Trialkylsulfonium Fluorohydrogenate Giving the Highest Conductivity in Room Temperature Ionic Liquids

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Synthesis and characterization of tertiary sulfonium fluorohydrogenate ionic liquids (trimethylsulfonium (S_{111}^+), dimethylethylsulfonium (S_{112}^+), diethylmethylsulfonium (S_{122}^+), and triethylsulfonium (S_{222}^+)) are reported. The vacuum–stable HF composition in the anion differs, depending on the cationic structure ($S_{111}(FH)_{1.9}F$, $S_{112}(FH)_{2.0}F$, $S_{122}(FH)_{2.0}F$, and $S_{222}(FH)_{2.0}F$). The highest ionic conductivity at 298 K is observed for $S_{111}(FH)_{1.9}F$ (131 mS cm^{-1}) and ionic conductivity decreases in the order of $S_{111}(FH)_{1.9}F$ > $S_{112}(FH)_{2.0}F$ (111 mS cm^{-1}) > $S_{122}(FH)_{2.0}F$ (91 mS cm^{-1}) > $S_{222}(FH)_{2.0}F$ (83 mS cm^{-1}). Electrochemical windows of $S_{111}(FH)_{1.9}F$, $S_{112}(FH)_{2.0}F$, $S_{122}(FH)_{2.0}F$, and $S_{222}(FH)_{2.0}F$ are 4.09, 4.20, 4.37 and 4.93 V, respectively.
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Ionic liquids (ILs) composed of alkylammonium cations and fluoroanions have been widely studied.[1] Unique properties including non–flammability, negligible vapor pressure, wide liquid temperature range, high thermal and electrochemical stability are often found for ILs and have attracted many interests of researchers in the fields of electrochemistry and organic chemistry.[2–4] Applications of ILs as safe electrolytes in electrochemical devices such as lithium batteries, solar cells, fuel cells, double–layer capacitor, and plating have been investigated to replace presently used aqueous and organic solvents.[4–8] Imidazolium cation is an aromatic cation and often gives a salt with lower melting point and higher ionic conductivity than those of nonaromatic cation–based salts (e.g. pyrrolidinium, tetraalkylammonium, piperidinium, and phosphonium), whereas their electrochemical stability is sometimes insufficient especially against reduction because of the high acidity of hydrogen at the C2–carbon of imidazolium ring.[9,10] According to previous reports, small aliphatic trialkylsulfonium–based ILs have relatively low melting points and high ionic conductivity comparable to imidazolium–based ILs, (cf. T_m = 218 K and σ = 15.7 mS cm^{-1} at 298 K for $S_{122}N(SO_2F)_2$,[11] T_m = 250 K and σ = 5.8 mS cm^{-1} at 298 K for $S_{122}N(SO_2CF_3)_2$,[12] no melting point and σ = 26.8 mS cm^{-1} at 298 K for $S_{122}N(CN)_2$,[13] T_m = 260 K and σ = 16.5 mS cm^{-1} at 298 K for EMImN(SO_2F)_2,[14] T_m = 257 K and σ = 8.4 mS cm^{-1} at 298 K for EMImN(SO_2CF_3)_2,[14] and T_m = 261 K and 27 mS cm^{-1} at 293 K for EMImN(CN)_2,[15] where EMIm, T_m and σ denote 1-ethyl-3-methylimidazolium, melting point, and ionic conductivity, respectively).

Fluorohydrogenate (($FH)_nF^-$) ILs based on aromatic and nonaromatic cations have been prepared and characterized by spectroscopic, physicochemical, and electrochemical methods.[16–19] These ILs are nonvolatile at room temperature when they are thoroughly evacuated at room temperature and exhibit high ionic conductivities and low viscosities compared to other ILs based on popular anions (e.g. EMIm(FH)_{2.3}F possessing T_m = 208 K, σ = 100 mS cm^{-1} and η = 4.9 cP at 298 K), where η denotes viscosity.[16]

Considering the properties of the previously reported ILs of fluorohydrogenate anion or alkylsulfonium cation, combination of these two species is interesting to obtain low melting point and high ionic conductivity. This study reports synthesis and properties of ILs composed of a fluorohydrogenate anion ($(FH)_2F^-$) and a trialkylsulfonium (S_{111}, S_{112}, S_{122}, or S_{222}) cation. Effects of cationic structure and alkyl chain length on physicochemical properties of the ILs are discussed.

Experimental

Trimethylsulfonium bromide (Tokyo Chemical Industry Co., Ltd., < 98%) was recrystallized from acetonitrile by adding ethyl acetate and dried at 353 K under vacuum for one day. The three iodide salts,

$S_{112}I$, $S_{122}I$, and $S_{222}I$, were synthesized as previously reported and washed several times with ethyl acetate.[20] Purification of $S_{112}I$ and $S_{222}I$ were performed by recrystallization from acetonitrile by adding ethyl acetate, followed by drying at 353 K. The salt, $S_{122}I$, was washed with ethyl acetate after removal of acetonitrile under vacuum, followed by drying at 298 K. All the trialkylsulfonium halides were obtained as white powdery samples. Trialkylsulfonium fluorohydrogenate ILs were prepared by the reaction of large excess of anhydrous HF and trialkylsulfonium halides ($S_{111}Br$ (10.28 g, 65.5 mmol), $S_{112}I$ (12.90 g, 59.1 mmol), $S_{122}I$ (7.78 g, 33.5 mmol), and $S_{222}I$ (8.16 g, 33.1 mmol)) as previously described.[16–19] The HF contents in the four ILs were checked by weight change and neutralization titration using an aqueous NaOH solution (Aldrich, 0.200 N); $S_{111}(FH)_{1.9}F$ (8.84 g, 65.9 mmol), $S_{112}(FH)_{2.0}F$ (8.80 g, 58.7 mmol), $S_{122}(FH)_{2.0}F$ (5.47 g, 33.4 mmol), and $S_{222}(FH)_{2.0}F$ (5.90 g, 33.1 mmol). Testing for the presence of residual Br$^-$ or I$^-$ with an aqueous AgNO_3 solution gave no precipitation of silver halides. Infrared spectroscopy (FTS–165, BIO–RAD Laboratories) identified trialkylsulfonium cations for $S_{111}Br$, $S_{112}I$, $S_{122}I$, and $S_{222}I$, and trialkylsulfonium cations and fluorohydrogenate anions for $S_{111}(FH)_{1.9}F$, $S_{112}(FH)_{2.0}F$, $S_{122}(FH)_{2.0}F$ and $S_{222}(FH)_{2.0}F$. Karl–Fischer measurements (MKC–510N, Kyoto Electronics Mfg. Co.) showed water contents of the fluorohydrogenate ILs around 100 ppm. Thermogravimetric analysis (Shimadzu DTG–60H) was performed on the sample in a nickel cell under argon gas flow using the Shimadzu DTG–60H. The scanning rate was 10 K min^{-1}. Differential scanning calorimetric analysis was performed on the sample in a stainless steel seal cell under argon gas flow using the Shimadzu DSC–60. The scanning rate was 5 K min^{-1}. Density, ionic conductivity, viscosity, and electrochemical windows were measured as previously described.[17]

Results and Discussion

When the sample was evacuated at room temperature, the vacuum-stable HF content (n for $(FH)_nF^-$) in fluorohydrogenate ILs was 2.3 for most alkylammonium and phosphonium cations according to previous studies.[16–19] There are some exceptions such as the salts of 1-alkyl-3-methylimidazolium cations with a long alkyl chain.[21] The present study showed that the n value for trialkylsulfonium fluorohydrogenate ILs is below 2.3 ($S_{111}(FH)_{1.9}F$, $S_{112}(FH)_{2.0}F$, $S_{122}(FH)_{2.0}F$, and $S_{222}(FH)_{2.0}F$). These results show fluorohydrogenate anions which work as a Lewis base decrease their vacuum-stable HF composition to become a smaller anion with stronger Lewis basicity so that the small sulfonium countercation is stabilized. Alkyl chain length also seems to influence the n value since the decrease in alkyl chain length slightly decreases the HF content (compare the case of $S_{111}(FH)_{1.9}F$ to the other cases).

Physicochemical properties of $S_{111}(FH)_{1.9}F$, $S_{112}(FH)_{2.0}F$, $S_{122}(FH)_{2.0}F$, and $S_{222}(FH)_{2.0}F$ are summarized in Table I. Thermogravimetric curves of the present trialkylsulfonium fluorohydrogenate

Table I. Physicochemical properties of trialkylsulfonium fluorohydrogenate ILs.[a]

	Fw	T_m/K	T_d/K	ρ/g cm^{-3}	η/cP	σ/mS cm^{-1}	λ/S cm^2 mol^{-1}	/ V vs Fc$^+$/Fc E_{ca}	E_{an}
$S_{111}(FH)_{1.9}F$	134	242	447	1.18	7.8	131	14.9	−1.64	2.45
$S_{112}(FH)_{2.0}F$	150	227	437	1.14	8.2	111	14.6	−1.73	2.47
$S_{122}(FH)_{2.0}F$	164	–	431	1.11	8.9	91	13.4	−1.86	2.51
$S_{222}(FH)_{2.0}F$	178	217	420	1.09	8.3	83	13.6	−2.10	2.83

[a] Fw: Formula weight, T_m: melting point, T_d: decomposition temperature (onset), ρ: density, η; viscosity, σ; conductivity, λ; molar conductivity, E_{ca}; cathode limit potential, E_{an}; .anode limit potential.

ILs are shown in Figure 1. Thermal decomposition temperatures based on the onset of large weight loss for $S_{111}(FH)_{1.9}F$, $S_{112}(FH)_{2.0}F$, $S_{122}(FH)_{2.0}F$, and $S_{222}(FH)_{2.0}F$ are 447, 437, 431, and 420 K, respectively. Gradual weight loss below the decomposition temperature is caused by reversible HF dissociation from $(FH)_nF^-$. Decomposition products are considered to be fluoroalkane and dialkylsulfide. This decomposition reaction results from the attack of $(FH)_nF^-$ as an nucleophile to the α–carbon in trialkylsulfonium cations, leaving dialkylsulfide as an elimination group.[22] Decomposition temperature of the present alkylsulfonium fluorohydrogenate salts tends to increase with decrease in alkyl chain length and are lower than those for previously reported alkylammonium fluorohydrogenate ILs, (e.g. around 540 K for EMIm(FH)$_{2.3}$F and 500 K for EMPyr(FH)$_{2.3}$F)[16,17,23] because of the weaker C–S bond than C–N bond.[24] Differential scanning calorimetry showed melting points of $S_{111}(FH)_{1.9}F$, $S_{112}(FH)_{2.0}F$, and $S_{222}(FH)_{2.0}F$ are 242, 227, and 217 K, respectively, whereas $S_{122}(FH)_{2.0}F$ does not show a melting point above 140 K.

Arrhenius plots of ionic conductivity and viscosity for $S_{111}(FH)_{1.9}F$, $S_{112}(FH)_{2.0}F$, $S_{122}(FH)_{2.0}F$, and $S_{222}(FH)_{2.0}F$ are shown in Figure 2. Viscosity at 298 K increases in the order of $S_{111}(FH)_{1.9}F$ (7.8 cP) < $S_{112}(FH)_{2.0}F$ (8.2 cP) < $S_{222}(FH)_{2.0}F$ (8.3 cP) < $S_{122}(FH)_{2.0}F$ (8.9 cP). There are two factors that can influence viscosity of ILs except columbic interactions; van der Waals interactions and conformational degrees of freedom.[11] Increase of the former increases viscosity, whereas increase of the latter decreases viscosity. In the present cases, the viscosity of $S_{222}(FH)_2F$ is lower than that of $S_{122}(FH)_2F$. Similar behavior was reported in the cases of $S_{222}N(SO_2F)_2$ (20 cP) and $S_{122}N(SO_2F)_2$ (24 cP).[11] Such behavior arises from the larger effect of conformational degrees of freedom than that of van der Waals interaction. When compared to previously known fluorohydrogenate ILs, viscosities of trialkylsulfonium fluorohydrogenate ILs are higher than those of EMIm(FH)$_{2.3}$F (4.9 cP) and lower than those of EMPyr(FH)$_{2.3}$F (N-ethyl-N-methylpyrrolidinium fluorohydrogenate, 11.5 cP).[17,23]

The highest ionic conductivity in the presently known ILs is observed for $S_{111}(FH)_{1.9}F$ (131 mS cm^{-1}) and ionic conductivity at 298 K decreases in the order of $S_{111}(FH)_{1.9}F$ > $S_{112}(FH)_{2.0}F$ (111 mS cm^{-1}) > $S_{122}(FH)_{2.0}F$ (91 mS cm^{-1}) > $S_{222}(FH)_{2.0}F$ (83 mS cm^{-1}) with increase in the size of cation. Although the high ionic conductivity of fluorohydrogenate ILs is derived from the exchanging HF unit working as a dielectric spacer,[25] the values for the present trialkylsulfonium fluorohydrogenate ILs are particularly high. Since the viscosities of trialkylsulfonium fluorohydrogenate ILs are not the lowest in the known fluorohydrogenate ILs, their high ionic conductivities arise from the large number of ions per volume because of the small size of the cations.

Linear sweep voltammograms of a glassy carbon electrode in trialkylsulfonium fluorohydrogenate ILs are shown in Figure 3. The anode and cathode limit potentials are determined when the absolute value of the current density exceeds 0.5 mA cm^{-2} at a scan rate of 10 mV s^{-1}. The cathode limit potentials range between −1.64 ~ −2.10 V and the anode limit potentials between +2.45 ~ +2.83 V. Electrochemical windows of $S_{111}(FH)_{1.9}F$, $S_{112}(FH)_{2.0}F$, $S_{122}(FH)_{2.0}F$, and $S_{222}(FH)_{2.0}F$ are 4.09, 4.20, 4.37, and 4.93 V, respectively. Replacement of methyl group with ethyl group slightly increases the electrochemical window as shown for other fluorohydrogenate ILs in previous reports.[16] Trialkylsulfonium cations in $S_{122}N(SO_2F)_2$ and $S_{222}N(SO_2F)_2$ are reduced around −2.18 V vs. Fc$^+$/Fc, whereas $(FH)_nF^-$ in fluorohydrogenate ILs are reduced at −1.0 to −2.9 V on a glassy carbon electrode.[11,17–20,23] Consequently, the cathode reaction of trialkylsulfonium fluorohydrogenate ILs probably involves reduction of both or either the cation and anion.[17,18,23] The reaction at the anode limit is considered to be a decomposition of the cation including its fluorination by the anion.[17,18,23] Electrochemical windows of sulfonium fluorohydrogenate ILs are larger than alkylimidazolium fluorohydrogenate ILs (about 3 V) and smaller than alkylpyrrolidinium or alkylphosphonium fluorohydrogenate ILs (4.6 ~ 6.0 V).[17,18,23]
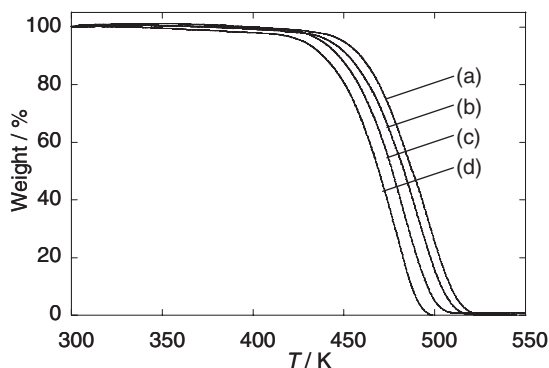
Figure 1. Thermogravimetric curves of (a) $S_{111}(FH)_{1.9}F$, (b) $S_{112}(FH)_{2.0}F$, (c) $S_{122}(FH)_{2.0}F$, and $S_{222}(FH)_{2.0}F$.
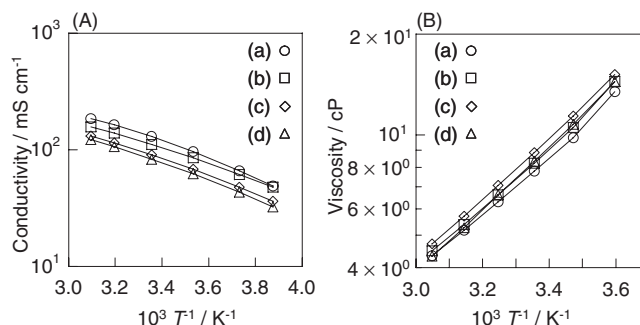
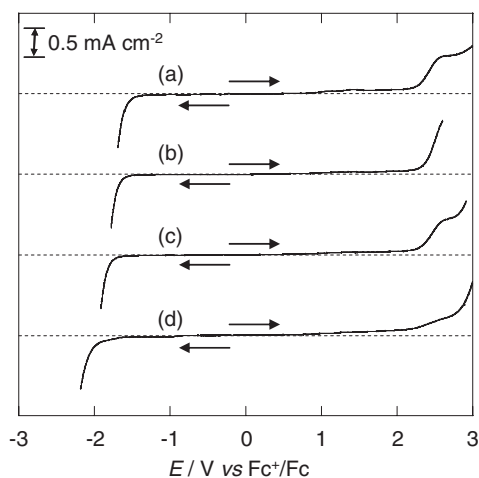**Figure 2.** Arrhenius plots of (A) conductivity and (B) viscosity of (a) $S_{111}(FH)_{1.9}F$, (b) $S_{112}(FH)_{2.0}F$, (c) $S_{122}(FH)_{2.0}F$, and (d) $S_{222}(FH)_{2.0}F$.

Figure 3. Linear sweep voltammograms of (a) $S_{111}(FH)_{1.9}F$, (b) $S_{112}(FH)_{2.0}F$, (c) $S_{122}(FH)_{2.0}F$ and (d) $S_{222}(FH)_{2.0}F$ on a glassy carbon electrode. Potential (E) was referenced to the ferrocenium (Fc^+)/ferrocene (Fc) redox couple.

Conclusions

Trialkylsulfonium fluorohydrogenate ILs were synthesized and their physicochemical properties were investigated. These ILs have high ionic conductivities and the highest value of 131 mS cm^{-1} in the known room temperature ILs was observed for $S_{111}(FH)_{1.9}F$ at 298 K. Sufficiently large electrochemical windows and high thermal stabilities of them are advantageous for electrolytes in electrochemical devices.

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