

# Conductivity and Viscosity Behavior of Asymmetric Phosphonium Iodides

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In this work, we report the physicochemical properties of a variety of aliphatic phosphonium iodide (API) salts, including thermal degradation. Also, we compared the conductivity, viscosity, and fragility behavior of APIs to similar molten systems and related these properties to their structure. Our investigation has found that APIs have an intermediate fragility behavior. We plotted the conductivity and viscosity data of APIs according to Walden's rule and found that they can be classified as an associated ionic liquid (AIL), an intermediate between a true ionic liquid and a molecular species. Lastly, we correlated the structure and behavior of APIs and similar polarizable anions, such as the diacetamide anion.

## Introduction

Currently, there is a great demand for the development of clean and renewable energy sources.<sup>1</sup> For example, nanocrystalline cells, introduced by Grätzel,<sup>2</sup> have a high application potential due to their low cost. Nevertheless, an important aspect regarding cell stability is the electrolyte volatility<sup>3</sup> at the working temperature range of the cell. The redox couple  $\text{KI}/\text{I}_2$  in isopropyl alcohol has been found to be an excellent electrolyte; however, a  $\text{KI}/\text{I}_2$  system exhibits poor performance related to electrochemical cyclability,<sup>4</sup> due to solvent evaporation. To overcome this problem, the use of ionic liquids (ILs) has been proposed by Bonhôte.<sup>5</sup> The most common ionic liquids are<sup>6</sup> imidazolium, ammonium, pyridinium, picolinium, and phosphonium salts. These compounds have melting points below 100 °C, and it has been shown that ILs can be used in a wide variety of electrochemical applications, where high conductivity and ionic mobility<sup>7</sup> are required. Due to the strong ionic nature of IL, their volatility is considered very close to zero. However, recent discoveries showed that, at relatively high temperatures, a certain amount of decomposition<sup>8</sup> and volatility<sup>9</sup> is expected.

Recently, phosphonium salts have found use in electrochemical applications. For instance, these salts have successfully been used for electrodeposition of  $\text{CdS}$ ,<sup>10</sup> alkali metals,<sup>11</sup>  $\text{Ti}$ <sup>12</sup> and  $\text{Al}$ ,<sup>13</sup> among others. Additionally, phosphonium ionic liquids have been proposed in electrochemical devices as capacitors by Ue,<sup>14</sup> Xu,<sup>15</sup> Frackowiak,<sup>16</sup> and Hagiwara.<sup>17</sup> Matsumoto proposed<sup>18</sup> their use in lithium batteries, and later, Tsunashima<sup>19</sup> extended this potential use to a variety of low viscosity phosphonium salts. Our research group proposed the application of asymmetric phosphonium iodides to nanocrystalline solar cells.<sup>20</sup> In addition, the Tsunashima<sup>21</sup> group has approached similar compounds for dye-sensitized solar cell applications.

In this work, we report several physicochemical properties of a variety of aliphatic phosphonium iodide salts. Specifically, we compared their conductivity, viscosity, and fragility behavior to similar molten systems and attempt to explain these properties using structural considerations. Furthermore, their conductivity and viscosity data are plotted under Walden's rule, where ion

association plays a major role. We plotted the glass transition temperatures versus molar volume and related the compound structure to intermolecular considerations.

## Experimental Section

Chemicals for the synthesis of phosphonium salts included tri-*n*-octylphosphine (90%), 1-iodoethane (99%), 1-iodobutane (99%), 1-iodo-2-methylpropane (97%), 1-iodohexane (98%), and 1-iodooctane (98%) from Aldrich and tri-*n*-hexylphosphine from TCI Tokyo Kasei (90%). All reactants were used without further purification. In Table 1, we list the combination of all quaternary phosphonium iodides synthesized, and labeled all of the products with an acronym to facilitate reading. Stoichiometric quantities of reagents were poured and mixed inside a dark vial (iodoalkenes are photosensitive) until a homogeneous mixture was obtained. In a few cases, the above reaction occurred spontaneously. Otherwise, these reactions were completed using an ultrasonic bath (Branson 1510R-MTH) at  $42 \pm 6\%$  kHz frequency. Specific details on the synthesis and characterization of the products have been published elsewhere.<sup>22</sup>

Ionic conductivity was determined using a potentiostat/galvanostat, equipped with a frequency response analyzer (Gamry PC4/750). A 2 mL portion of each liquid sample was poured inside a 4 mL vial, and a dip-in platinum electrode cell was used for impedance spectroscopy (IS) measurements. The IS scans were carried out from 100 kHz down to 7 mHz, using a small amplitude of 10 mV. The cell constant was determined before each analysis, using a standard solution of 0.1 N KCl, and was calculated according to the following equations:

$$K_{\text{cell}} = \sigma_{\text{KCl}} R_{\text{CD}} \quad (1)$$

$$\sigma_{\text{sample}} = \frac{K_{\text{cell}}}{R_{\text{CD}}} \quad (2)$$

where  $K_{\text{cell}}$  is the cell constant,  $\sigma_{\text{KCl}}$  is the conductivity of the KCl solution at a certain temperature,  $R_{\text{CD}}$  is the resistance at direct current on the Nyquist plot, and  $\sigma_{\text{sample}}$  is the sample conductivity. Impedance measurements were carried out at

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TABLE 1: Quaternary Phosphonium Compounds and Acronyms Synthesized on This Work

trialkylphosphine	iodoalkane	phosphonium compounds	acronym
tri- <i>n</i> -hexylphosphine	1-iodoetane	ethyl-tri- <i>n</i> -hexylphosphonium iodide	EH <sub>3</sub> PI
	1-iodobutane	butyl-tri- <i>n</i> -hexylphosphonium iodide	BH <sub>3</sub> PI
	2-methyl-1-iodopropane	isobutyl-tri- <i>n</i> -hexylphosphonium iodide	iBH <sub>3</sub> PI
	1-iodohexane	tetra- <i>n</i> -hexylphosphonium iodide	H <sub>4</sub> PI
	1-iodooctane	octyl-tri- <i>n</i> -hexylphosphonium iodide	OH <sub>3</sub> PI
tri- <i>n</i> -octylphosphine	1-iodoetane	ethyl-tri- <i>n</i> -octylphosphonium iodide	EO <sub>3</sub> PI
	1-iodobutane	butyl-tri- <i>n</i> -octylphosphonium iodide	BO <sub>3</sub> PI
	2-methyl-1-iodopropane	isobutyl-tri- <i>n</i> -octylphosphonium iodide	iBO <sub>3</sub> PI
	1-iodohexane	hexyl-tri- <i>n</i> -octylphosphonium iodide	HO <sub>3</sub> PI
	1-iodooctane	tetra- <i>n</i> -octylphosphonium iodide	O <sub>4</sub> PI

TABLE 2: Melting Points and Cation Molar Weights of Tetralkylphosphonium Iodides

compound	melting points (°C)	cation molar weight (g/mol)
EH <sub>3</sub> PI	49.03	315.54
BH <sub>3</sub> PI	−5.5	343.59
iBH <sub>3</sub> PI	−79.25	343.59
H <sub>4</sub> PI	50.57 (48–50) <sup>28</sup>	371.64
OH <sub>3</sub> PI	11.15	399.70
EO <sub>3</sub> PI	57.25	399.70
BO <sub>3</sub> PI	57.07	427.77
iBO <sub>3</sub> PI	−80.45	427.77
HO <sub>3</sub> PI	62.47	455.81
O <sub>4</sub> PI	91.09 (87–88) <sup>28</sup>	483.86

different temperatures, ranging from 23 to 72 ± 0.1 °C. Viscosity measurements were taken using a digital viscometer (Viscolab Model 3000), at temperatures ranging from 40 to 90 °C, at 10 °C intervals. Melting points ( $T_m$ ) and glass transitions ( $T_g$ ) of the ionic liquids were measured by differential thermal analysis (DTA), using an instrument customized for low temperature measurements, as previously reported.<sup>22</sup> The melting points of solid samples were determined by differential scanning calorimetry (DSC, Shimadzu DSC-50), and the thermal decomposition of ionic liquids was measured by thermogravimetric analysis (TGA, TA Instruments SDT 2960).

## Results and Discussion

In this study, two series of phosphonium iodides were prepared. The phosphonium cation formula is represented by  $[R'PR_3]^+$  where  $R = n$ -triethyl or  $n$ -trioctyl and  $R' =$  ethyl, butyl, isobutyl, hexyl, or octyl. The full names and their corresponding acronyms are presented in Table 1. In Table 2, we observe that, in general, tri-*n*-octyl-based phosphonium salts have higher melting points than tri-*n*-hexyl compounds. On the other hand, symmetrical compounds, such as O<sub>4</sub>PI and H<sub>4</sub>PI, have higher melting points, and this is attributed to the greater symmetry of the cation, which provides the stability needed for crystalline lattice formation. In quasi-symmetrical phosphoniums (where  $R' = n$ -alkyl, but different from  $R$ ), there is a reduction in melting points due to steric hindrance in the formation of crystals. Furthermore, asymmetric cations (where  $R' =$  iso-butyl) promote the lowest density crystalline lattices, so only a small amount of thermal energy is needed to overcome the ionic bonding that maintains the solid phase. In fact, these asymmetric salts (such as iBH<sub>3</sub>PI and iBO<sub>3</sub>PI) do not crystallize readily.<sup>22</sup>

In Figure 1, we present the thermal decomposition behavior of the four phosphonium iodides discussed. We observe that all compounds start to decompose (5% weight loss) at about 300 °C. Beginning around 340 °C, there is a fast and total weight loss. These results suggest a one-step thermal degradation; however, we are confident about the thermal stability at 100 °C, where there is only 1% degradation, on average. The

temperature for 10% weight loss varies from 338 to 348 °C, and it is comparable to other phosphonium halides previously reported.<sup>23</sup>

Ionic conductivities of liquid phosphoniums at room temperature are depicted in Figure 2. Fitted lines are based on the Arrhenius equation ( $\sigma = \sigma_0 \exp(-E_a/RT)$ ) for the sake of simplicity, and the corresponding activation energy values are listed in Table 3. Hexyl-based phosphonium iodides show higher conductivity compared to octyl-based. This behavior can be attributed to their higher dipole moments, longer, more ionic

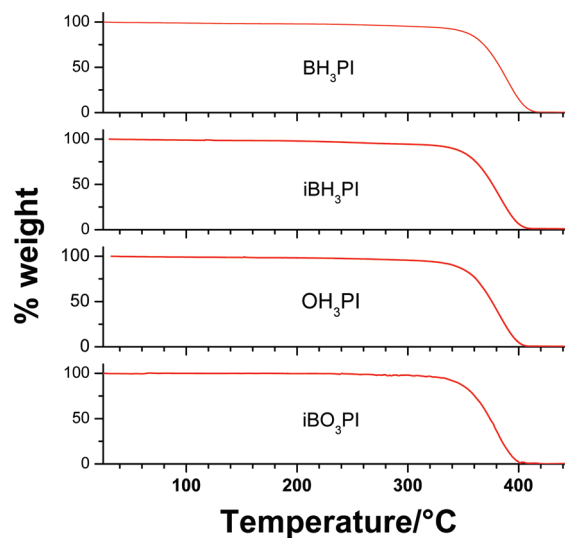
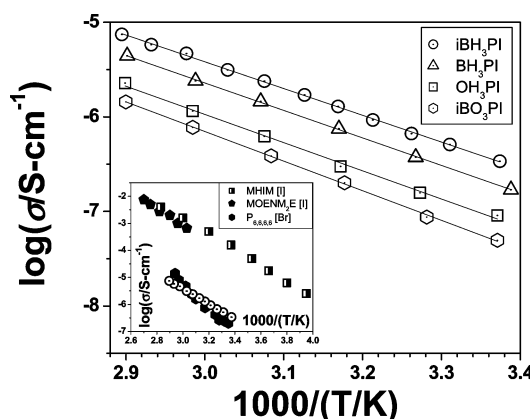


Figure 1. Thermal decomposition of room temperature liquid phosphonium iodides.

Figure 2. Conductivity Arrhenius plot of room temperature liquid phosphonium iodides. Inset: conductivity plot comparing data of our iBH<sub>3</sub>PI and other IL iodides (methyl hexyl imidazolium iodide,  $\blacksquare$ , MHIM[I];<sup>5</sup> methoxy ethyl dimethyl ethyl iodide, solid  $\circ$ , MOENM<sub>2</sub>E[I];<sup>27</sup> tetrahexyl phosphonium bromide,  $\bullet$ , P<sub>6,6,6,6</sub>[Br]).<sup>28</sup>

**TABLE 3: Physical Properties of Room Temperature Molten Phosphonium Iodides**

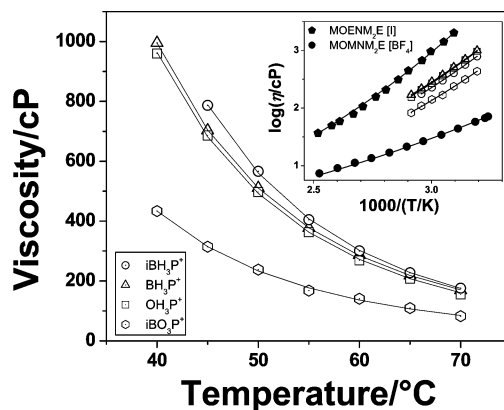
property	BH <sub>3</sub> PI	iBH <sub>3</sub> PI	OH <sub>3</sub> PI	iBO <sub>3</sub> PI
glass transition temperature $T_g$ (°C)	−94	−98.5	−84	−106
melting temperature $T_m$ (°C)	−5.5	−79.25	11.5	−80.4
$T_{dec}^a$ (°C)	348	339	338	341
conductivity $\sigma_{25^\circ C}$ ( $\mu S/cm$ )	0.213	0.380	0.0933	0.055
activation energy $E_a$ (kJ/mol)	55.6	54.2	57.1	60.0
viscosity <sup>b</sup> (cP)	995	787 <sup>c</sup>	960	433
density <sup>d</sup> (g/cm <sup>3</sup> )	1.05	1.12	1.07	1.08
molecular weight (g/mol)	470.5	470.5	526.6	554.7

<sup>a</sup> Thermal decomposition temperature of 10% weight loss. <sup>b</sup> At 40 °C. <sup>c</sup> At 45 °C. <sup>d</sup> At room temperature.

P–I bonds, and lower HOMO–LUMO energy gaps, as recently pointed out by Benavides et al.<sup>24</sup> In particular, iBH<sub>3</sub>PI has a calculated P–I bond length of 4.38 Å (the longest of this group) and a calculated dipole moment of 15.89 D (again, the largest in this group). These characteristics account for the largest ionic conductivity found in this class of compounds. On the other hand, BO<sub>3</sub>PI has a calculated P–I bond length of 4.00 Å and a dipole moment of 14.59 D, which can be extrapolated from the iBO<sub>3</sub>PI conductivity results. BH<sub>3</sub>PI has an intermediate P–I bond length and dipole moment, compared to iBH<sub>3</sub>PI and BO<sub>3</sub>PI, and this is reflected in conductivity values that are in the median.

There are few conductivity results for molten iodide salts in the literature. In Figure 2, we present an Arrhenius plot of some IL with iodide as the anion. At first glance, we observe a drastic difference between methyl hexyl imidazolium iodide<sup>25</sup> (MHImI) and phosphonium halides. This could be attributed to differences in cation size and structure, among other physical characteristics. Matsumoto et al.<sup>26</sup> reported a comparative IL study with different cations of  $\pi$ -bonded flat structures, such as imidazolium and pyrrolidinium salts, to aliphatic quaternary ammonium salts, using the same anion (TFSI, trifluoromethylsulfonimide) and similar molecular weight. They concluded that the  $\pi$ -bonded, flat cation structure is significant for high conductivity and low viscosity. In fact, the positive charge on the imidazolium cation is distributed throughout its entire structure, due to  $\pi$ -bond resonance, which lowers the ion pair attraction to the polarizable iodide anion. Also, low  $\eta$  behavior is attributed to the ease of movement of planar structures compared to aliphatic moieties, which must transport four long and bulky alkyl chains that may entangle the cations themselves. Both factors may enhance the ion conductivity. Smaller alkyl chains will decrease chain entanglement and van der Waals interactions, therefore increasing ion conductivity, as is the case of methoxyethyl-dimethyl ethyl iodide (MOENM<sub>2</sub>E-I) reported by Angell.<sup>27</sup> However, smaller cations have a tendency to crystallize at higher temperatures, reducing their conductivities and narrowing their temperature application range. Tetrahexyl phosphonium bromide<sup>28</sup> (H<sub>4</sub>PBr) has a similar conductivity to iso-butyl-trihexyl phosphonium iodide (iBH<sub>3</sub>PI), likely due to the similar aliphatic chain size and anion polarizabilities of both salts.

We observe similar values for viscosity (Figure 3) among the three hexyl-based phosphonium salts, where the iBH<sub>3</sub>P<sup>+</sup> cation exhibits the highest viscosity. Also, their  $\eta$  significantly decreases with temperature. We also observe an unexpectedly low viscosity for iBO<sub>3</sub>PI, and a softer decrease in viscosity upon change in temperature. At 70 °C, all liquids have achieved lower  $\eta$  values, in the 90–180 cP range. To explain this behavior, structural interactions of the iodide ion with the aliphatic chains should be accounted for. According to Benavides,<sup>24</sup> the hexyl



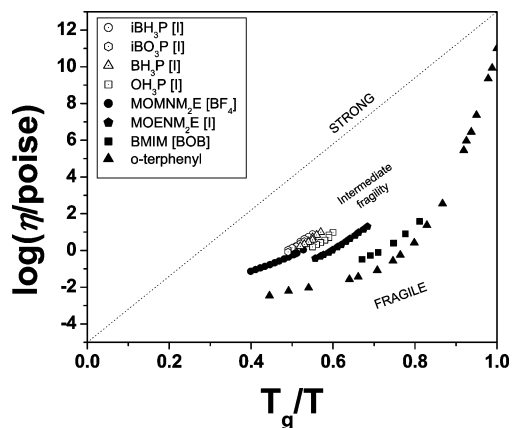
**Figure 3.** Viscosity VTF plot of four molten phosphonium iodides from the present work. Inset: Arrhenius plot of viscosities, comparing our phosphonium iodides with alternative compounds (methoxy methyl dimethyl ethyl ammonium tetrafluoroborate, ●, MOMNM<sub>2</sub>E[BF<sub>4</sub>];<sup>27</sup> butyl methyl imidazolium bis(oxalato)borate, ■, BMIM[BOB].<sup>31</sup>

**TABLE 4: VTF Equation Parameters for Viscosity Data**

	$\eta = \eta_0 e^{(B/(T-T_0))}$			
	$\eta_0/10^{-2}$ cP	$B/10^3$ K	$T_0/K$	$D$
iBO <sub>3</sub> P[I]	4.79	1.25	175.9	7.1
BH <sub>3</sub> P[I]	4.91	1.37	174.6	7.9
iBH <sub>3</sub> P[I]	2.90	1.48	173.5	8.5
OH <sub>3</sub> P[I]	1.98	1.63	162.4	9.9

aliphatic chains tend to form coplanar molecular structures and longer chains (octyl) have almost planar structures, favoring lower intermolecular interactions and lowering viscosity values. In the inset of Figure 3, we display the Arrhenius plot for the viscosity of our phosphonium iodides along with MOENM<sub>2</sub>E[I] and MOMNM<sub>2</sub>E[BF<sub>4</sub>] for comparison.<sup>27</sup> We observe a decrease in viscosity when phosphonium cations are used, compared to MOENM<sub>2</sub>E<sup>+</sup>, which is significant. This behavior can be explained by the fact that the strength of the iodide–phosphonium interactions in the smaller molecules exceeds the van der Waals interactions of the long aliphatic chains. However, a bigger anion, such as BF<sub>4</sub><sup>−</sup>, should have lower anion–cation interactions, and the van der Waals interactions may predominate, as in MOMNM<sub>2</sub>E[BF<sub>4</sub>], leading to lower viscosities than the selected iodides. Fitting lines were calculated using the Vogel–Tammann–Fulcher equation ( $\eta = \eta_0 \exp(B/(T - T_0))$ ) and their corresponding  $\eta_0$ ,  $B$ , and  $T_0$  values are listed in Table 4. From this data, the strength parameter,  $D$ , was calculated as  $D = B/T_0$  and could be used as a measure of fragility.<sup>29</sup> In the strength–fragility scheme, originally proposed by Angell,<sup>30</sup> a  $D$  value lower than 10 represents fragile behavior, and higher values (around 100) are typical for strong liquids, similar to SiO<sub>2</sub>. The three hexyl-based phosphonium iodides have fragility values in the range 8–10, indicating an intermediate response. The octyl-based iBO<sub>3</sub>PI has a  $D$  value around 7, indicating a higher fragility. However, these values are significantly higher than previously reported for ionic liquids, such as dicyanamide<sup>29</sup> and orthoborates.<sup>31</sup> Therefore, an extended analysis of their fragility was conducted.

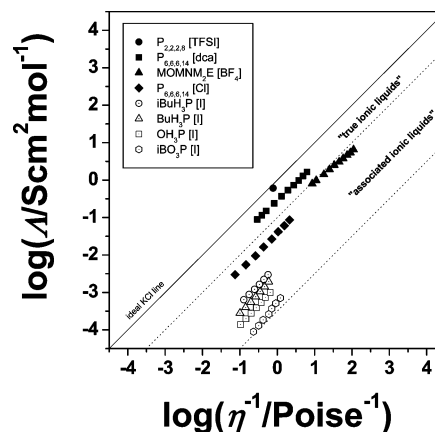
A fragility plot is shown in Figure 4. Here, we present the viscosity data vs the adjusted temperature ( $T_g/T$ ) to the glass transition. We indicate with a dotted line the extreme behavior of glass forming liquids, whose viscosity behavior does not change abruptly with temperature, as is the case of SiO<sub>2</sub>. On the other side, we present data for *o*-terphenyl,<sup>32</sup> a model molecular liquid with a high degree of fragility. Also, we have included data for BMIM[BOB], a proposed<sup>31</sup> glass forming ionic



**Figure 4.** Fragility plot for viscosity data versus adjusted temperature ( $T_g/T$ ) to glass transition, along with data from the literature and prepared phosphoniums (methoxy methyl dimethyl ethyl ammonium tetrafluoroborate, ●, MOMNM<sub>2</sub>E[BF<sub>4</sub>];<sup>27</sup> methoxy ethyl dimethyl ethyl iodide, solid ○, MOENM<sub>2</sub>E[I];<sup>27</sup> butyl methyl imidazolium bis(oxalato)borate, ■, BMIM[BOB];<sup>31</sup> ▲, *o*-terphenyl).<sup>32</sup>

liquid model, which is one of the more fragile ionic liquids reported. We included the previously discussed MOENM<sub>2</sub>E[I] and MOMNM<sub>2</sub>E[BF<sub>4</sub>] for comparison.<sup>27</sup> In the graph, we observe that the reported phosphonium iodides could be considered as possessing intermediate fragile behavior, comparable to MOENM<sub>2</sub>E[I] and MOMNM<sub>2</sub>E[BF<sub>4</sub>]. This is an important finding due to the structural differences among the phosphonium compounds. At this point, we believe that, despite their low glass transition (Table 3), the long aliphatic chains of phosphonium iodides interact to allow low fluidity at room temperature, compared to more fragile systems. The ammonium–iodide interactions, as in MOENM<sub>2</sub>E[I], are stronger and lead to a higher glass transition, promoting a shift to the right of the plot. This is an indication of more fragile behavior than the phosphonium iodides. On the other hand, MOMNM<sub>2</sub>E[BF<sub>4</sub>] has one of the lowest glass transitions reported, and, despite its low temperature viscosity, an intermediate fragile behavior is observed. This situation could be verified if more data on viscosity/glass transition for molten iodides becomes available.

It is clear now that the midsize aliphatic chains in the phosphonium iodides have low ionic conductivity. To clarify the relationship between our results and those reported in the literature regarding conductivity and viscosity, we constructed a Walden plot, and the outcome is presented in Figure 5. According to Angell,<sup>27</sup> all compounds that lie below 1 order of magnitude of the ideal behavior of diluted KCl must be classified as “poor ionic liquids”, indicating that the ionic conductivity is lower than expected due to substantially higher viscosity values. However, MacFarlane proposed<sup>23</sup> a new and clarifying approach. Salts that possess strongly interacting ions in ionic liquids are usually located below the KCl line, due to partial association of neighboring ions. Indeed, this is a broader approach to the ion pair concept originally proposed by Fuoss.<sup>33</sup> Therefore, different cations and anions will have different levels of attractive forces, reducing the degree of ionicity. Consequently, there is a possibility for the formation of ion pairs<sup>34</sup> or aggregates. These associated species do not contribute to the overall conductivity; thus, there must be a permanent effort to reduce their presence in electrolyte applications. Trihexyl-tetradecyl phosphonium diacetamide<sup>34</sup> has long aliphatic chains, yet it lies near the ideal KCl line on the Walden plot and is classified as a “true” ionic liquid. Similar behavior is found in phosphonium salts with shorter aliphatic chains,<sup>19</sup> as is the case

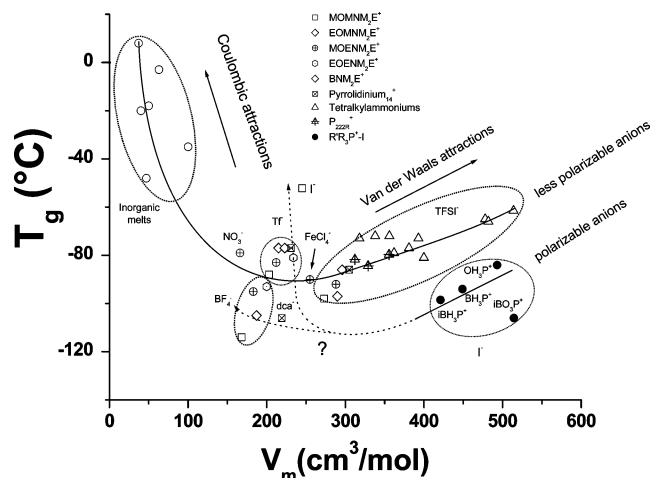


**Figure 5.** Walden plot presenting our phosphonium iodides, along with similar compounds (triethyl octyl phosphonium imide, ●, P<sub>2,2,2,8</sub>[TFSI];<sup>19</sup> trihexyl tetradecyl phosphonium dicyanamide, ■, P<sub>6,6,6,14</sub>[dca];<sup>34</sup> methoxy methyl dimethyl ethyl ammonium tetrafluoroborate, ▲, MOMNM<sub>2</sub>E[BF<sub>4</sub>];<sup>27</sup> trihexyl tetradecyl phosphonium chloride, ◆, P<sub>6,6,6,14</sub>[Cl]);<sup>34</sup>

of triethyl-R phosphonium bis(trifluoromethanesulfonyl)imides (where R = dodecyl, dodecyl, and pentyl). On the other hand, trihexyl-tetradecyl phosphonium chloride lies below the ideal KCl line and, according to MacFarlane, this phosphonium must be classified as an associated ionic liquid (AIL), which should be considered an intermediate between a true ionic liquid and a molecular species. Bulky diacetamide or bis(trifluoromethanesulfonyl)imide anions are larger than the spherical chloride anion and are closer to the phosphorus cation, increasing the electrostatic attraction and the number of ion pairs. The iBH<sub>3</sub>PI lies well below the ideal KCl line and even lower than the AIL, [P<sub>6,6,6,14</sub>][Cl], implying a larger amount of associated ions that decrease the overall conductivity. Thus, iBH<sub>3</sub>PI should be considered an AIL as well. This may be explained in terms of the structure of iBH<sub>3</sub>PI, where the large iodide anion straightens out the aliphatic chains, exposing the phosphorus cation to stronger cation–anion interactions, as recently was pointed out by Benavides.<sup>24</sup>

At the present time, for electrochemical applications, ionic liquids with low viscosity and high conductivity at room temperatures are desirable. This objective could be reached by decreasing cohesive forces in the liquids up to an optimal point. The high energy of cohesion, associated with electrostatic forces, which increases as ion size decreases, induces the formation of viscous liquids. Therefore, if the sum of effective ionic radii is increased, the Coulombic attraction forces decrease, to achieve a lower viscosity. However, as particle size increases, the van der Waals interactions become more important. Recently, Angell<sup>27</sup> proposed a relation of these effects by plotting glass transition temperatures ( $T_g$ ) of a wide variety of ionic liquids vs their molar volume ( $\bar{V} = M_w/\rho$ ), and a partial replica of this plot is depicted in Figure 6. Accordingly, at low  $\bar{V}$ , we find a group of inorganic molten salts, whose main characteristic is a very high electrostatic ion attraction in their crystal lattices. On the other side, we find a wide variety of alkyl ammonium salts and some alkylphosphonium<sup>19</sup> and bis(trifluoromethanesulfonyl)imide salts. We should note the relatively long aliphatic chains of these compounds, and an increase in  $T_g$  as chain size increases as well. This behavior is a clear indication of the dominance of van der Waals interactions. In this graph, there is a middle region around 200–250 cm<sup>3</sup>/mol, where the ILs with lowest  $T_g$  are located and should be interpreted as a region where the Coulombic and van der Waals attractions are at their





**Figure 6.** Glass transition ( $T_g$ ) versus molar volume for a wide variety of ionic liquids. This plot is partially reproduced from Angell.<sup>27</sup> Here, we have marked several islands where certain anion “families” are found and a solid line that indicates a suggested trend for ILs with less polarizable anions. On the lower part, we have marked a region for our more polarizable phosphonium iodides. A dashed line is plotted as a suggestive behavior for a broader approach, dependent on more experimental data.

lowest level. One characteristic of this plot is that most of the ILs have low polarizabilities. We wondered where our new asymmetric phosphonium iodides would fit on this plot. Angell<sup>27</sup> has pointed out that polarizable ions should be left out of this plot because a different effect of the van der Waals attraction is expected. Observing Figure 6, we immediately notice that phosphonium iodides have a lower  $T_g$  than ammonium bis(trifluoromethanesulfonyl)imide salts of a similar size, which may indicate that the phosphonium iodides may be part of a different tendency for polarizable ionic liquids. Unfortunately, there is very little data available on other iodides to confirm this possibility. However, the three hexylphosphonium iodides ( $i\text{BH}_3\text{PI}$ ,  $\text{BH}_3\text{PI}$ , and  $\text{OH}_3\text{PI}$ ) plotted follow a linear trend, according to their increase in  $\bar{V}$ , and are positioned in the van der Waals dominance region. The  $\text{HO}_3\text{PI}$  is apart from this trend, as longer octyl chains have almost planar structures<sup>24</sup> favoring lower van der Waals interactions that lessen their structural associations ( $T_g$  indeed). Alternatively, there are reports<sup>35</sup> on very low  $T_g$  pyrrolidinium salts with polarizable dicyanamides that could potentially follow the same trends as these phosphonium iodides. Further research on thermal properties is suggested on lower molar weight phosphonium or ammonium iodides to define a possible trend for polarizable ILs.

## Conclusions

In general, thermal stability is acceptable for these molten iodides. Ionic conductivity is relatively low compared to other aliphatic and aromatic ILs. Viscosity data is comparable to similar aliphatic nitrogen-based ILs. We can classify these salts as having intermediate fragility and being comparable to other aliphatic ILs. Under Walden’s rule, we observe data well below the ideal KCl line, and this is explained in terms of associated ionic liquid interactions. Lastly, we remark that polarizable anions, such as iodides, have considerable deviations from less polarizable ions in a glass transition vs molar volume plot.

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