Effect of Aromaticity in Anion on the Cation—Anion Interactions and Ionic Mobility in Fluorine-Free Ionic Liquids

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ABSTRACT: Ionic liquids (ILs) composed of tetra(n-butyl)phosphonium [P4444]⁺ and tetra(n-butyl)ammonium [N4444]⁺ cations paired with 2-furoate [FuA]⁻, tetrahydro-2-furoate [HFuA]⁻, and thioephene-2-carboxylate [TpA]⁻ anions are prepared to investigate the effects of electron delocalization in anion and the mutual interactions between cations and anions on their physical and electrochemical properties. The [P4444]⁺ cations-based ILs are found to be liquids, while the [N4444]⁺ cations-based ILs are semi-solids at room temperature. Thermogravimetric analysis revealed higher decomposition temperatures and differential scanning calorimetry analysis showed lower glass transition temperatures for phosphonium-based ILs than the ammonium-based counterparts. The ILs are arranged in the decreasing order of their ionic conductivities as [P4444][FuA] > [P4444][FuA'] > [P4444][TpA] > [P4444][HFuA] > [P4444][HfA'], as measured by linear sweep voltammetry. This order can be attributed to the electrons’ delocalization in [FuA]⁻ and in [TpA]⁻ aromatic anions, which has enhanced the oxidative limit potentials and the overall electrochemical stabilities.

INTRODUCTION

Ionic liquids (ILs), especially room-temperature ionic liquids (RTILs), as emerging electrolytes have been extensively studied in numerous electrochemical applications owing to their exceptional physicochemical and electrochemical properties. Some of the adoptable properties, which are common to ILs, are negligible vapor pressure, nonflammability, wide temperature range of liquid phase, high thermal stability, high solvating behavior, high ionic conductivity, and wide electrochemical stability window. ILs composed of bis-(trifluoromethyl sulfonyl)imide (TFSI) anion with different nitrogen-based aromatic and aliphatic cations such as imidazolium, pyridinium, pyrrolidinium, and quaternary ammonium derivatives are widely used in different electrochemical applications. The quaternary ammonium cations and their derivatives coupled with TFSI anion have good electrochemical stability at room temperature but are thermally less stable than quaternary phosphonium counterparts, and they would not be good electrolytes at high temperatures.

There has been considerable interest in the synthesis and electrochemical characterization of phosphonium-based RTILs due to their advantages in simultaneously providing chemical, thermal, and electrochemical stabilities. The phosphonium ILs have been used as electrolytes for various applications such as electrochemical sensing, electro-polymerization of organic monomers, and electrolytes in supercapacitors and in dye-sensitized solar cells. Many of these reported phosphonium ILs are based on large molecular weight cations derived from tris(n-hexyl)phosphine, and the resulted ILs have relatively high viscosities and low ionic conductivities. Low viscosity is a main requisite for electrochemistry since viscosity pointedly affects the ionic conductivity, diffusivity, dispersion, mixing, filtration, and even equipment selections. Despite the importance of lower viscosity and higher ionic conductivity, there have been limited attempts on lowering liquid viscosities of phosphonium ILs. In this regard, we have designed tetra(n-butyl)ammonium and tetra(n-butyl)-phosphonium-based ILs containing relatively smaller heterocyclic anions with a motivation to achieve the following desirable properties: (i) enhanced thermal stability (phosphonium-based ILs are known for their high chemical and thermal stabilities and comparatively low toxicity than their ammonium analogues); (ii) faster diffusivity of ions (the investigation of ions self-diffusions is of great importance for ILs as electrolytes for electrochemical devices); (iii) higher electrochemical stability (phosphonium-based ILs have wide electrochemical windows and higher ionic conductivities and in some cases better electrochemical properties than their ammonium counterparts). The lowest-viscosity phosphonium-based IL for electrochemical application is tri(n-butyl)octylphosphonium TFSI...
ILs, however, the viscosity is still higher in comparison to conventional TFSI-based ILs. Tsunashima and Sugiyama have reported a series of ILs comprising triethylphosphine (TEP)-based cations and TFSI anions having relatively higher ionic conductivity and lower viscosity. The main limitation of ILs with TFSI anions in electrochemical systems is their high fluorine content, which would lead to toxicity and environmental concerns. There have been a number of salts developed to substitute the LIBs’ electrolyte salt LiPF$_6$, but many of these salts were thermally or electrochemically unstable. In the mid-1990s, a successful attempt was made toward the synthesis of salts based on aromatic anions (following the Hückel rule) as potential battery electrolytes. This concept was strongly supported by molecular modeling. Among the possible aromatic anions using the cyclization synthesis approach, LiTDI salt (lithium 4,5-dicyano-2-(trifluoromethyl)imidazolate) was made at a large scale. Similar aromatic analogs, LiPDI (lithium 4,5-dicyano-2-(pentfluoroethyl)imidazolate) and LiHDI (lithium 4,5-dicyano-2-(n-heptafluoropropyl)imidazolate) were also synthesized. The newly synthesized unique salts were thermally stable, and unlike LiPF$_6$, they were stable in the presence of moisture as well. Further, the aromatic salts (LiTDI and LiPDI) electrolytes were also highly stable on the surface of Pt electrode even in a wide potential window of 4.8 V versus Li$^+$/Li as confirmed by voltammetric measurements. Swiderski et al. studied the effect of metal cations, including Li and Na, on the electrochemical stability windows (ESW) of these ILs. The onset of the DSC peak was considered as the glass transition temperature ($T_g$). Nitrogen gas was supplied at 20 mL min$^{-1}$ to maintain a dry environment inside the sample chamber.

**Electrochemical Measurements.** Metrohm Autolab (PGSTAT302N) electrochemical workstation, with FRA32 M module for impedance, was used for the electrochemical studies. About 80 μL of the electrolyte was placed in the TSC 70 closed cell. The cell was mounted onto the Microcell HC cell stand, which is connected to a temperature controller. In the Microcell HC setup, the temperature is controlled through a Peltier element which enables adjusting the temperature from −20 to 100 °C. A two-electrode cell assembly, glassy carbon electrode as working and Pt cup as counter electrodes, was used for electrochemical impedance to measure IL ionic conductivity. Impedance measurements were performed in the frequency range of 0.1 Hz to 1 MHz with an alternating current (AC) amplitude of 10 mV. Heating and cooling impedance responses were recorded from −20 to 100 °C. The cell was thermally equilibrated for at least 10 min before each measurement. The cell constant of the Pt cup was determined by means of a 100 μS cm$^{-1}$ KCl standard solution from Metrohm ($K_{cell} = 1.486$ cm$^{-1}$). Prior to each experiment, the working electrode was polished with a Kemet diamond paste (0.25 μm). For data acquisition, Nova 2.02 software was used. In case of the ILs electrochemical stability windows (ESW) tests, linear sweep voltammetry (LSV) was run at different temperatures from −20 to 80 °C using a three-electrode cell assembly: glassy carbon (GC) as working, Ag wire (coated with AgCl) as pseudoreference, and Pt cup as counter
electrodes, respectively. The LSV scan rate was 20 mV s⁻¹, and the applied potential was from -3 to +3 V. Ferrocene was used as an internal reference, and the potentials were converted to Fe/Fe⁺ couple standard.⁴⁶ Ferrocene was poorly soluble in the IL, and an ultrasonic bath (VWR USC-TH) was employed to assist the dissolution. The current was converted to current density using the working electrode surface area (2 mm diameter). The electrochemical window of the IL was considered as the potential at 0.10 mA cm⁻² cutoff current density.

**NMR Diffusometry.** Pulsed gradient spin–echo—nuclear magnetic resonance (PGSE-NMR) measurements were performed on a Bruker Avance III (Bruker BioSpin) NMR spectrometer. The working frequency for ¹H analysis was 400.27 MHz. Data were processed using Bruker Topspin 3.1 software. NMR self-diffusion measurements were performed on ¹H with a PGSE-NMR probe Diff50 (Bruker) with a maximum amplitude of the magnetic field gradient pulse of 29.73 T m⁻¹. The sample was placed in a standard 5 mm glass sample tube and closed with a plastic stopper to avoid air contact. Prior to measurements, the samples were equilibrated at a specific temperature for 30 min.

**Simulation Methodology.** Density functional theory (DFT) calculations were first performed to obtain optimized molecular geometries of three anions, and thereafter their tightly bound ion pair structures with tetra(n-butyl)ammonium and tetra(n-butyl)phosphonium cations, respectively, using the Gaussian 16 package (Revision B.01) at the B3LYP/6-311+g(d,p) level of theory,⁴⁸ with Grimme’s-D3 dispersion correction.⁴⁹ Only molecular geometries with all positive vibration frequencies were taken into consideration to ensure that the obtained ion and ion pairing structures are in fact true minima in the corresponding energy landscapes.

Atomic force field parameters for three anions based on the AMBER framework were developed in a procedure similar to that described in previous publications.⁵⁰ The CHELPG atomic partial charges for three anions were determined by fitting molecular electrostatic potentials generated from DFT calculations of individual anions at the same level of theory,⁴⁸ with Grimme’s-D3 dispersion correction.⁴⁹ Only molecular geometries with all positive vibration frequencies were taken into consideration to ensure that the obtained ion and ion pairing structures are in fact true minima in the corresponding energy landscapes.

In the current work, all simulation systems are composed of 400 ion pairs having ~26000 atoms. Atomistic molecular dynamics simulations were performed using the GROMACS package with cubic periodic boundary conditions.⁵¹ The equations of motion were integrated using a classical velocity Verlet leapfrog integration algorithm with a time step of 1.0 fs. A cutoff distance of 1.6 nm was set for short-ranged van der Waals interactions and real-space electrostatic interactions between atomic partial charges. The particle-mesh Ewald summation method with an interpolation order of 5 and a Fourier grid spacing of 0.2 nm was employed to handle long-range electrostatic interactions in reciprocal space.

All simulation systems were first energetically minimized using a steepest descent algorithm and thereafter annealed gradually from 800 to 300 K within 20 ns. All annealed simulation systems were equilibrated in an isothermal—isobaric ensemble for 40 ns maintained using the Nose—Hoover thermostat and the Parrinello—Rahman barostat with time coupling constants of 0.5 and 0.2 ps, respectively, to control the temperature at 300 K and the pressure at 1 atm. Atomistic simulations were further performed in a canonical ensemble for 100 ns, and simulation trajectories were recorded at an interval of 100 fs for further microstructural and dynamical analyses.

### RESULTS AND DISCUSSION

The synthesized ILs, namely, tetra(n-butyl)phosphonium furoate ([P₄₄₄₄][FuA]), tetra(n-butyl)phosphonium tetrahydrofuroate ([P₄₄₄₄][HFuA]), tetra(n-butyl)phosphonium thiophencarboxylate ([P₄₄₄₄][TpA]), tetra(n-butyl)ammonium furoate ([N₄₄₄₄][FuA]), tetra(n-butyl)ammonium tetrahydrofuroate ([N₄₄₄₄][HFuA]), and tetra(n-butyl)ammonium thiophencarboxylate ([N₄₄₄₄][TpA]), are obtained in good yields. The structures and abbreviations of the ions in these ILs are shown in Figure 1.

![Chemical structures and abbreviations of the ionic components of the synthesized ILs.](https://dx.doi.org/10.1021/acs.jpcb.0c08421)

The synthesized ILs were characterized by ¹H, ¹³C, and ³¹P NMR analyses to confirm the structures and purity of the products. The ¹H NMR spectra (SI Figure S1, Figure S4, and Figure S7) of [P₄₄₄₄][FuA], [P₄₄₄₄][TpA], and [P₄₄₄₄][HFuA] have three resonance lines associated with the alkyl chains of the phosphonium cation; a triplet in the range from 0.90 to 0.95 ppm is for the terminal methyl groups, a multiplet between 1.46 and 1.54 ppm is for all of the methylene protons, and another multiplet between 2.30 and 2.46 ppm is due to the 8 α-protons. The downfield resonance lines of varying multiplicity in the ranges of 6.32–6.34 ppm (multiplet) and 6.88–6.90 ppm (multiplet) and at 7.34 ppm (singlet) are assigned to the three non-equivalent protons of the furoate anion (Figure S1). Similar varying multiplicities were also observed for the three non-equivalent protons of thiophencarboxylate anion at 6.97–6.99 ppm (triplet), 7.32–7.33 pm (doublet), and 7.66–7.67 ppm (doublet), as shown in Figure S4. The protons in tetrahydrofuroate ring have a different pattern of resonance lines because of the saturated structure and chiral conformation. The resonance multiplicity at 4.38–4.42 ppm is assigned to the single proton attached to the carbon at position 2. The second more deshielded protons attached to carbon at position 5 have multiple resonance lines from 3.79 to 4.01 ppm. The third deshielded protons attached to carbon at position 3 have two separate multiplicities, one from 2.19 to 2.26 ppm and another from 1.97 to 2.02 ppm. Protons attached to carbon at position 4 have a resonance line (multiple) at 1.85–1.92 ppm, Figure S7. In the ¹H NMR
In the 13C NMR spectra, the absence of a resonance line corresponds to -OH of 2-furoic acid, tetrahydro-2-furoic acid, and thiophene-2-carboxylic acid in the range of 8.54–10.00 ppm, confirming the successful synthesis and purity of the respective ILs.

The 13C NMR spectra of the ILs (Figure S2, Figure S5, and Figure S8) have upfield resonance lines from 13.61 to 24.21 ppm associated with the aliphatic carbon chains of the phosphonium cation. For [P[4444][FuA] (Figure S2), the downfield resonance lines at 610.8, 112.2, 142.4, and 152.93 ppm are accounted for by the four carbon atoms in the furan ring, while the resonance line at 163.9 ppm is attributed to the carboxylate carbon. In case of [P[4444][TpA] (Figure S5), the resonance line at 166.1 ppm is for the carboxylate carbon. For [P[4444][HFuA] (Figure S8), the 13C resonance lines at 127.2, 129.1, 130.5, and 142.4 ppm are assigned to the carbons in the thiophenecarboxylate ring, while the resonance lines at 116.1 ppm is for the carboxylate carbon. The synthesized ILs are also characterized by electrospray ionization mass spectrometry (ESI-MS) to further confirm synthesis and purity. The ESI-MS mass to charge ratio values and spectra are given in the Supporting Information (Figures S10–S15). The mass to charge ratios detected are assigned to phosphonium (m/z 259.25), ammonium (m/z 242.28) cations and fuorate (m/z 111.01), thiophene-2-carboxylate (m/z 126.99), and tetrahydrofuorate (m/z 115.04) anions. The mass to charge ratio values are very much close to the calculated values.

The ATR-FTIR spectra of the ILs (Figure S16) have stretching bands at 2957–2870 cm−1 due to the sp2 and sp3 C–H functional groups. The vibrational bands in the range of 650 to 570 cm−1 can be assigned to the P–C stretching in the phosphonium cation. A strong band at 1100–1083 cm−1 is assigned to the stretching of the C–O functional group. The FTIR band of C=O stretching generally appears at about 1700 cm−1. However, the exact position of this band is dependent on the nature of the functional groups such as carboxylic acid, ester, aldehyde, and ketone and the chemical environment of C=O such as aromatic delocalization of electrons and electron-withdrawing effect. Figure 3 shows the FTIR spectra of ILs in the region of 1850 to 1150 cm−1. The infrared bands observed at 1750–1720 cm−1 (with shoulders at 1666 cm−1) in the spectra of [N[4444][FuA], [N[4444][HFuA], [N[4444][TpA], and [P[4444][HFuA] are assigned to the carbonyl stretching of [HFuA]− and [FuA]− anions. The carbonyl stretching is shifted to lower wavenumber of 1704 cm−1 in [FuA]− anion and of 1680 cm−1 in [TpA]− anion in [P[4444][FuA] and [P[4444][TpA] ILs.

Figure 2. 13C NMR spectra in the range from 100 to 180 ppm: (a) 2-furoic acid, (b) [P[4444][FuA] showing peaks of furoate anion, (c) thiophene-2-carboxylic acid, and (d) [P[4444][TpA] showing peaks of thiophene-2-carboxylic acid anion.
The charge density distribution on carboxylate moieties. The charge density distribution on conjugated structure between the heteroaromatic rings and the attributed to $\delta^-$ cm$^{-1}$ respectively. An IR band characteristic of OH (3400 cm$^{-1}$) with the C phosphonium-based ILs, the vibrational frequencies associated electron circulation over the conjugated ring. Similarly in electron density more toward the cation, and restrict the more electronegative nitrogen atom that can polarize the formation of anion. The electron delocalization is further manifested on the HOMO (highest occupied molecular framework (Figure 4c). However, both $[\text{FuA}]^-$ and $[\text{TpA}]^-$ anions. This indicates that the charge density distribution in $[\text{FuA}]^-$ is more delocalized than that on $[\text{HFuA}]^-$ anion. The replacement of oxygen atom on heteroaromatic ring moiety with sulfur atom can further strengthen the charge delocalization around the whole anion framework (Figure 4c).

The charge delocalization effects on these three anions are further manifested on the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies. Figure 5 presents the molecular orbital energies from HOMO–5 to LUMO+5, the HOMO–LUMO energy gap, and the charge density contours of three anions at HOMO and LUMO states. The charge delocalization effect for three anions are characterized by $[\text{HFuA}]^- < [\text{FuA}]^- < [\text{TpA}]^-$, and therefore the HOMO energies are gradually lowered from $[\text{HFuA}]^-$ to $[\text{TpA}]^-$ with a concomitant increase in LUMO energies and the enlarged energy gaps ($E_{\text{LUMO}}-E_{\text{HOMO}}$), indicating that the former is relatively easier and the latter is harder to oxidize. This is further confirmed by the thermo-electrochemical stabilities (the LSV curves shown in Figure 10) of ILs consisting of these anions coupled with $[\text{P4444}]^+$ cations. The variations of HOMO and LUMO energies are detailed in the corresponding electron density contours shown in Figure 6. The NMR, FTIR, and the DFT calculations confirmed the electrons’ delocalizations in $[\text{FuA}]^-$ and $[\text{TpA}]^-$ anions over the aromatic rings that might have a pronounced impact on the physicochemical and electrochemical properties of the synthesized ILs.

The properties of ILs such as thermal behavior and stability, viscosities, ionic conductivity, diffusivity, and electrochemistry are significantly affected by impurities of IL samples. Among all possible impurities, water holds a peculiar significance. Therefore, the water content in IL samples was determined, and it was found to be within the acceptable limits such as 300 ppm in $[\text{P4444}][\text{FuA}]$, 280 ppm in $[\text{P4444}][\text{HFuA}]$, and 360 ppm in $[\text{P4444}][\text{TpA}]$. The ammonium-based ILs are semi-solids at room temperature; therefore, their viscosities and ionic conductivities are not measured. However, the phosphonium-based ILs are viscous liquids at room temperature and their densities and viscosities in the temperature range from 20 to 60 °C are presented in Table S1. In addition, the liquid density data for tetra(n-butyl)phosphonium-based ILs obtained from atomistic simulations are consistent with experimental results. As expected, the densities of these ILs are linearly decreased with increasing temperature. The comparatively high density of $[\text{P4444}][\text{TPA}]$ at all temperatures is consistent with the presence of high atomic mass sulfur atom in $[\text{TPA}]^-$ anion. As shown in Table S1, viscosity decreases with temperature; i.e., the viscosity of $[\text{P4444}][\text{FuA}]$ is 955.6 mPa s at 25 °C, which is decreased to 98.32 mPa s at 60 °C.

![Figure 4. Molecular electrostatic potential contours of (a) $[\text{HFuA}]^-$, (b) $[\text{FuA}]^-$, and (c) $[\text{TpA}]^-$ anions obtained from DFT calculations.](https://dx.doi.org/10.1021/acs.jpcb.0c08421)
interactions among ionic species, hydrogen bonding, and alkyl-chain stacking interactions are the main factors affecting the physical state and viscosity of these synthesized ILs. The radial distribution functions (RDFs) for the cation–anion and cation–cation pairs are presented in Figure 6a,b. The cations’ central atoms N and P while the anions’ central atoms O or S were taken as reference to calculate the site–site RDFs that would present the microscopic structure between ionic species. In the RDFs presented in Figure 6a, two distinct solvation shells are observed at around 0.5 and 1.3 nm for the \([\text{N}_{4444}]^+\) and \([\text{P}_{4444}]^+\) cations with \([\text{FuA}]^-\), \([\text{HfuA}]^-\), and \([\text{TpA}]^-\) anions. Comparatively broader distribution is observed for \([\text{HFuA}]^-\)-based ILs. A higher first peak and lower first minimum have been observed in the cation–anion RDFs for the same anion with alkylammonium and alkylphosphonium cations, showing a well-defined solvation shell of the anions around cations and vice versa. This means that the aromatic anions such as \([\text{FuA}]^-\) and \([\text{TpA}]^-\) have stronger intermolecular interactions with the tetra(n-butyl)ammonium and tetra(n-butyl)phosphonium cations than the nonaromatic.

Figure 5. Molecular orbital energies from HOMO−5 to LUMO+5, the HOMO–LUMO energy gap, and the electron density contours of anions at HOMO and LUMO states: (a, c, and e) HOMOs for \([\text{HfuA}]^-\), \([\text{FuA}]^-\), and \([\text{TpA}]^-\) anions, and (b, d, and f) LUMOs for these three anions.

Figure 6. Intermolecular RDFs of (a) N/P in cations with O/S atoms on aromatic rings of anions and (b) N–N and P–P pairs between cations.

Figure 7. TGA thermograms (a) and DSC scan curves (b) of the ILs.
[HFuA]− anion. Similar cation–anion RDFs calculations have been reported for the alklyphosphonium orthoborate ILs.50 The cation–cation RDFs (Figure 6b) exhibit a broad first maxima with some distance shoulder which is presenting an ionic system dominated by a long-range electrostatic interaction.50 This is specially observed for tetra(n-butyl)-ammonium cations having stronger interactions with neighboring cations than their phosphonium counterparts (Figure 6b) when they are coordinated with the same anion. This supports the semi-solid nature of the tetra(n-butyl)ammonium ILs at room temperature. The RDFs calculations clearly show that the local ionic structures of the ILs are affected by the nature of the cations and anions.

Thermal properties of the ILs are determined using TGA and DSC. The most significant descriptor in TGA analysis is the decomposition onset temperature (Td), which is the intersection of the baseline and the tangent of the weight versus temperature (Figure S17). The Td depends on the intrinsic stability and mutual interactions between ions.55 The TGA curves of the ILs shown in Figure 7a indicate that these ILs have two inflection points, corresponding to two decomposition steps. The majority of the weight loss for [P4444][FuA] (79%) and [P4444][TpA] (71%) comes from the first inflection, while most of the weight loss for [P4444][HFuA] (70%) comes from the second inflection that corresponds to the cation decomposition. The Td (onset temperatures from the first inflection point) of [P4444][FuA], [P4444][HFuA], and [P4444][TpA] are 291, 208, and 262 °C, respectively (Table 1).

Table 1. Molecular Weights, Glass Transition Temperatures, Decomposition Temperatures, and Ionic Conductivity of the Synthesized ILs

| IL            | MW (g mol−1) | Tg (°C) | Td (°C) | σ (mS cm−1)   | Td (°C)   |
|--------------|-------------|---------|---------|---------------|-----------|
| [P4444][FuA] | 370.5       | −55.62  | 291     | 0.032         | 197       |
| [P4444][HFuA]| 374.5       | −68.21  | 208     | 0.069         |           |
| [P4444][TpA]| 386.6       | −55.65  | 262     | 0.028         |           |
| [N4444][FuA]| 353.5       | −45.41  | 197     |               |           |
| [N4444][HFuA]| 357.6       | −66.25  | 201     |               |           |
| [N4444][TpA]| 369.6       | −37.43  | 197     |               |           |

Conversely, the ammonium-based ILs exhibit single-step decomposition TGA curves (Figure 7a) with Td at about 200 °C. Ohno and co-workers have reported a series of tetra(n-butyl)phosphonium-based amino acid ILs having higher thermal stabilities than imidazolium- and ammonium-based ILs.56 [P4444][succinate] and [P4444][maleate] are liquids, while [P4444][fumarate] is solid at room temperature.50 The Tg temperatures reported for the phosphorym-based ILs were 276, 264, and 265 °C with succinate, maleate, and fumarate anions,56 while, with choline-based ILs, have the Td temperatures of 212, 223, and 219 °C with succinate, maleate, and fumarate anions,57 respectively. On the other hand, choline-based ILs with a range of amino acids anions are known to decompose at temperatures < 200 °C.58 The effect of cations on the thermal decomposition of furoate-based ILs have also been reported.59 A decrease in thermal stability was observed by changing the cation from phosphonium to ammonium; i.e., the [P4442][FA] IL has Td of 289 °C, while [N4444][FA] IL has Td of 198 °C.59 The DSC heating scans at a rate of 10 °C min−1 are shown in Figure 7b, where we can see that each IL exhibits a heat capacity change that corresponds to a glass transition temperature (Tg). In comparison to the phosphorym counterparts, the Tg values are positively shifted with ammonium cations, Figure 7b and Table 1. The subzero Tg values of the ILs indicate the very low crystallization rate and fairly stable supercooling state. The thermal analysis shows that the synthesized ILs have relatively high thermal stability and lower glass transition temperatures. The high thermal stability and subzero glass transition temperatures of these ILs make them excellent electrolytes for electrochemical devices operating at variable temperatures.

Figure 8 shows temperature-dependent ionic conductivities of the phosphonium-based ILs. The original ionic conductivity data as a function of temperature are provided in Figure S18 in the SI. At 20 °C, the ionic conductivities of ILs with a common cation can be arranged in decreasing order as [P4444][HFuA] (0.069 mS cm−1) > [P4444][FuA] (0.032 mS cm−1) > [P4444][TpA] (0.028 mS cm−1) (Table 1). The ionic conductivities of [P4444][FuA] and [P4444][TpA] are lower than [P4444][HFuA] over the whole temperature range. The ionic conductivity of [P4444][TpA] is slightly lower than [P4444][FuA]. The difference in ionic conductivities of these ILs for the same cation is attributed to the variations in microstructures of the three anions and their varied charge delocalization effect, which in turn affect their ionic mobility.

The Vogel–Fulcher–Tamman (VFT) equation (eq 1) was used to fit the temperature (K) versus ionic conductivity plots of the phosphorym-based ILs in the temperature range from −20 °C (253 K) to 100 °C (373 K).

\[
\sigma = \sigma_o \exp \left(\frac{\sigma_o \cdot B}{T - T_o}\right)
\]

where \(\sigma_o\) (S cm−1), \(B\) (K), and \(T_o\) (K) are the fitting parameters. \(\sigma_o\) is a pre-exponential factor, \(B\) is a factor related to the activation energy (E), and \(T_o\) is the ideal glass transition temperature, respectively. The plots of temperature versus ionic conductivities for [P4444][HFuA], [P4444][FuA], and [P4444][TpA] are well-fitted to the VFT model over the whole temperature range, Figure 8. The best-fit parameters of eq 1 are given in Table 2. \(T_o\) is found to be about 60 K below the experimental Tg values, which is typical for ionic liquids.50 There is a direct relation between B and activation energy for ion conduction (Ea = BR). As can be seen in Table 2, the Ea value is increasing from 12.1 kJ mol−1 for [P4444][TpA] to 13.6 kJ mol−1 for [P4444][HFuA] due to the slower mobility of ions.
as a result of heterogeneous interactions among neighboring ions and the specific microstructures in the IL matrices.

The self-diffusion coefficients of the phosphonium-based ILs is evaluated using PGSE-NMR technique. The self-diffusion coefficients of cations and anions in each IL can be separately determined since these ILs have NMR active proton (¹H) nuclei in their respective ion groups. In addition, the self-diffusion coefficients of [P₄₄₄₄][FuA] cation and their coupled three anions are also calculated from atomistic simulations. Tables S2 and S3 show that the experimental and computational self-diffusion coefficients of the [P₄₄₄₄][FuA], [P₄₄₄₄][HFuA], and [P₄₄₄₄][TpA] ILs with increasing temperature.

The experimental and computational self-diffusion coefficients of the anions and cations in [P₄₄₄₄][FuA], [P₄₄₄₄][HFuA], and [P₄₄₄₄][TpA] ILs versus temperature are fitted to VFT equation for diffusion (eq 2), and the data are shown in Figure 9.

\[
D = D_0 \exp \left(\frac{-B}{T - T_0}\right)
\]  

where \(D_0\) (m² s⁻¹), \(T_0\) (K), and \(B\) (K) are adjustable parameters. Energy of activation for diffusion is related to \(B\) (\(E_D = BR\)). The values of the best-fit parameters are tabulated in Table 3. The solid and dashed lines in Figure 9 are the calculated curves using eq 2. It is worth mentioning that the experimental and simulated diffusion coefficients for the anions in each IL are larger than those for the corresponding cations. This is due to the smaller sizes of these anions as compared with the [P₄₄₄₄]⁺ cation. The diffusivities of the cation and anions in [P₄₄₄₄][FuA] and [P₄₄₄₄][HFuA] are comparable with and higher than [P₄₄₄₄][TpA]. This is due to the enhanced intermolecular interactions of [TpA]⁻ anions with neighboring ionic species than those in the other two ILs. The experimental values of \(T_0\) and \(E_D\) are slightly larger than the simulated values. This can be attributed to the fact that the simulation measurements may not include all of the smaller interactive forces which exist between the ions in experimental measurements. In the case of [P₄₄₄₄][HFuA], the simulated \(T_0\) value for the cation (145 K) is larger than that for the anion (115 K), which means that the [HFuA]⁻ anions are clustered and have adopted a glassy physical state at earlier temperature than the [P₄₄₄₄]⁺ cation (Table 3).

The ESW of an IL is the potential range in which it does not get oxidized or reduced, which can be calculated by subtracting the oxidation potential limit (anodic limit, \(E_A\)) from the reduction potential limit (cathodic limit, \(E_C\)). In order to make a base for the ESW determination, a current density called cutoff current density must be selected to evaluate the redox potentials. Water content and the operating temperatures are among the main factors affecting the ESW of an IL. Generally, increasing temperature and water content results in narrowing of both \(E_C\) and \(E_A\) and subsequently the ESW of ILs.²⁴,⁶¹

The LSV characterization at variable temperatures is carried out to evaluate the thermo-electrochemical stabilities of the synthesized ILs. The LSV curves of the phosphonium-based ILs at 20 °C are shown in Figure 10a. Both the [P₄₄₄₄][FuA]...
and [P4444][TpA] ILs are evidently more electrochemically stable than [P4444][HFuA] at the surface of glassy carbon electrode. The $E_A$ is shifted to more negative by changing the anions from [FuA]$^-$ and [TpA]$^-$ to [HFuA]$^-$ and, therefore, the [P4444][FuA] and [P4444][TpA] ILs have wider ESW than the [P4444][HFuA]. This is attributed to the distinct electron delocalization in [FuA],$^-$ and [TpA]$^-$ anions, which is confirmed by the $^{13}$C NMR data in Figure 2, stretching shifts of C=O in the FTIR spectra in Figure 3 and the molecular electrostatic potential contours of these three anions shown in Figure 4 and Figure 5.

The temperature-dependent LSV profiles of these ILs in the temperature from ~20 to 80 °C are shown in Figure S19 and the ESW values are given in Table S4. The ESWs of [P4444][FuA] and [P4444][TpA] are much wider than [P4444][HFuA] in the whole studied temperature range. For instance, the ESW of [P4444][FuA], [P4444][TpA], and [P4444][HFuA] are 4.60, 4.60, and 3.95 V, respectively, at 20 °C. The ESW for each IL is getting narrower with increasing temperatures; i.e., the [P4444][FuA] has ESW of 4.60 V at 20 °C, 3.69 at 40 °C, 2.43 V at 60 °C, and 2.18 V at 80 °C. A continuous decrease in the ESWs with an increase in temperature is previously observed for ether and siloxane functionalized imidazolium TFSI ILs. Figure 10b shows the decrease in ESW as a function of temperature, with a large decrease observed between 10 and 70 °C. The decrease in ESW with temperature can be associated with the decrease in viscosity resulting in a higher ionic conductivity and diffusivity of ions and thus frequent interactions of ions with the electrode surface. Both the $E_A$ and $E_C$ are affected with temperature, showing that both anions and cations are sensitive to the temperature increase.

Traces of water can also decrease the ESW of ILs. It is well-known that water molecules present heterogeneous structures and dynamics in the cavities of IL matrices and are strongly bounded to neighboring ionic groups via preferential hydrogen bonding interactions. In most cases, such interactions are so strong that it is impossible to completely remove traces of these dispersed water molecules even by using high temperature and vacuum. Hence, a shoulder around 1.7 V versus Fe/Fe$^+$ in the LSV curves of both [P4444][FuA] and [P4444][TpA] (Figure S19a,c) that is more obvious at 60 and 80 °C might be due to the trapped water molecules’ electrolysis at the electrode surface. The LSV thermo-electrochemical stabilities are in very good agreement with the TGA thermal stabilities of the synthesized ILs. On the basis of these physicochemical and electrochemical investigations, it is worth mentioning that the halogen-free phosphonium-based ILs of this study can be promising electrolytes for high-temperature electrochemical devices in particular to supercapacitors and batteries.

**CONCLUSIONS**

A combined experimental and theoretical study has found that the nature of cation and anion, and an electron delocalization in the anion, has significant effect on the physical and electrochemical properties of ILs. The thermal analysis revealed that the tetra(n-butyl)phosphonium-based ILs are thermally more stable and have lower glass transition temperatures than the tetra(n-butyl)ammonium-based ILs having common anions. The aromatic structure of 2-furoate and thiophene-2-carboxylate anions enhanced the electrostatic interaction with cations that resulted in highly stable ILs. The aromatic anions ([FuA]$^-$ and [TpA]$^-$) based ILs are more thermally stable and presented a wider electrochemical window than nonaromatic anion ([HFuA]$^-$) based IL. This is probably due to the aromatic stability of the 2-furoate and thiophene-2-carboxylate anions that enhanced the overall stability of the ILs. As expected, the mobility of anion containing sulfur atom, [TpA]$^-$, is found to be slower than the anion with an oxygen atom, [FuA]$^-$.

The new anions presented in this study can be promising electrolytes for high-temperature electrochemical devices in particular to supercapacitors and batteries.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcb.0c08421.

$^1$H, $^13$C, $^31$P NMR, MS-EIS, and FTIR spectra and data, details of synthesis procedures, and physicochemical and electrochemical characterizations of the ILs

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