Preparation and Properties of High Mass Tetraalkylphosphonium Ionic Liquids

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Abstract

Most of the molten salts now identified as ionic liquids have either large cations or large anions with many degrees of freedom that inhibit crystallization. We describe here ionic liquids that have both massive cations and massive anions. The formula mass for some of these liquids exceeds 2000 g/mole, yet they are still liquids. The cations used are tetraalkylphosphoniums; ranging in size from tetrabutylphosphonium to tetradecyltrihexylphosphonium. The anions range in size from chloride (reported by others) to the C_{60} fulleride dianions and the tetrasulfonated copper phthalocyanine. The massive ionic liquids are viscous, but there is a poor correlation with anion size. Cation size appears to have a greater effect on properties. The liquids are significantly less dense than the more common imidazolium ionic liquids. Nearly all examples undergo glass transitions, rather than crystallization. The thermal stability and electrochemistry are determined by the nature of the anion. Some of the ionic liquids have interesting optical and magnetic properties.

Introduction

Salts with melting temperatures less than 100°C were once thought to be rare, but now we know of hundreds (perhaps thousands) of examples. A very commonly used cation in ionic liquids (ILs) is 1-ethyl-3-methylimidazolium, which now is listed in Chemical Abstracts as the cation in 315 different salts. Many of those salts are ILs, but not all are room temperature ionic liquids (RTILs). Salts that are liquid at room temperature and below have a special attraction for many applications.

While the N,N'-dialkylimidazolium cation has been the prevalent type of cation in ionic liquids, quite a variety of anions have been employed. The first imidazolium-based ionic liquids had chloroaluminate (AlCl_4^- and Al_2Cl_7^-) anions, which are water-reactive (1). Later, several water-stable anions were found to make good ionic liquids (2). The most popular early (i.e. more than 10 years ago) ionic liquids had relatively small anions. Table 1 lists the sizes of anions that may be classified as “small,” and compares them with two “larger” anions discovered later. We define “larger” arbitrarily as ions with mass greater than 200 g/mol. The larger anions gave ionic liquids some interesting solvent properties. The bis(trifluoromethylsulfonyl)amide (Tf_2N^- and tris(trifluoromethylsulfonyl)methide (Tf_3C^-) anions result in more hydrophobic (i.e.
dissolves less water) ionic liquids.(3,4) Not unexpectedly the masses and volumes do not correlate particularly well. (5)

Table 1. Small and Larger Anions

| Anion  | Ion Mass/g mol⁻¹ | Ion Volume*/Å³ |
|--------|------------------|---------------|
| Cl⁻    | 35.45            | 22.44         |
| BF₄⁻   | 86.80            | 40.55         |
| PF₆⁻   | 144.96           | 57.75         |
| AlCl₄⁻ | 168.79           | 108.73        |
| Tf₂N⁻  | 280.15           | 133.66        |
| Tf₃C⁻  | 411.22           | 189.78        |

*Volumes were calculated by the AM1 method

Our interest in large anions is based on the design of ionic liquids with third-order nonlinear optical properties. Calculations of the second hyperpolarizability of anions show that the strongest third-order polarization occurs in anions of multiple negative charge and with higher row elements (i.e. more massive elements have more electrons to polarize). Delocalization of the electron density also is important (6).

There are two general ways to obtain more massive anions; 1) make anions that contain heavy metal atoms, and 2) make anions with many light atoms. In this paper we describe new ionic liquids with both classes of anions, and some that use both strategies (heavy atoms and many light atoms).

The heavy-atom approach to massive anions has produced some impressively heavy ionic liquids in recent years. Table 2 lists some examples of anions of ionic liquids reported in the literature that employ the 1-ethyl-3-methylimidazolium cation. Unfortunately most of the papers describing the compounds do not report melting points, and we believe that none are room temperature ionic liquids.
Table 2. Heavy Atom Anions in 1-Ethyl-3-methylimidazolium Ionic Liquids

| Anion               | Ion Mass/g mol⁻¹ | Reference                  |
|---------------------|------------------|----------------------------|
| MoS₄²⁻              | 224.20           | Temansky et al. 2004 (7)   |
| BiCl₄⁻              | 350.79           | Gmouth et al. 2003 (8)     |
| ZnBr₄⁻              | 385.01           | Kim et al. 2003 (9)        |
| {{Cd(SCN)₃}₂}²⁻    | 573.32           | Liu et al. 2002 (10)       |
| {{UO₂(NO₃)₂}(μ-C₂O₄)}²⁻ | 876.09         | Hardacre et al. 2004 (11)  |
| PW₁₂O₄₀³⁻           | 1696.45          | Antonio et al. 2004 (12)   |

The many-light-atom approach to massive anions is more successful in generating room temperature ionic liquids. Table 3 lists some such examples from the literature, where the cation is 1-ethyl-3-methylimidazolium. The last and most massive entry in the table is remarkable in that such a large anion can result in a liquid. That anion is a bis(sulfonyl)amide much like Tf₂N⁺, but it has two cholesteryl groups linked to the amide by polyether carbonate linkages. The structure must be seen to be appreciated. The ionic liquid is a liquid crystal.

Table 3. Many-light-atom Anions in 1-Ethyl-3-methylimidazolium Ionic Liquids

| Anion               | Ion Mass/g mol⁻¹ | Reference                  |
|---------------------|------------------|----------------------------|
| CH₂O.SO₃⁻           | 209.28           | Wasserscheid et al. 2002 (13) |
| CH₃CH₂CHCH₂CH₂CH₂CH₃ |                 |                            |
| CF₃CF₂CF₂CF₂SO₃⁻    | 299.09           | Grätzel et al. 1996 (4)    |
| C₆₈H₁₁₄NO₁₄S₂⁻      | 1233.76          | Yasuda & Koji, 2003 (14)   |

The nature of the cation in a nonlinear optical salt is also a factor in the design of such materials. Molecular orbital calculations have shown that a small cation will interact strongly and specifically with a cation with the diffuse charge of the kinds of anions we thought make effective third-order NLO salts. This interaction affects the delocalization of electron density in the anion, thus removing the basis of the anion's high second hyperpolarizability. Also, some of the anions we proposed are quite basic, so the cation must not be acidic. This is a problem for the N,N'-dialkylimidazolium cations. With these constraints in mind we selected phosphonium cations of the form...
[PR₃RⱼR₃R₄]⁺, where the Rs may be alkyl or aryl, and all of the substituents need not be different.

EXPERIMENTAL

Materials and Equipment

See Figures 1-5 for the abbreviations. The alkali metal salts Na(ddtc) (Fluka), Li(Tf₂N) (Aldrich), K(CF₃SO₃) (Aldrich), Na[N(CN)₂] (Fluka), K[C(CN)₃] (Strem), K₄[Fe(CN)₆] (Strem), Na₄(CuPc) (Aldrich), and Na₂(ThY) (ACROS) are all commercially available, and were used as received. The [PC₆C₆C₆C₆Cl], [PC₆C₆C₆C₆Cl], [PC₆C₆C₆C₆Cl], and [PC₆C₆C₆C₆Br] salts were prepared by Cytec Specialty Chemicals, and dried under vacuum at 90°C before being used.

For those that were not available, the K-salt (15), Na(xan) (16), Na₂(dtmn) and Na₂[M(dtmn)₂] (17) were synthesized by known methods. The Cs(CoCB) salt was provided by Los Alamos National Laboratory.

The metal complexes K₂[Co(NCS/Se)₄], K₄[Co(NCS)₆], and Na₂[Co(N(CN)₂)₄] were made by simple substitution by reacting the MCl₂ salt with excess sodium or potassium salts of the desired ligands in water. The aqueous solutions were used without isolation of the salt.

Viscosities of the samples were measured on a Cambridge Applied Systems ViscoLab 4000 Viscometer and measured over the range of 20-90°C. The densities were determined by a Mettler-Toledo DE40 Density Meter at 20, 45, 60 and 80°C. Absorptions were measured on an HP 8452A diode array spectrophotometer, using neat samples in a 0.01mm (10µm) etched quartz cuvette. Thermal characterization was carried out using a TA Instruments Q100 DSC and SDT 2960 SDT-TGA. Alkali metal and halide impurities were determined using a Varian VistaPro ICP-OES with CCD detector. Water content of the RTILs was measured with a Mettler Toledo DL38 Karl-Fischer titrator.

Syntheses of RTILs

To make the [PR₃RⱼR₃R₄] phosphonium RTILs from the above alkali metal salts (all except the dtc, dtmn, [C₆F₅SO₃], and CoCB RTILs), metathesis reactions were carried out in which the [PR₃RⱼR₃R₄]Cl (except in the case of the [PC₆C₆C₆C₆]Cl, which is only available as the Br salt) was dissolved in excess CHCl₃ and added to an aqueous solution of the above salts. The solution was rapidly stirred for 24 hours, and the organic layer containing the RTIL product was separated and washed several times with water. The solvent was removed under vacuum, and the resulting RTIL dried at 90-120°C, typically for 12 hours.

The dtc and dtmn RTILs were synthesized by mixing the [PR₃RⱼR₃R₄]Cl and respective alkali metal salt in ethanol. The NaCl precipitate was filtered, the ethanol evaporated, and the resulting crude RTIL purified by redissolving in CHCl₃ and washing with water as above. The [C₆F₅SO₃] and [CoCB] RTILs were made in a similar fashion except CHCl₃ and THF were the reaction solvents, respectively.
RESULTS AND DISCUSSION

The Phosphonium Cations

Large quaternary phosphonium cations were chosen, because the hydrocarbon substituents can shield the positive charge of the cation from the negative charge of the anion. Also, there is reason to expect that the phosphonium cations are compatible with basic anions. Figure 1 shows the structures of the phosphonium cations we used in the preparation of ionic liquids with large anions. All of the cations are available commercially as halide salts. The one cation we found to be most useful is [PC₆C₆C₆Cu⁺], where C₆ = n-hexyl and C₁₄ = n-tetradecyl. All of the abbreviations for the phosphonium salts follow this scheme.

The Large Anions

Figures 2-5 and Table 4 show the structures, our abbreviations, formula masses, and glass transition temperatures (Tg) for single salt massive ionic liquids that have the [PC₆C₆C₆C₁₄⁺] cation and large anions. Some noteworthy features of the salts listed are:

- Nearly all are room temperature ionic liquids.
- A few have true melting temperatures as designated by Tm values
- The large phosphonium cations produce high formula mass ionic liquids even when the anion is relatively small
- A 2- or 4- charge on the anion multiplies the mass greatly
- Heavy-atoms, many-light-atoms or a combination can produce massive RTILs

Table 4. Ionic Liquids With Various Phosphonium Cations

| Anion      | Cation             | Formula Mass/ g mol⁻¹ | Tg or Tm/ °C |
|------------|--------------------|------------------------|---------------|
| [dtmn]²⁻   | [PC₆C₆C₆C₁₄⁺]    | 1107.9                 | -71           |
|            | [PC₄C₄C₄C₁₄⁺]    | 939.6                  | -46           |
|            | [PC₆C₆C₆C₂⁺]     | 1107.9                 | -69           |
|            | [PC₆C₆C₆C₄⁺]     | 659.1                  | -35           |
|            | [PPPh₄⁺]          | 818.9                  | +154(Tm)      |
|            | [PC₆C₆C₆C₁₄⁺]    | 764.0                  | -76           |
| [Tf₂N]⁻    | [PC₆C₆C₆C₂⁺]     | 679.8                  | -60           |
|            | [PC₆C₆C₆C₄⁺]     | 764.0                  | +2            |
|            | [PC₄C₄C₄C₄⁺]     | 539.6                  | +65(Tm)       |
|            | [PPPh₄⁺]          | 619.5                  | +160(Tm)      |
|            | [PC₄C₄C₄Bz⁺]     | 573.6                  | -67           |
Properties

Density. The densities of ionic liquids are the most frequently reported property after $T_g$ or $T_m$. This property has a simple linear temperature dependence illustrated by Figure 6. The parameters for the linear fit of density to temperature are listed in Table 5 for most of the ionic liquids presented above. The tetraalkylphosphonium ionic liquids generally have densities less than most others, probably due to the high hydrocarbon content of the cations.

Viscosity. All of the ionic liquids described here are quite viscous, undoubtedly due to the bulky ions. As with most ionic liquids the temperature deviates from simple Arrhenius behavior, so the viscosities were modeled with the three-parameter VTF equation (Equation 1).

$$\ln(\eta) = \ln A + \frac{E}{(T-T_0)}$$  \[1\]

$\eta$ is dynamic viscosity in cP. $A$, $E$, and $T_0$ are the adjustable parameters in the VTF equation.

Figure 7 shows the very large range of viscosities seen in the phosphonium-based ionic liquids, and Table 6 lists the VTF parameters. There does not appear to be any trend between the viscosities of the $[PC_6C_6C_6C_14]^+$ salts with varying anion size or charge, presumably due to the effects of the anion morphology and functionalities. Varying the cations with a common anion, such as with the different phosphonium $[dtmn]$ and $[Tf_2N]$ salts, does show some correlation, in which the smaller cations result in salts with higher room temperature viscosities. However, this is most likely a result of the effect of cation size on the $T_g$ of the salt, with the smaller cations resulting in salts with $T_g$'s closer to room temperature.

| Ionic Liquid | $a/\text{g cm}^{-3}$ | $b \times 10^4/\text{g cm}^{-3} \cdot \text{oC}^{-1}$ |
|--------------|-----------------------|-----------------------------------------------|
| $[PC_6C_6C_6C_14]_2[dtnm]$ | 0.9571 | -6.540 |
| $[PC_4C_4C_4C_14]_2[dtnm]$ | 0.9660 | -6.456 |
| $[PC_6C_6C_6C_14]_2[dtnm]$ | 0.9613 | -6.397 |
| $[PC_6C_6C_6C_14][Tf_2N]$ | 1.099 | -8.005 |
| $[PC_4C_4C_4C_14][Tf_2N]$ | 1.127 | -7.415 |
| $[PC_6C_6C_6C_14][Tf_2N]$ | 1.086 | -7.272 |
| $[PC_6C_6C_6C_14][Ni(dtmm)_2]$ | 1.009 | -6.378 |
| $[PC_6C_6C_6C_14][Ni(dtmn)_2]$ | 1.015 | -6.728 |
| $[PC_6C_6C_6C_14][K \text{salt}]$ | 0.9792 | -7.522 |
| $[PC_6C_6C_6C_14][Xan]$ | 0.9356 | -6.465 |
| $[PC_6C_6C_6C_14][\text{dtc}]$ | 0.9585 | -6.983 |
| $[PC_6C_6C_6C_14][\text{CoCB}]$ | 1.018 | -7.077 |
| $[PC_6C_6C_6C_14][N(\text{CN})_2]$ | 0.9182 | -6.206 |
| $[PC_6C_6C_6C_14][\text{Ni} (\text{NCSe})_4]$ | 0.9161 | -6.289 |
| $[PC_6C_6C_6C_14][\text{NfO}]$ | 1.023 | -6.715 |
| $[PC_6C_6C_6C_14][\text{Ni(ncse}_4]$ | 1.098 | -7.573 |
Table 6. Temperature Parameters Viscosity

| Ionic Liquid | Viscosity $A/\text{g cm}^{-3}$ | $\ln(\eta) = \ln A + \frac{E}{(T-T_0)}$ | $T_0/K$ |
|--------------|-------------------------------|------------------------------------------|---------|
| [PC6C6C6C14] [dtmnn] | 0.0210 | 1816 | 140.8 |
| [PC6C6C6C8]2 [dtmnn] | 0.0111 | 2098 | 130.9 |
| [PC6C6C6C14] [Tf2N] | 0.0427 | 1327 | 144.9 |
| [PC6C6C6C14] [Tf2N] | 0.0521 | 1193 | 163.1 |
| [PC6C6C6C8]2 [Tf2N] | 0.0625 | 1177 | 161.0 |
| [PC6C6C6C14] [K salt]** | 0.0477 | 1295 | 154.5 |
| [PC6C6C6C14] [Xan] | 0.0227 | 1647 | 143.6 |
| [PC6C6C6C14] [Tf2N] | 0.0271 | 1531 | 149.0 |
| [PC6C6C6C14] [Tf2N] | 0.0308 | 1601 | 155.8 |
| [PC6C6C6C14] [Xan] | 0.0347 | 1468 | 145.8 |
| [PC6C6C6C14] [CoCB] | 0.0156 | 1984 | 127.3 |
| [PC6C6C6C14] [Ni(NCS)6] | 0.0626 | 1311 | 152.3 |

**Viscosities were measured over the temperature range of 20 – 70°C**

**Thermal Stability.** The thermal stability is usually reported as the temperature of the onset of the first decomposition in a TGA experiment. It is well known that there is some decomposition of the sample below the onset temperature, but the onset temperature is a fairly reproducible number when the experiments are done at similar scan rates and sample size. We report the decomposition onset temperatures for our ionic liquids in Table 7. We performed isothermal decomposition experiments on some of the salts to estimate better the true long term stability at elevated temperatures. It appears that ionic liquids are generally stable for the long-term at temperatures 100 °C below the TGA onset.

Table 7. Thermal Stability

| Ionic Liquid | TGA Onset/ °C |
|--------------|---------------|
| [PC6C6C6C14] [dtmnn] | 360 |
| [PC6C6C6C8]2 [K-salt] | 350 |
| [PC6C6C6C14] [dtc] | 255 |
| [PC6C6C6C14] [Xan] | 290 |
| [PC6C6C6C14] [N(CN)2] | 395 |
| [PC6C6C6C14] [Tf2N] | 400 |
| [PC6C6C6C14] [NfO] | 390 |
| [PC6C6C6C14] [Co(NCS)4] | 405 |
| [PC6C6C6C14] [Ni(NCS)6] | 380 |
| [PC6C6C6C14] [Co(dtmnn)2] | 370 |
| [PC6C6C6C14] [Ni(dtmnn)2] | 380 |
| [PC6C6C6C14] [CoCB] | 440 |
| [PC6C6C6C14] [CuPc] | 400 |
| [PC6C6C6C14] [ThY] | 395 |
Absorption. All of the ionic liquids presented above that have transition metal atoms or extended π-delocalization absorb in the UV and visible spectrum. The absorbance maxima and are listed in Table 8. The visible absorption is entirely due to the anions, since the phosphonium cations have no chromophore. The colors of the ionic liquids are very intense, because they are neat liquids with very high concentrations of the absorbing ions.

| Ionic Liquid                     | \( \lambda_{\text{max}} \) nm |
|----------------------------------|-------------------------------|
| \([\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]_2 \text{[dtmn]}\) | 394                           |
| \([\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]_2 \text{[K-salt]}\) | 396                           |
| \([\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]_2 \text{[dtc]}\) | 305                           |
| \([\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]_2 \text{[xan]}\) | 345                           |
| \([\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]_2 \text{[Co(NCS)]}_4\) | 626                           |
| \([\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]_2 \text{[Co(NCSe)]}_4\) | 628                           |
| \([\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]_4 \text{[Ni(NCS)]}_6\) | 345                           |
| \([\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]_2 \text{[Ni(dtmm)]}_2\) | 380, 475                      |
| \([\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]_2 \text{[Ni(dtmm)]}_2\) | 460                           |
| \([\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]_2 \text{[CoCB]}\) | 290                           |
| \([\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]_4 \text{[CuPc]}\) | 598 (sh 698)                  |
| \([\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]_2 \text{[ThY]}\) | 405                           |
| \([\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]_2 \text{[C}_{60}\text{Cl]}\) | 825, 950                      |

CONCLUSIONS

Large asymmetric tetraalkylphosphonium cations are useful in creating ionic liquids with large to extremely large anions. As a class, these ionic liquids are very viscous.

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The historic progression from small to large anions in ionic liquid development is not quite right. Ionic liquids with the $\text{Al}_{2}\text{Cl}_7^-$ anion were described in the literature more than a decade earlier than the $\text{Tf}_2\text{N}^-$ and $\text{Tf}_2\text{C}^-$ ionic liquids.

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Figure 1. Quaternary Phosphonium Cations. $C_n$ specifies the length of each normal alkyl chain. Bz is benzyl.
Figure 2. Ionic liquids with the [PC\textsubscript{6}C\textsubscript{6}C\textsubscript{4}]+ cation. The abbreviations are [K salt]\textsuperscript{2-} = dithionitroacetate, [dtmn]\textsuperscript{2-} = dithiomaleonitrile, [xan]' = methylxanthate, [dtc]' = diethyldithiocarbamate, [M(dtmn)\textsubscript{2}]\textsuperscript{2-} are the two dithiomaleonitrile complexes of the metal ions indicated. FM is formula mass of the ionic liquid.

Figure 3. More ionic liquids with the [PC\textsubscript{6}C\textsubscript{6}C\textsubscript{4}]+ cation. The abbreviations are [NfO]' = nonafluorobutanesulfonate, [N(CN)\textsubscript{2}]' = dicyanamide, [Tf\textsubscript{2}N]' = bis(trifluoromethylsulfonyl)amide, [CoCB]' = cobalt dicarbollide. FM is formula mass of the ionic liquid.
Figure 4. Still more ionic liquids with the [PC₆C₆C₆C₄]⁺ cation. The abbreviations are [Co(NCS)₄]²⁻ = tetrathiocyanatocobaltate(II), [Ni(NCS)₆]⁴⁻ = hexathiocyanatonicelate(II), [Co(NCSe)₄]⁺ = tetraselenocyanatocobalt(II).
Figure 5. Yet more ionic liquids with the $[\text{PC}_{66}C_4C_4C_4]^{+}$ cation. The abbreviations are $[\text{CuPc}]^{4+} = \text{Cu(II)phthalocyaninetetrasulfonate}$, $[\text{ThY}]^{2-} = \text{thiazolium yellow}$. 

$[\text{CuPc}]^{4+}$
- FM = 2823.8 g/mol
- Tg = -45°C

$[\text{ThY}]^{2-}$
- FM = 1617.5 g/mol
- Tg = +65°C

$[\text{C}_{66}^{4+}][\text{Cl}]^{-}$
- FM = 2207.7 g/mol
- Tg = -56°C
Figure 6. Densities of [PC6C6C6C14] ionic liquids. ● - [NTf2], ○ - [dmtn], ▼ - [Ni(dtmm)], ▽ - [K salt], ■ - [Xan], □ - [dtc], ● - [CoCB], ◇ - Co(NCS)4, ▲ - [Ni(NCS)3], △ - [NfO], ● - [Co(NCS)3].
Figure 7. Viscosities of high, medium, and low viscosity phosphonium ionic liquids. 

A – [PC₆C₆C₆C₄][CoCB], B – [PC₆C₆C₆C₁₄] [Xan], C - [PC₆C₆C₆C₁₄] [N(CN)₂].