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An ionic liquid containing arsonium cation

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Cations in ionic liquids (ILs) are typically derived from ammonium or phosphonium structures with long alkyl chains, and it is well established that the central atom significantly influences the properties of the resulting ILs. In this study, an arsonium-based IL, trihexylmethylarsonium bis(trifluoromethylsulfonyl)amide, was synthesized. The arsonium cation was found to contribute to lower viscosity and higher ionic conductivity, while maintaining sufficient stability compared to its phosphonium counterpart.

Ionic liquids (ILs) are salts with melting points below 100 °C.[1,2] They possess desirable properties, such as flame retardancy, low volatility, and high ionic conductivity, making them useful for applications in extraction, organic synthesis, and electrochemistry. The properties of ILs can be tuned by altering the combination of cations and anions, which can be synthetically modified.[3] Freemantle referred to ILs as "designer solvents" in 1998 because of their versatility.[4] Achieving low melting points in ILs requires weak interactions between the cations and anions. Consequently, alkyl-substituted cations and weakly coordinating anions are typically used, as shown in Figure 1a.

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Ammonium and phosphonium cations are predominantly employed in cation design. Phosphonium cations tend to reduce the viscosity of ILs compared to their ammonium counterparts (Figure 1b).[5] Because low viscosity is beneficial for practical applications, both experimental and computational studies have been conducted to examine the effects of the central elements nitrogen and phosphorus. One crucial factor influencing viscosity is the molecular flexibility around the central atoms.[5c,d] The larger molecular orbitals of phosphorus provide flexible bonds and dihedral angles, enhancing the molecular mobility.

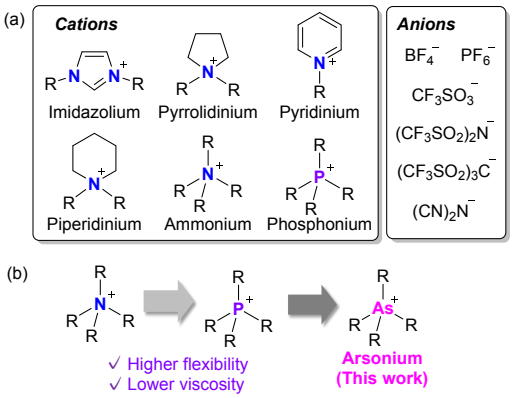


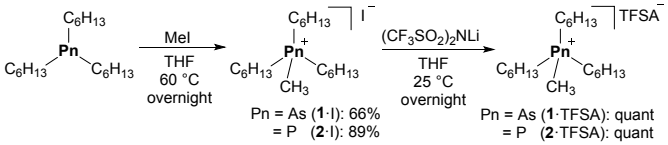
Fig. 1 (a) Representative ions for ILs. (b) Effects of central element in cations.

In this context, arsonium cations are hypothesized to be more effective in producing ILs with low viscosity because of their heavier pnictogen (Pn), arsenic. Notably, certain natural products containing quaternary arsonium cations, such as arsenobetaine, are non-toxic, suggesting potential for the development of arsonium-based ILs.[6] May and coworkers reported the electrochemical stability of tetramethylarsonium bis(trifluoromethylsulfonyl)amide (TFSA),[7] though it exhibited a relatively high melting point (~140 °C) and was not investigated further as an IL candidate. The limited exploration of arsonium-containing ILs can likely be attributed to the

challenges associated with synthesizing tertiary arsines, the key precursors to arsonium salts. Trichloroarsine ($AsCl_3$) is typically used in this synthesis; however, it is highly toxic and volatile.[8] We have developed a safe method to prepare tribromoarsine ($AsBr_3$), a less volatile precursor, for the synthesis of tertiary arsines.[9] This synthetic strategy has significantly advanced the development of functional materials including metal complexes, conjugated molecules, and organocatalysts. Other researchers have also explored functional arsenic compounds using practical As–C bond formation methods.[10]

Recent progress in organoarsenic chemistry has encouraged the investigation of arsonium-containing ILs. In this study, we synthesized TFSA salts of trihexylmethylarsonium (**1**) and trihexylmethylphosphonium (**2**) cations, selecting TFSA for its stability, low viscosity, and hydrophobicity. The resulting salts (**1**·TFSA and **2**·TFSA) are liquids at 25 °C, qualifying them as room-temperature ionic liquids (RTILs). Their thermal properties, viscosity, alkali resistance, ionic conductivity, and electrochemical window were also examined.

Compounds **1**·TFSA and **2**·TFSA were synthesized as shown in Scheme 1. Trihexylarsine was prepared from $AsBr_3$ and hexylmagnesium bromide ($C_6H_{13}MgBr$) following a previously reported procedure.[11] Quaternization of trihexylarsine and trihexylphosphine with iodomethane (MeI) produced iodide salts **1**·I and **2**·I in 66% and 89% yields, respectively. Anion exchange with TFSA was conducted by using Li(TFSA) to quantitatively produce **1**·TFSA and **2**·TFSA. The crude products were washed four times with water to remove any remaining lithium salts. To remove water, the products were dried in a vacuum oven at 100 °C for 5 h, then stored in a glovebox for 1 week at 25 °C. Karl Fischer titration revealed that the water contents of **1**·TFSA and **2**·TFSA were 235 ppm and 189 ppm, respectively. The purified and dried products were liquid at 25 °C , suggested that **1**·TFSA and **2**·TFSA are RTILs. We also tried to synthesize the antimony analogs of **1**·TFSA (Scheme S1). However, the obtained iodide salt intermediate immediately decomposed under ambient conditions, and yellow precipitates were generated, though they were colorless in an inert atmosphere. Therefore, further investigation of their properties was avoided.



Scheme 1. Synthesis of **1**·TFSA and **2**·TFSA.

The phase transition temperatures of the ILs were measured over the range −150 to 100 °C using differential scanning calorimetry (DSC). The DSC curves of the ILs are shown in Figure 2a. Glass transition temperatures (T_g) were observed at −94 °C (**1**·TFSA) and −83 °C (**2**·TFSA), consistent with the observation that **1**·TFSA and **2**·TFSA are RTILs. A decrease in T_g of more than 10 °C was observed for **1**·TFSA compared to **2**·TFSA. A lower T_g is desirable for transport properties such as fluidity and ionic conductivity in ILs. The weaker Coulombic interaction between the cation and anion, attributed to the larger atomic radius of arsenic in **1**·TFSA, likely reduces cohesive forces,[12] contributing to the lower T_g. This feature aligns with the enhanced thermal stability of **1**·TFSA compared to **2**·TFSA, as discussed below (*vide infra*). The viscosity of **1**·TFSA and **2**·TFSA was subsequently measured over the range 25 to 95 °C (Figure 2b). Notably, the viscosity of **1**·TFSA (85 mPa·s) is significantly lower than that of **2**·TFSA (184 mPa·s) at 25 °C. For practical applications, a viscosity below 20 mPa·s is generally preferred, highlighting the need for further modifications to the arsonium cation structure for optimal performance.[13]

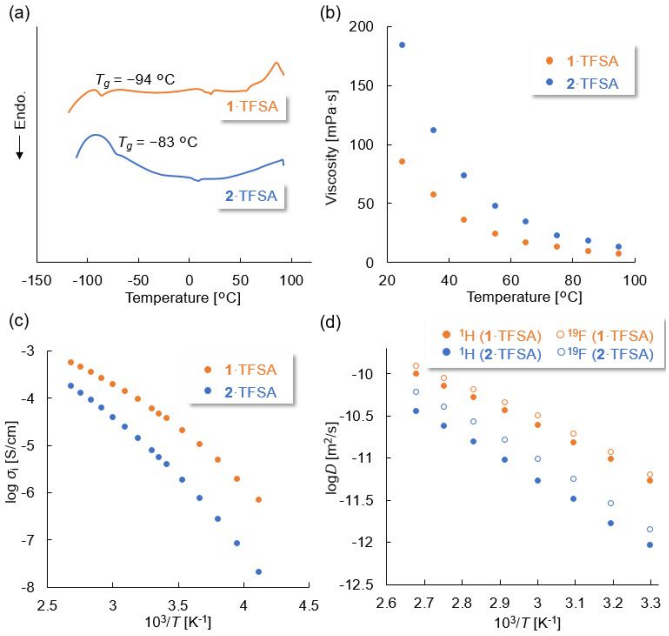


Fig. 2 (a) DSC curves (second scan, under N_2, 10 °C/min) and (b) variable temperature viscosity of **1**·TFSA and **2**·TFSA. (c) Arrhenius plots of ionic conductivities for the ILs. (d) Arrhenius plots of self-diffusion coefficients for the ILs.

Figure 2c presents the Arrhenius plots of the ionic conductivities for **1**·TFSA and **2**·TFSA. Both ILs exhibit convex upward curves, indicating that the ion conduction process in these ILs can be described by the Vogel-Fulcher-Tammann (VFT) equation, which accounts for the temperature dependence of viscosity in amorphous materials.[14] The ionic conductivity values of **1**·TFSA (25 °C: 4.7×10^{-5} S/cm; 100 °C: 5.8×10^{-4} S/cm) were significantly higher than those of **2**·TFSA (25 °C: 5.6×10^{-6} S/cm; 100 °C: 1.8×10^{-4} S/cm). The lower viscosity and higher molecular mobility of **1**·TFSA contribute to its superior ionic conductivity. These findings suggest that arsonium-containing ILs are promising electrolytes for rechargeable batteries.

To further investigate the ion transport properties in the ILs, we measured the self-diffusion coefficients (D) of **1**·TFSA and **2**·TFSA using the pulsed field gradient (PFG)-NMR method over the temperature range 30–100 °C. ^{1}H- and ^{19}F-NMR analyses were used to determine the D values of the cations (D_H) and anions (D_F), respectively. Figure 2d shows the self-diffusion coefficients of the ^{1}H and ^{19}F nuclei in the ILs. In both **1**·TFSA and **2**·TFSA, the D_F value was higher than the D_H value, due to the smaller size of the TFSA anion compared to the arsonium or phosphonium cation, which has long hexyl chains. The D value of cation **1** was consistently higher than that of cation **2** at all

measured temperatures, indicating that the molecular mobility of **1**·TFSA is greater than that of **2**·TFSA, in agreement with the results of the ionic conductivity and viscosity measurements.

To confirm the reason for the lower viscosity of **1**·TFSA over **2**·TFSA, density functional theory (DFT) calculations were conducted to compare ammonium- and phosphonium-containing ILs.[5c,d] Flexibility around the pnictogen center is one of the most crucial factors determining viscosity, according to previous studies. Thus, the C–Pn–C bond angles and C–Pn–C–C torsion angles were varied to estimate the energy increase in the optimized structures. To simplify the calculations, triethylmethylarsonium (**1'**) and triethylmethylphosphonium (**2'**) cations were selected as model cations for **1** and **2**, respectively, and the long hexyl groups were replaced by short ethyl groups. The structures were optimized by freezing C(Me)–Pn–C(Et) bond angles (ϑ_1:190–130°) or C(Me)–Pn–C(Et)–C(Et) torsion angles (ϑ_2: −20–140°) employing the B3LYP/def2svp method extended with Grimme's dispersion correction (D3) and the Becke-Johnson damping (D3BJ) version. The energy profiles of **1'** and **2'** were plotted based on the energies of the fully optimized structures (Figure 3). The energy increase for **1'** was lower than that for **2'** when changing ϑ_1 values from the optimized structures ($\vartheta_1 \approx 109°$). This is because the As–C bonds are relatively flexible owing to the larger molecular orbitals of the As center. The energy barriers for As–C bond rotation in **1'** (7.1 and 8.9 kJ/mol) are smaller than those for P–C bond rotation in **2'** (11.3 and 14.8 kJ/mol) when changing ϑ_2 values. The relatively long As–C bonds relieve steric repulsion and lower the energy barrier. These DFT studies indicate that arsonium cation **1** is more flexible than phosphonium cation **2**, resulting in a lower viscosity for **1**·TFSA.

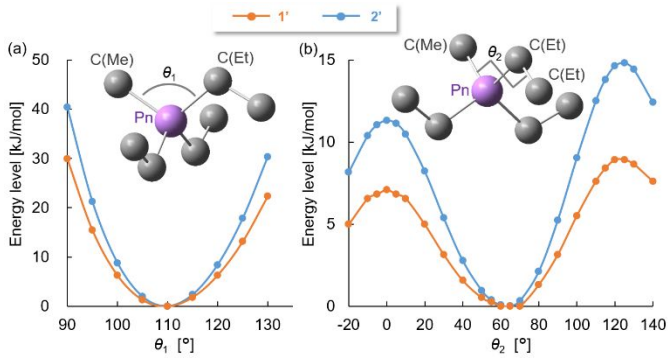


Fig. 3 Energy profiles of **1'** and **2'** with varying (a) C(Me)–Pn–C(Et) bond angles (ϑ_1) and (b) C(Me)–Pn–C(Et)–C(Et) torsion angles (ϑ_2).

The stability of **1**·TFSA and **2**·TFSA was compared. The thermal stability was evaluated using thermogravimetric analysis (TGA, Figure 4a). The decomposition temperatures corresponding to 5 wt% loss (T_{d5}) of **1**·TFSA and **2**·TFSA were 365 and 330 °C, respectively. Thus, the arsonium-containing IL exhibits heat resistance equal to or greater than that of its corresponding phosphonium counterpart.

Subsequently, the alkali resistance was evaluated. Methanol (CD_3OH/CH_3OH = 1/9 v/v) solutions of **1**·TFSA and **2**·TFSA were prepared separately and heated at 80 °C in the presence of 1 M KOH. The residual amounts of cations were monitored by ^{1}H-NMR spectroscopy (Figures 4b, S10, and S11), with 1,3,5-tri-*tert*-butylbenzene as the internal standard. No significant decomposition of cations **1** and **2** was observed even after eight weeks. In contrast, benzyltrimethylammonium (BTMA), a cationic functional group commonly used in anion exchange membranes under alkaline conditions,[15] showed more than 20% decomposition in a 1 M KOH CD_3OD solution within 1 week. In addition, the stabilities of **1** and **2** are comparable to that of tetrabutylammonium, according to a previous study that also examined BTMA.[16] These results indicate that the arsonium cation **1** possesses sufficiently high alkali resistance.

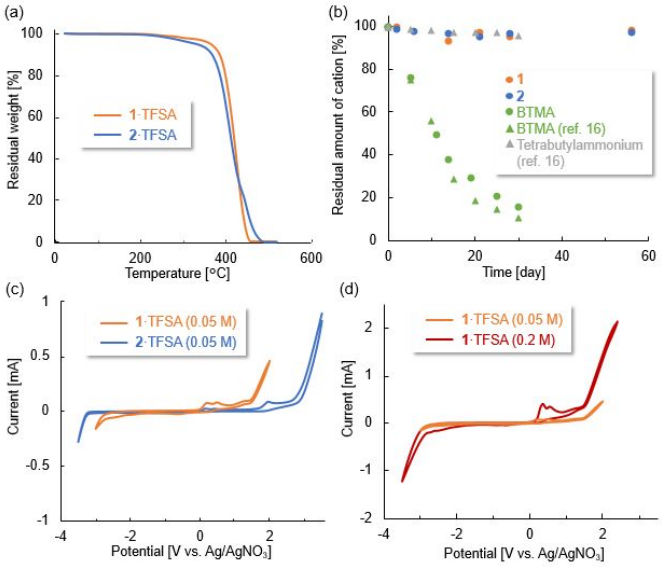


Fig. 4 (a) TGA thermograms (under N_2, 10 °C/min) of **1**·TFSA and **2**·TFSA. (b) Residual amounts of **1**, **2**, BTMA, and tetrabutylammonium detected by ^{1}H-NMR spectroscopy (1 M KOH in CD_3OH/CH_3OH (9/1), heated at 80 °C).[16] (c, d) Cyclic voltammograms (in MeCN, scan rate: 100 mV/s) of **1**·TFSA ((c) 0.05 M and (d) 0.05 and 0.2 M) and **2**·TFSA ((c) 0.05 M).

Finally, the electrochemical windows of **1**·TFSA and **2**·TFSA were evaluated using cyclic voltammetry (CV) measurements. Acetonitrile (MeCN) solutions (0.05 M) of **1**·TFSA and **2**·TFSA were prepared separately, and CV measurements (Figure 4c) were conducted under the same conditions as previous studies (100 mV/s, Ar atmosphere).[7] An irreversible redox peak for **1**·TFSA was observed near 0.5 V (vs Ag/Ag^+), whereas for **2**·TFSA, it appeared near 2.0 V. To confirm the origin of the peak near 0.5 V in the CV curve of **1**·TFSA, a 0.2 M MeCN solution of **1**·TFSA was also subjected to CV measurement (Figure 4d). The current near 0.5 V increased compared to that of the 0.05 M solution, indicating that the peak at 0.5 V is associated with the oxidation of **1**·TFSA. The CV study suggests that the arsonium-containing IL is more sensitive to electrochemical oxidation than its phosphonium analog. May et al. proposed that the lower electronegativity of As contributes to a narrower electrochemical window.[7] The present results appear to align with those reported in the literature.

In this study, we synthesized a novel arsonium-containing IL, **1**·TFSA, and compared its properties with those of its phosphonium counterpart, **2**·TFSA. We found that **1**·TFSA exhibited a lower glass transition temperature and viscosity

than **2**·TFSA, attributed to its relatively flexible structure. This flexibility also contributed to the higher ionic conductivity observed for **1**·TFSA compared to that of **2**·TFSA. Despite the narrower electrochemical window of **1**·TFSA, its thermal and alkali resistance were comparable to those of **2**·TFSA. These findings suggest that arsonium cations are promising candidates as high-performance ILs. Furthermore, our results demonstrate the efficacy of employing heavy elements as cation centers to broaden the chemical scope of IL research. We are currently expanding our investigation to a series of arsonium-containing ILs using safe and efficient synthetic protocols.

Author contributions

R. Inaba: Synthesis, structural analysis, data curation, writing – original draft; T. Imai: alkali resistance evaluation, data curation, writing – original draft; S. Kitajima: evaluation of electrochemical stability, data curation, writing – original draft; H. Kasai: evaluation of electrochemical stability, data curation, writing – review and editing; K. Oka evaluation of electrochemical stability, data curation, writing – review and editing; R. Hifumi: alkali resistance evaluation, data curation, writing – review and editing; I. Tomita: alkali resistance evaluation, data curation, writing – review and editing; M. Yoshizawa-Fujita: evaluation of IL properties, data curation, writing – review and editing; K. Naka: conceptualization, investigation, writing – review and editing, supervision; H. Imoto: conceptualization, investigation, writing – original draft, writing – review and editing, funding acquisition project administration, supervision.

Data Availability Statement

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials.

Conflicts of interest

There are no conflicts to declare.

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Data Availability Statement
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The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials.

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