Ferrocenium ionic liquids containing 3,4,5-tri(dodecyloxy)benzene sulfonate and bis(2-ethylhexyl)sulfosuccinate (AOT) anions

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(Citation)
Journal of Organometallic Chemistry,725:34-36

(Issue Date)
2013-02-01

(Resource Type)
journal article

(Version)
Accepted Manuscript

(URL)
https://hdl.handle.net/20.500.14094/90001815

Note

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Keywords: Ferrocenium salts; Ionic liquid; 3,4,5-tri(dodecyloxy)benzene sulfonate; bis(2-ethylhexyl)sulfosuccinate

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Abstract

The salts of the dodecyloctaferrocenium cation (**1**) and decamethylferrocenium cation (**2**) with the mesogenic anions of 3,4,5-tri(dodecyloxy)benzene sulfonate [$(C_{12}H_{25}O)_3C_6H_2SO_3$] and bis(2-ethylhexyl)sulfosuccinate (AOT) were prepared. The resulting materials, [**1**][$(C_{12}H_{25}O)_3C_6H_2SO_3$], [**2**][$(C_{12}H_{25}O)_3C_6H_2SO_3$], and [**1**][AOT] were ionic liquids exhibiting glass transitions at –53, –41, and –51°C, respectively, whereas [**2**][AOT] was a solid with a high melting point (T_m = 122°C). The melting points and glass transition temperatures correlated with the flexibility of the substituents and the size of the constituent molecules. None of the salts exhibited liquid crystal phases.

1. Introduction

Ionic liquids are salts with melting points below 100°C [1–3], and they have attracted considerable attention in several fields of research, including electrochemistry and green chemistry [4–6]. Although most ionic liquids are composed of onium cations, we have recently developed metallocenium ionic liquids [7–12], which are the salts of a variety of different metallocenium cations and the Tf_2N anion (Tf_2N = bis(trifluoromethane)sulfonylamide). These ionic liquids exhibit interesting magnetic properties as a consequence of the magnetic anisotropy of the ferrocenium cation [10,11]. Although imidazolium ionic liquids with neutral ferrocenyl substituents have been reported in the literature [13–15], they are diamagnetic.

In this paper, we report the synthesis and thermal properties of salts composed of the ferrocene-based cations dodecyloctamethylferrocene (**1**), decamethylferrocene (**2**), and formyloctamethylferrocene (**3**) (Fig. 1a), and the anions 3,4,5-tri(dodecyloxy)benzene sulfonate ($(C_{12}H_{25}O)_3C_6H_2SO_3$) and bis(2-ethylhexyl)sulfosuccinate (AOT) (Fig. 1b). These anions can act as mesogens [16], and liquid-crystal salts containing $(C_{12}H_{25}O)_3C_6H_2SO_3$ [17,18] and AOT [19–21] have been reported in the literature. The 1-butyl-3-methylimidazolium salt of AOT is an ionic liquid with a melting point of 25°C [22]. The polymethylated ferrocenium cations are stable in air, whereas ferrocenium cations are generally sensitive to these conditions [10,23]. In the current study, we found that [**1**][$(C_{12}H_{25}O)_3C_6H_2SO_3$], [**2**][$(C_{12}H_{25}O)_3C_6H_2SO_3$], and [**1**][AOT] were ionic liquids, whereas [**2**][AOT] was a solid with a high melting point. None of the salts exhibited liquid crystal phases.

2. Results and discussion

The ferrocenium salts with mesogenic anions were prepared by anion exchange from the corresponding nitrate salts. The salts [**1**][$(C_{12}H_{25}O)_3C_6H_2SO_3$], [**2**][$(C_{12}H_{25}O)_3C_6H_2SO_3$], and [**1**][AOT] were obtained as green liquids under ambient conditions, whereas [**2**][AOT] and [**3**][AOT] were isolated as green solids. The salts with the $(C_{12}H_{25}O)_3C_6H_2SO_3$ anion were soluble in several polar solvents, including ethanol, acetone, and dichloromethane, and insoluble in water and several non-polar solvents, including hexane and diethyl ether. The AOT salts were soluble in water and several organic solvents, such as ethanol, acetone, dichloromethane, hexane, and diethyl ether.

The glass transition temperatures (T_g) and melting points (T_m) of these salts, together with those of the Tf_2N salts [11,24] are listed in Table 1. These data were determined by differential scanning calorimetry (DSC). A comparison of the salts of **1** and **2** showed the effect of the alkyl chain in the cation. The liquids of [**1**][$(C_{12}H_{25}O)_3C_6H_2SO_3$] and [**2**][$(C_{12}H_{25}O)_3C_6H_2SO_3$] showed similar glass transition temperatures at –53 and –41°C, respectively, upon cooling, and exhibited no crystallization. However, the cation had a greater effect on the thermal behavior in the AOT salts. [**1**][AOT] was a liquid with a glass transition temperature of –51°C, whereas [**2**][AOT] was a solid with a melting point of 122.2°C (ΔS = 66.4 J mol^{-1} K^{-1}). The difference was even more pronounced for the Tf_2N salts, where the melting points of [**1**][Tf_2N] and [**2**][Tf_2N] were 26.2 and 343°C, respectively [11,24], with the latter being more than 200°C higher than the former. Therefore, the introduction of the long alkyl chain into the cation effectively decreased the melting points in the salts with smaller anions, with the size decreasing according to the order $(C_{12}H_{25}O)_3C_6H_2SO_3$ > AOT > Tf_2N. Furthermore, although the melting points and glass transition temperatures of [**1**][X] were not much affected by the anion, those in [**2**][X] decreased significantly according to the order X = Tf_2N > AOT > $(C_{12}H_{25}O)_3C_6H_2SO_3$. Both of these tendencies were consistent with the flexibility of the alkyl chains in the cations and anions as well as the molecule sizes. Namely, the melting points and the glass transition temperatures were lower for the larger ions because of the reduction of intermolecular Coulombic interactions, and they were lower for molecules with a larger number of methylene groups because of the increase in the entropy of the liquid phase. The effects were less pronounced when the counter ions were larger. The salt [**3**][AOT] decomposed at 110°C without melting.

These salts did not exhibit liquid-crystal phases, which may be attributed to the bulkiness of the cations. Most AOT salts that exhibit liquid-crystal phases are composed of small cations or divalent cations [19–21], which might increase the level of their intermolecular interactions. We also prepared the cobaltocenium salt of AOT, which contained a smaller cation, but no further investigation was carried out because the salt was deliquescent. We failed to isolate the carboxylate salt [**2**][$(C_{12}H_{25}O)_3C_6H_2CO_2$] because the salt was found to decompose during the anion exchange procedure.

In conclusion, ferrocenium ionic liquids with the mesogenic anions of 3,4,5-tri(dodecyloxy)benzene sulfonate and AOT have been prepared, and the effect of the anion has been investigated. The development of ferrocenium ionic liquid-crystals, together with an understanding of both the anisotropic magnetic response based on the ferrocenium cation [10] and the electric field response of the mesogens, remain interesting target for future research.

3. Experimental

The nitrate salts with **1–3** [11, 25] and sodium 3,4,5-tri(dodecyloxy)benzene sulfonate [18] were prepared according to methods previously published in the literature. Sodium bis(2-ethylhexyl)sulfosuccinate (NaAOT, purity 98%) was purchased from Sigma-Aldrich. Elemental analyses were carried out using a Yanaco MT5 analyzer. DSC measurements were performed using a TA Instrument Q100 differential scanning calorimeter over a temperature range of 90–430 K and a scan rate of 10 K min^{-1}.

The salt [**1**][$(C_{12}H_{25}O)_3C_6H_2SO_3$] was prepared according to the following procedure. A solution of sodium 3,4,5-tri(dodecyloxy)benzene sulfonate (25.0 mg, 0.06 mmol) in $CHCl_3$ was added in a dropwise manner to a solution of [**1**][NO_3] (11.3 mg, 0.03 mmol) in water and the resulting mixture was stirred for 10 min. The organic phase was then separated and washed carefully with water to avoid emulsification. This washing procedure was typically repeated 10 times at 30 min intervals, until the presence of sodium ions could no longer be detected by the flame coloration test. In the final cycle, the organic phase was separated, dried over magnesium sulfate, and evaporated to give the desired ionic liquid, which was dried under vacuum at 60°C overnight. The product salt [**1**][$(C_{12}H_{25}O)_3C_6H_2SO_3$] was obtained as a green liquid in 8.5% yield. Anal. Calcd (%) for $C_{72}H_{127}O_6FeS$ (1176.67): C, 73.49; H, 10.88; N; 0. Found: C, 73.32; H, 11.13; N, 0. [**2**][$(C_{12}H_{25}O)_3C_6H_2SO_3$] was prepared by the same method using [**2**][NO_3] (11.7 mg, 0.03 mmol) and sodium 3,4,5-tri(dodecyloxy)benzene sulfonate (25.0 mg, 0.06 mmol). A green liquid was obtained in 9.2% yield. Anal. Calcd (%) for $C_{62}H_{107}O_6FeS$ (1035.71): C, 71.85; H, 10.41; N, 0. Found: C, 71.39; H, 10.71; N, 0.

The salt [**1**][AOT] was prepared as described for [**1**][$(C_{12}H_{25}O)_3C_6H_2SO_3$] using [**1**][$NO_3$] (70.2 mg, 0.197 mmol) and NaAOT (44.6 mg, 0.217 mmol). A green solid was obtained in 67% yield. Anal. Calcd (%) for $C_{50}H_{87}O_7FeS$ (887.55): C, 67.62; H, 9.87; N, 0. Found: C, 67.31; H, 9.64; N, 0. The salt [**2**][AOT] was prepared by the same method using [**2**][NO_3] (69.8 mg, 0.197 mmol) and NaAOT (44.6 mg, 0.217 mmol). A green solid was obtained in 62% yield. Anal. Calcd (%) for $C_{40}H_{67}O_7FeS$ (747.40): C, 64.24; H, 9.03; N, 0. Found: C, 64.03; H, 8.93; N, 0. The salt [**3**][AOT] was prepared by the same method using [**3**][NO_3] (65.4 mg, 0.197 mmol) and NaAOT (44.6 mg, 0.217 mmol). A green solid was obtained in 59% yield. Anal. Calcd (%) for $C_{39}H_{63}O_8FeS$ (747.36): C, 62.64; H, 8.49; N, 0. Found: C, 62.33; H, 8.15; N, 0. This salt gradually decomposed to give black solids when allowed to stand for over a week in air at ambient temperature.

Acknowledgements

We would like to thank Y. Furuie (Kobe University) for the elemental analysis and M. Nakama (Crayonsoft Inc., Tokyo) for providing a Web-DB system. This work was financially supported by KAKENHI (No. 24350073) from the Japan Society for the Promotion of Science (JSPS).

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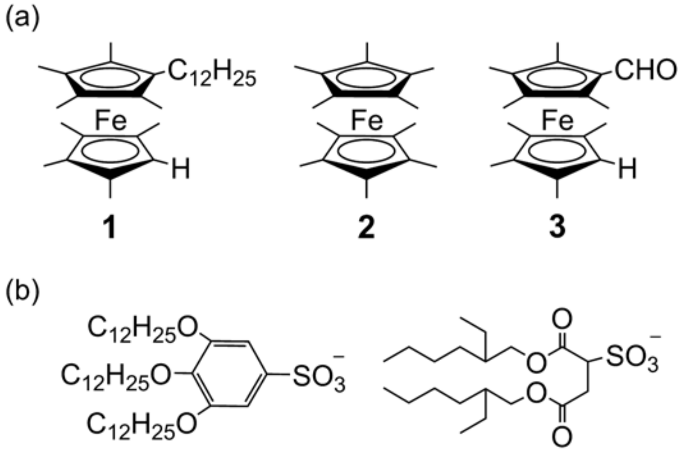


Fig. 1. Chemical structures of (a) ferrocene derivatives (**1**–**3**) used in this study and (b) 3,4,5-tri(dodecyloxy)benzene sulfonate (left) and AOT (right).

Table 1.

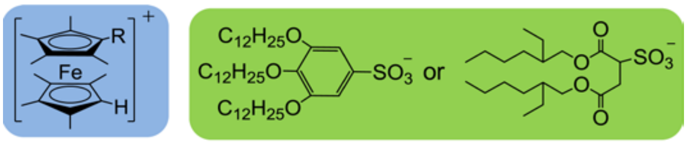
Glass transition temperatures (T_g) and melting points (T_m) of ferrocenium salts with mesogenic anions and with Tf_2N anions.

Compounds	T_g [°C]	T_m [°C]
[**1**]($(C_{12}H_{25}O)_3C_6H_2SO_3$)	–53	
[**2**]($(C_{12}H_{25}O)_3C_6H_2SO_3$)	–41	
[**1**](AOT)	–51	
[**2**](AOT)		122.2
[**1**](Tf_2N)[a]		26.2
[**2**](Tf_2N)[b]		343

[a] Ref. 11

[b] Ref. 24

TOC



Ferrocenium ionic liquids with mesogenic anions