



TITLE:

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Mixed Anions, (FH)F, BF, and N(SOCF)

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**Physical and electrochemical properties of
1-ethyl-3-methylimidazolium ionic liquids of mixed anions, $(\text{FH})_n\text{F}^-$,
 BF_4^- , and $\text{N}(\text{SO}_2\text{CF}_3)_2^-$**

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Abstract

Physical and electrochemical properties of 1-ethyl-3-methylimidazolium ionic liquids of mixed anions, $(\text{FH})_{2.3}\text{F}^-$, BF_4^- , and $\text{N}(\text{SO}_2\text{CF}_3)_2^-$, have been investigated. Molar volume shows almost linear behavior, whereas molar conductivity is decreased by mixing for the systems involving $(\text{FH})_{2.3}\text{F}^-$ due to the enhancement of ion association in spite of the decrease in viscosity. The currents at the anode and cathode limits in the cyclic voltammogram of $\text{EMIm}(\text{FH})_{2.3}\text{F}$ decreases with decrease in the molar ratio of $(\text{FH})_n\text{F}^-$, suggesting the involvement of $(\text{FH})_n\text{F}^-$ for both electrode reactions. Electrochemical stability of the BF_4 -TFSA mixture is unchanged by mixing.

Introduction

Room temperature ionic liquids (RTILs) are now widely studied as potential electrolytes for energy storage devices and plating, as well as media for extraction and separation processes, organic syntheses, and catalysis.¹⁻⁴⁾ Most alkylimidazolium based RTILs are versatile and most widely used due to their favorable characteristics such as nonvolatility, wide liquid-phase temperature range, nonflammability, high ionic conductivity, low viscosity, and high electrochemical stability. Physical properties of RTILs are changed by the combination of cationic and anionic structures. The tetrafluoroborate (BF_4^-) and bis(trifluoromethylsulfonyl)amide ($\text{N}(\text{SO}_2\text{CF}_3)_2^-$ or TFSA^-) anions are most widely used for syntheses of RTILs owing to their abilities to form low melting salts with high conductivity.⁵⁻⁷⁾ Fluorohydrogenate anion ($(\text{FH})_n\text{F}^-$) also forms RTILs combined with a variety of quaternary ammonium cations, exhibiting remarkably high ionic conductivities.^{8,9)} The vacuum-stable HF composition, n , for $(\text{FH})_n\text{F}^-$ in the fluorohydrogenate RTILs depends on the temperature, giving $n = 2.3$ at 25°C regardless of the cationic structure.¹⁰⁾ The anions of the vacuum stable fluorohydrogenate RTILs at 25°C are regarded as a mixture of $(\text{FH})_2\text{F}^-$ and $(\text{FH})_3\text{F}^-$.

In previous reports, mixing of RTILs was examined for several systems to improve the physical or chemical properties as electrolytes.¹¹⁾ This communication reports the physical and electrochemical properties of 1-ethyl-3-methylimidazolium (EMIm) ionic liquids of mixed anions, $(\text{FH})_{2.3}\text{F}^-$, BF_4^- , and $\text{N}(\text{SO}_2\text{CF}_3)_2^-$.

Experimental

All the nonvolatile materials were handled in the dry Ar atmosphere of a glovebox. Room temperature ionic liquids, $\text{EMIm}(\text{FH})_{2.3}\text{F}^-$ ⁸⁾ and EMImTFSA ,⁶⁾ were prepared

according to the literature method. The tetrafluoroborate salt, EMImBF₄, was used as purchased (Kanto Kagaku Co., Inc.). Physical and electrochemical properties were measured as previously reported.⁹⁾

Results and discussion

Physical properties of neat EMIm(FH)_{2,3}F, EMImBF₄, and EMImTFSI are listed in Table 1. The values obtained for EMImBF₄ and EMImTFSI agree well with those previously reported.⁵⁻⁷⁾ Physical properties of EMIm ionic liquids of the mixed anions are shown in Fig. 1.

3. 1 Density and molar volume

Density of the (FH)_{2,3}F-BF₄ system shows a linear relationship with $x((\text{FH})_{2,3}\text{F})$, whereas those of the other two systems involving TFSI⁻ show convex curvatures. Since the formula weight of EMImTFSI (391.3) is significantly larger than those of EMIm(FH)_{2,3}F (176.2) and EMImBF₄ (198.0), the contribution of EMImTFSI to the weight in the mixture is larger than the other salts, resulting in the increase in the apparent density with respect to the molar ratio. The almost linear relationship is obtained in molar volume for all the mixtures, where the deviation observed for the (FH)_{2,3}F-BF₄ system is within error. This observation indicates that there is little volume change by mixing these ionic liquids, in other words, the volume which each ion occupies in the neat ionic liquid is preserved in the mixture.

3. 2 Conductivity, molar volume, and viscosity

In all the three systems, both conductivities and molar conductivities exhibit concave curvatures by mixing the anions. The largest drop of the conductivity was observed for the TFSI-(FH)_{2,3}F system, where the conductivity of the 50:50 mixture is only 42% of

the estimated value from the neat RTILs. According to the previous study, the high conductivity for fluorohydrogenate RTILs is explained by their low viscosity, leading to the large diffusion coefficients of both the cation and anion compared to the ions in other RTILs although the anion moves faster than the cation.¹²⁾ The decrease of the conductivity by mixing BF_4^- and TFSA^- is explained by the increase in viscosity as the viscosity shows the corresponding convex curvature. In the cases of the other two systems involving $(\text{FH})_n\text{F}^-$, the association of the ions, that is, formation of ion pair or aggregate, is significantly enhanced by mixing the anions, since the viscosity shows concave curvatures violating Walden's rule.^{7,8,12)} It was reported that the molar conductivity for the EMImOSO₂CF₃-EMImTFSA system is enhanced by mixing the anions, showing a remarkably convex curvature,¹³⁾ whereas such behavior was not observed for the present cases.

3.3 Thermal properties

Phase behavior of the mixed ionic liquids was studied by differential scanning calorimetry (DSC) in a Ni cell under a dry N₂ atmosphere at the scan rate of 10 K min⁻¹. Both EMIm(FH)_{2,3}F and EMImBF₄ are super-cooled to form a glass phase in the cooling process, followed by glass transition, crystallization, and melting in the heating process.^{7,8)} The (FH)_{2,3}F-BF₄ mixture does not show any exo- or endothermic peak for the entire composition range, suggesting the stable super-cooled state. Although EMImTFSA showed an exothermic peak of crystallization in the cooling process followed by the melting in the heating system, the BF₄-TFSA mixture does not show any exo- or endothermic peak for the entire composition range. These observations suggest that BF_4^- facilitates the formation of the super-cooled state and prevent the system from crystallizing. As shown in Fig. 2, the (FH)_{2,3}F-TFSA mixture show both

glass transition and melting in any composition. Since the mixture with a high ratio of EMIm(FH)_{2,3}F did not show a clear peak, the slow scan rate (2 K min⁻¹) was applied. The glass transition temperature gradually decreases with increase in the molar ratio of (FH)_{2,3}F⁻ in the range of $0 \leq x((\text{FH})_{2,3}\text{F}) \leq 0.6$ and becomes almost constant in the range of $0.6 \leq x((\text{FH})_{2,3}\text{F}) \leq 1.0$. The eutectic point of EMIm(FH)_{2,3}F-EMImTFSI was determined to be 203 K at the composition of EMIm(FH)_{2,3}F : EMImTFSI = 90 : 10.

Thermal decomposition was examined by thermogravimetric analysis (TGA) in a Ni cell under a dry N₂ atmosphere at the scan rate of 10 K min⁻¹. The neat EMIm(FH)_{2,3}F slowly loses HF at elevated temperatures and decomposes around 550 K, whereas EMImBF₄ and EMImTFSI have higher thermal stabilities up to about 650 K and 700 K, respectively. Thermogravimetric analysis revealed that thermal decomposition of the component in the (FH)_{2,3}F-BF₄ or TFSI-(FH)_{2,3}F ionic liquid mixture occurs sequentially, giving two stages in the curve at the temperature corresponding to the decomposition of EMIm(FH)_{2,3}F and that of EMImBF₄ or EMImTFSI. The BF₄-TFSI system showed a gradual weight loss at and above the decomposition temperature of EMImBF₄.

3. 4 Electrochemical stability

Electrochemical stability was examined by cyclic voltammetry using a glassy carbon electrode at the scan rate of 5 mV s⁻¹. Neat EMImBF₄ or EMImTFSI shows a similar electrochemical stability with the cathode limit of -2.5 V vs. Fc⁺/Fc and anode limit of +2.1 V vs. Fc⁺/Fc. Mixing of these two RTILs do not change the electrochemical stability in any ratio. Cyclic voltammogram of EMIm(FH)_{2,3}F-EMImBF₄ is shown in Fig. 3. The anode limit of neat EMIm(FH)_{2,3}F is +1 V vs. Fc⁺/Fc, which is probably ascribed to the oxidation of the cation accompanied by fluorination according to the

previous study for neat liquids.⁸⁾ The reaction of the cathode limit is considered to be the reduction of $(\text{HF})_n\text{F}^-$ to give H_2 evolution. Although the potential of H_2 evolution depends on the electrode material, it is -1.8 V vs. Fc^+/Fc on a glassy carbon electrode. In the mixed RTILs, the currents at the anode and cathode limits observed for $\text{EMIm}(\text{FH})_{2,3}\text{F}$ are decreased with decrease in molar ratio of $(\text{FH})_n\text{F}^-$, suggesting the involvement of $(\text{FH})_n\text{F}^-$ in both the limits. The cyclic voltammogram of the $\text{EMIm}(\text{FH})_{2,3}\text{F}$ - EMImTFSI mixture is essentially the same as that of $\text{EMIm}(\text{FH})_{2,3}\text{F}$ - EMImBF_4 , although the peak current density is slightly different.

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Table 1 Physical properties^a of neat EMIm(FH)_{2.3}F, EMImBF₄, and EMImTFSA

	T_m	T_g	ρ	$M.V.$	σ	Λ	η
	/ K	/ K	/ g cm ⁻³	/ cm ³ mol ⁻¹	/ mS cm ⁻¹	/ S cm ² mol ⁻¹	/ cP
EMIm(FH) _{2.3} F ^b	208	148	1.13	155.9	100	15.8	4.9
EMImBF ₄	288	194	1.27	155.9	13.0	2.02	34
EMImTFSA	254	-	1.51	259.3	7.6	1.98	31

^a T_m : melting point, T_g : glass transition, ρ : density at 298 K, $M.V.$: molar volume at 298 K, σ : conductivity at 298

K, Λ : molar conductivity at 298 K, η : viscosity at 298 K. ^b Ref. 8.

Figure captions

Fig. 1 Density (ρ), molar volume ($M.V.$), conductivity (σ), molar conductivity (Λ), and viscosity (η) at 298 K for EMIm ionic liquids of the mixed anions, (FH)_{2.3}F-BF₄, BF₄-TFSA, and TFSA-(FH)_{2.3}F.

Fig. 2 Phase diagram of the EMImTFSA-EMIm(FH)_{2.3}F system.

Fig. 3 Cyclic voltammograms of a glassy carbon electrode in the EMIm(FH)_{2.3}F-EMImBF₄ system. C.E.: glassy carbon, scan rate: 5 mV s⁻¹. The potential was referenced to the ferrocenium/ferrocene (Fc⁺/Fc) redox couple in each ionic liquid.

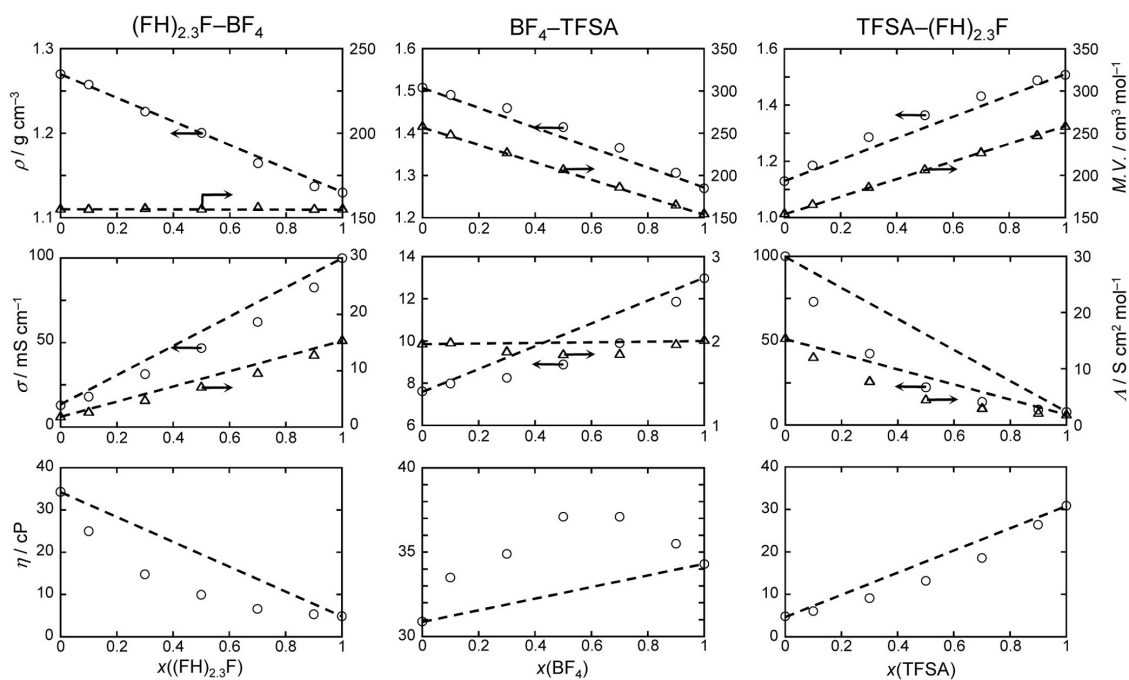


Fig. 1 Density (ρ), molar volume ($M.V.$), conductivity (σ), molar conductivity (Λ), and viscosity (η) at 298 K for EMIm ionic liquids of the mixed anions, $(\text{FH})_{2.3}\text{F}-\text{BF}_4$, BF_4-TFSA , and $\text{TFSA}-\text{FH}_{2.3}\text{F}$.

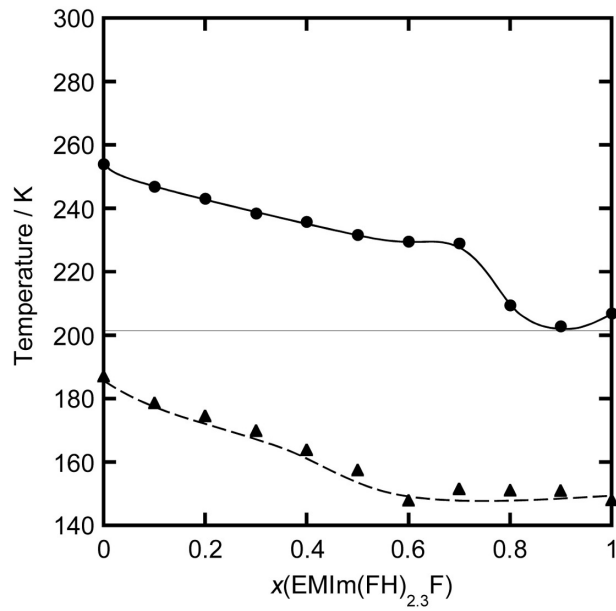


Fig. 2 Phase diagram of the EMIImTFSA-EMIIm(FH)_{2.3}F system.

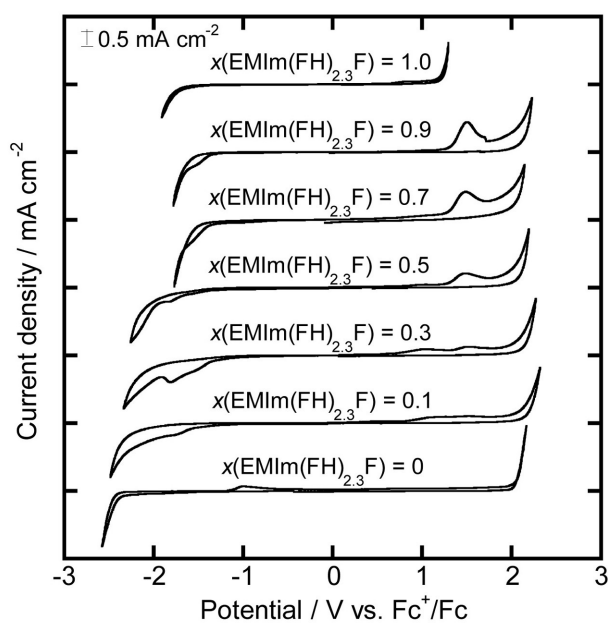


Fig. 3 Cyclic voltammograms of a glassy carbon electrode in the EMIm(FH)_{2.3}F-EMImBF₄ system. C.E.: glassy carbon, scan rate: 5 mV s⁻¹. The potential was referenced to the ferrocenium/ferrocene (Fc⁺/Fc) redox couple in each ionic liquid.