ionic liquid was involved as solvent.[15] Further bromination of **2g** using NBS in refluxing chloroform did not result in the desired hexabrominated product, but rather gave a mixture of **2g** and its syn isomer.

The other tetrabrominated liquids of **2h**, **2i**, and **2j** also were synthesized starting from 1-allylimidazole or 1-vinylimidazole; the densities range between 2.22 and 2.35 g cm^{-3} but do not exceed 2.40 g cm^{-3}. However, a liquid of exceptionally high density was achieved when iodine was introduced into the imidazolium ring. With the same synthesis protocol, starting from 1-methyl-4,5-diiodoimidazole (**1c**) or 1-allyl-4,5-diiodoimidazole (**1f**),[16] the diiododibrominated (**2f**) and diiodotetrabrominated (**2k**) compounds were prepared in moderate yields, having densities of 2.55 and 2.80 g cm^{-3}, respectively (Table 1). For **2h**, **2i**, **2j**, and **2k**, there are two isomers arising from the different relative configurations of two bromine atoms (2,2′- or 2,1′) on the N-substituents.

All of the products, except **2a** and **2b**, are liquids at 25 °C, and these hydrophobic ionic liquids are immiscible with water. After being pumped overnight, there is no water peak in the ^1H NMR and IR spectra, and good elementary analyses data were obtained. Compounds **2c**−**f** are miscible with methylene chloride, but difficultly soluble in chloroform, making them useful in separation science. All the new ionic liquids are water and air stable. All of the dense liquids except **2i** were stored at room temperature under atmosphere for 6 months without obvious changes in color. When **2c**,**e**,**f** were dissolved in DMSO-d_6/D_2O for 1 week at 25 °C and then heated at 60 °C for 12 h, no debromination product or deuterium exchange at 2-H of the imidazolium was detected by NMR.[17] The lack of exchange at C-2 is somewhat unusual. In addition, as shown in Table 1, all the compounds are thermally stable to >245 °C, and unexpectedly, when the halogen atoms are introduced on the imidazolium ring, the thermal stability is improved by 20−40 °C.

In summary, we have designed a family of new highly halogenated ionic liquids, whose densities range from 1.95 to 2.80 g cm^{-3}. These materials, which can be readily prepared by a one-pot procedure, are dense, viscous, water insensitive, and thermally stable liquids.

Experimental Section

General Methods. All the reagents used were analytical reagents purchased from commercial sources and used as received. ^1H, ^{19}F, and ^{13}C NMR spectra were recorded on a

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spectrometer operating at 300, 282, and 75 MHz, respectively, in acetone-d_6 unless otherwise stated. Chemical shifts are reported in ppm relative to the appropriate standard, $CFCl_3$ for ^{19}F and TMS for ^{1}H and ^{13}C NMR spectra. Differential scanning calorimetry (DSC) data were recorded in the range of −80 to 450 °C with a heating rate of 10 °C/min. The density was measured using a pycnometer.

General Procedure. An imidazole analogue (**1a**−**f**) and allyl bromide, propargyl bromide, or 1,1,2-trifluoro-4-bromobutene were placed in a Pyrex tube, which was evacuated, sealed, and heated at 65 °C for ~12 h. After being cooled to 25 °C, the tube was opened, and the volatile material was removed under reduced pressure. Crude products were washed with an acetone/pentane mixture (1:4) and then dissolved in CH_2Cl_2. To the organic solution was added bromine (1.3 equiv for each double bond), and the mixture was refluxed for about 5 h. After evaporation of the solvent, the residue was dissolved in acetone, an aqueous solution of $LiNTf_2$ was added, and the mixture was stirred for ~20 min. The acetone was removed under reduced pressure, and the remaining water and insoluble product were extracted with CH_2Cl_2 several times. The organic phase was combined, washed once with aqueous Na_2SO_3 (~10%) and three times with water, and then dried over Na_2SO_4. After removal of the solvent, and pumping overnight at 60 °C at 0.1 mmHg, the desired pure compounds were obtained in moderate to high yields.

1-(2,3-Dibromopropyl)-3-methylimidazolium hexafluorophosphate (2a): yield 81%; ^{1}H NMR δ 3.97 (dd, 1H, J = 11.4, 6.6 Hz), 4.08 (dd, 1H, J = 11.4, 4.7 Hz), 4.12 (s, 3H), 4.85 (dd, 1H, J = 13.8, 8.1 Hz), 4.90−4.97 (m, 1H), 5.05 (dd, 1H, J = 13.8, 3 Hz), 7.79 (s, 1H), 7.87 (s, 1H), 9.15 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 36.4, 37.2, 51.8, 54.5, 124.1, 125.1, 138.7; ^{19}F NMR δ −70.1 (d, J = 755.7 Hz). Anal. Calcd for $C_7H_{11}Br_2F_6N_2P$: C, 19.65; H, 2.59; N, 6.55. Found: C, 19.67; H, 2.59; N, 6.62.

1-(2,3-Dibromopropyl)-3-methylimidazolium hexafluoroantimonate (2b): yield 76%; ^{1}H NMR δ 3.96 (dd, 1H, J = 11.4, 6.6 Hz), 4.07 (dd, 1H, J = 11.4, 4.7 Hz), 4.12 (s, 3H), 4.85 (dd, 1H, J = 13.8, 8.1 Hz), 4.90−4.95 (m, 1H), 5.05 (dd, 1H, J = 13.8, 3 Hz), 7.78 (s, 1H), 7.87 (s, 1H), 9.16(s, 1H); ^{13}C NMR δ 34.4, 36.9, 49.9, 54.6, 124.1, 125.1, 138.3; ^{19}F NMR (CH_3CN-d_3) δ −105.3 to −140.6 (m). Anal. Calcd for $C_7H_{11}Br_2F_6N_2Sb$: C, 16.21; H, 2.14; N, 5.40. Found: C, 16.50; H, 2.22; N, 5.36.

1-(2,3-Dibromopropyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (2c): yield 90%; ^{1}H NMR (DMSO-d_6) δ 3.89 (s, 3H), 4.00 (dd, 1H, J = 11.3, 6.0 Hz), 4.04 (dd, 1H, J = 11.3, 5.3 Hz), 4.61 (dd, 1H, J = 14.6, 8.8 Hz), 4.78 (dd, 1H, J = 14.6, 4.1 Hz), 4.89−4.97 (m, 1H), 7.75 (s, 1H), 7.82 (s, 1H), 9.20 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 36.4, 37.3, 51.8, 54.5, 120.8 (q, $^{1}J_{C-F}$ = 320.0 Hz), 124.1, 125.1, 138.7; ^{19}F NMR (CH_3CN-d_3) δ −78.7 (s). Anal. Calcd for $C_9H_{11}Br_2F_6N_3O_4S_2$: C, 19.20; H, 1.97; N, 7.46. Found: C, 18.95; H, 1.96; N, 7.47.

1-(3,4-Dibromo-3,4,4-trifluorobutyl)-3-methylimidazolium Bis(trifluoromethanesulfonyl)amide (2d): yield 75%; ^{1}H NMR(DMSO-d_6) δ 3.01−3.31 (m, 2H), 4.06 (s, 3H), 4.77−4.94 (m, 2H), 7.71 (s, 1H), 7.91 (s, 1H), 9.18 (s, 1H); ^{13}C NMR δ 36.8, 38.6 (d, $^{2}J_{C-F}$ = 19.35 Hz), 46.1 (d, $^{3}J_{C-F}$ = 3.2 Hz), 105.1 (dt, J = 263.5, 30.0 Hz), 120.1 (td, J = 309.9, 33.1 Hz), 120.9 (q, J = 319.1 Hz), 123.8, 125.0, 138.2; ^{19}F NMR δ −118.9 to −119.2 (m, 1F), −79.9 (s, 6F), −60.8 (ddd, 2F, J = 386.6, 179.1, 14.6 Hz). Anal. Calcd for $C_{10}H_{10}Br_2F_9N_3O_4S_2$: C, 19.03; H, 1.60; N, 6.66. Found: C, 19.15; H, 1.63; N, 6.70.

1-(2,3-Dibromopropyl)-3-methyl-4,5-dibromoimidazolium bis(trifluoromethanesulfonyl)amide (2e): yield 85%; ^{1}H NMR(DMSO-d_6) δ 3.89 (s, 3H), 4.09 (dd, 1H, J = 11.0, 6.3 Hz), 4.14 (dd, 1H, J = 11.0, 5.0 Hz), 4.67 (dd, 1H, J = 14.0, 8.6 Hz), 4.75−4.82 (m, 1H), 4.84 (dd, 1H, J = 14.0, 3.6 Hz), 9.64 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 35.9, 38.0, 50.6, 54.6, 112.2, 113.3, 120.8 (q, J = 319.7 Hz), 140.9; ^{19}F NMR (DMSO-d_6) δ −78.7 (s). Anal. Calcd for $C_9H_9Br_4F_6N_3O_4S_2$: C, 14.99; H, 1.26; N, 5.83. Found: C, 15.39; H, 1.38; N, 5.86.

1-(2,3-Dibromopropyl)-3-methyl-4,5-diiodoimidazolium bis(trifluoromethanesulfonyl)amide (2f): yield 70%; ^{1}H NMR(DMSO-d_6) δ 3.89 (s, 3H), 4.09 (dd, 1H, J = 11.0, 6.4 Hz), 4.14 (dd, 1H, J = 11.0, 5.0 Hz), 4.64 (dd, 1H, J = 13.7, 8.6 Hz), 4.73−4.79 (m, 1H), 4.84 (dd, 1H, J = 13.7, 3.7 Hz), 9.62 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 35.9, 40.0, 51.1, 55.7, 94.8, 96.1, 120.8 (q, J = 319.9 Hz), 142.9; ^{19}F NMR (DMSO-d_6) δ −78.7 (s); Anal. Calcd for $C_9H_9Br_2F_6I_2N_3O_4S_2$: C, 13.26; H, 1.11; N, 5.16. Found: C, 13.64; H, 1.17; N, 5.17.

1-(*trans*-2,3-Dibromoallyl)-3-(2′,3′-dibromopropyl)imidazolium bis(trifluoromethanesulfonyl)amide (2g): yield 71%; ^{1}H NMR δ 3.98 (dd, 1H, J = 11.4, 6.8 Hz), 4.11 (dd, 1H, J = 11.4, 4.6 Hz), 4.94 (dd, J = 13.4, 8.5 Hz), 4.99−5.05 (m, 1H), 5.17 (dd, J = 13.4, 2.6 Hz), 5.64 (s, 2H), 7.36 (s, 1H), 7.92 (s, 1H), 8.05 (s, 1H), 9.51 (s, 1H); ^{13}C NMR δ 34.4, 50.0, 54.2, 55.0, 111.8, 117.4, 120.8 120.9 (q, J = 319.3 Hz), 124.2, 124.8, 138.7; ^{19}F NMR δ −79.7 (s). Anal. Calcd for $C_{11}H_{11}Br_4F_6N_3O_4S_2$: C, 17.69; H, 1.48; N, 5.63. Found: C, 18.01; H, 1.61; N, 5.90.

1,3-Di(2,3-dibromopropyl)imidazolium bis(trifluoromethanesulfonyl)amide (2h): yield 86%; isomer; ^{1}H NMR δ 3.94−4.00 (m, 2H), 4.06−4.12 (m, 2H), 4.88−5.03 (m, 4H), 5.12−5.17 (m, 2H), 8.01 (m, 2H), 9.46 (s, 0.5 H), 9.47 (s, 0.5 H); ^{13}C NMR ($CDCl_3$) δ 33.3, 48.4 (48.2), 54.9 (55.0), 120.6 (q, J = 319.2 Hz), 124.16 (124.19), 138.5; ^{19}F NMR ($CDCl_3$) δ −78.6 (s). Anal. Calcd for $C_{11}H_{13}Br_4F_6N_3O_4S_2$: C, 17.64; H, 1.75; N, 5.61. Found: C, 17.87; H, 1.81; N, 5.62.

1-(1,2-Dibromoethyl)-3-(2′,3′-dibromopropyl)imidazolium bis(trifluoromethanesulfonyl)amide (2i): yield 84%; isomer; ^{1}H NMR(DMSO-d_6) δ 4.02−4.08 (m, 2H), 4.55−4.57 (m, 1H), 4.63−4.73 (m, 2H), 4.87−4.97 (m, 2H), 7.09−7.15 (m, 1H), 8.06 (s, 1H), 8.29−8.31 (m, 1H), 9.75 (s, 0.5 H), 9.79 (s, 0.5H); ^{13}C NMR (DMSO-d_6) δ 34.4 (34.6), 36.12 (36.16), 51.6 (51.7), 55.21 (55.26), 56.3 (56.4), 48.4 (48.2), 54.9(55.0), 120.8 (q, J = 319.8 Hz), 122.1 (122.3), 125.9, 139.1 (139.2); ^{19}F NMR (DMSO-d_6) δ −78.7 (s). Anal. Calcd for $C_{10}H_{11}Br_4F_6N_3O_4S_2$: C, 16.34; H, 1.51; N, 5.72. Found: C, 16.44; H, 1.53; N, 5.64.

1-(2,3-Dibromopropyl)-3-(3′,4′-dibromo-3′,4′,4′-trifluorobutyl)-3-imidazolium bis(trifluoromethanesulfonyl)amide (2j): yield 69%; ^{1}H NMR δ 3.12−3.39 (m, 2H), 3.97 (dd, 1H, J = 11.3, 6.9 Hz), 4.08−4.14 (m, 1H), 4.89−5.03 (m, 4H), 5.14 (dd, 1H, J = 12.6, 1.7 Hz), 8.01 (t, 1H, J = 1.8 Hz), 8.12 (t, 1H, J = 1.8 Hz), 9.56 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 36.3, 38.0 (d, $^{2}J_{C-F}$ = 20.3 Hz), 46.2, 51.6, 54.6, 56.2, 105.6 (dt, J = 265.2, 29.5 Hz), 120.3 (td, J = 306.6, 32.78 Hz), 120.8 (q, J = 319.9 Hz), 124.2, 124.3, 139.1; ^{19}F NMR δ −119.0 to −118.8 (m, 1F), −79.8 (s, 6F), −60.6 (ddd, 2F, J = 384.2, 180.2, 13.8 Hz); HRMS for cation, calcd 536.7645, found 536.7620. Anal. Calcd for $C_{12}H_{12}Br_4F_9N_3O_4S_2$: C, 17.64; H, 1.48; N, 5.14. Found: C, 18.01; H, 1.69; N, 5.35.

1,3-Di(2,3-dibromopropyl)-4,5-diiodoimidazolium bis(trifluoromethanesulfonyl)amide (2k): yield 68%; isomer; ^{1}H NMR δ 4.11−4.16 (m, 2H), 4.18−4.22 (m, 2H), 4.92−5.00 (m, 4H), 5.20−5.25 (m, 2H), 9.86 (s, 0.5 H), 9.88 (s, 0.5 H); ^{13}C NMR δ 34.1 (34.3), 49.3 (49.4), 57.5 (57.6), 93.4 (93.6), 121.0 (q, J = 319.5 Hz), 143.0 (143.3); ^{19}F NMR δ-79.7 (s). Anal. Calcd for $C_{11}H_{11}Br_4F_6I_2N_3O_4S_2$: C, 13.20; H, 1.11; N, 4.20. Found: C, 13.52; H, 1.24; N, 4.08.

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