

An Ionic Liquid Consisting of Crown Ether–Coordinated Hydronium Cation and Amide Anion

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We first report an ionic liquid (IL) that consists of hydronium (H_3O^+) ion encapsulated by 18–crown–6–ether (18C6) and an amide anion. The composition of the crown ether–coordinated hydronium amide IL was estimated to be as $[\text{H}_3\text{O}^+\cdot 18\text{C6}][\text{Tf}_2\text{N}^-]$. The presence of H_3O^+ was revealed from the characteristic bands of the hydronium ion present in the infrared spectra. The melting point of $[\text{H}_3\text{O}^+\cdot 18\text{C6}][\text{Tf}_2\text{N}^-]$ was 68–70 °C. At 70 °C, the viscosity of $[\text{H}_3\text{O}^+\cdot 18\text{C6}][\text{Tf}_2\text{N}^-]$ was 39.5 mPa s, the conductivity was 1.9 mS cm^{-1} , and the density was about 1.32 g cm^{-3} . These bath properties of $[\text{H}_3\text{O}^+\cdot 18\text{C6}][\text{Tf}_2\text{N}^-]$ were similar to those of common ILs at room temperature.

Introduction

Ionic liquids (ILs) are salts which melt below 100 °C, and consist of a cation and an anion with low charge density. ILs have attracted remarkable attention as new materials for various chemical applications. There are reports on ILs which consist of strongly Lewis-acidic metal cations such as lithium ion and potassium ion coordinated by ether-ligands to decrease charge density (1–2). A cyclic hexamer of ethylene oxide 1,4,7,10,13,16–hexaoxacyclooctadecane (18–crown–6–ether, hereafter referred to as 18C6) has a suitable cavity for encapsulation of potassium ion and hydronium (H_3O^+) ion (3–4). Various compounds with H_3O^+ encapsulated by 18C6 ligand ($[\text{H}_3\text{O}^+\cdot 18\text{C6}]$ cation) have been reported, the counteranions of which are such as hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-) and trifluoromethylsulfonate (TfO^- ; $\text{Tf} = \text{CF}_3\text{SO}_2$) ions (3–4). However, their melting points are higher than 100 °C. Furthermore, as far as we know, nothing has been reported on combination of $[\text{H}_3\text{O}^+\cdot 18\text{C6}]$ cation and bis(trifluoromethylsulfonyl)amide (Tf_2N^-) anion. In this paper, we report a synthesis of a complex with $[\text{H}_3\text{O}^+\cdot 18\text{C6}]$ cation and an amide anion, whose melting point was about 70 °C.

Experimental

5 mmol of 18C6 (Kanto Chemical, 99% purity) and 5 mmol of HTf₂N (Aldrich, ≥95% purity) in 5 mL of water were stirred at 500 rpm and heated at 50 °C for 1 day, followed by vacuum-drying at 50 °C for 3 days. The obtained complex was a white solid at room temperature and a colorless transparent liquid at about 70 °C (see Figure 1). The composition of the complex was determined using elemental analysis and Karl–Fischer titration. The presence of H₃O⁺ was checked with infrared spectra (JASCO, FT/IR–460 plus). For the infrared measurement, Nujol and hexachlorobutadiene mulls painted on a barium fluoride window were used at room temperature. In order to evaluate the complex as an IL, we measured the density, the viscosity, the conductivity, and the melting point. The melting point of the complex was evaluated by differential scanning calorimeter (Shimadzu, DSC–60) with a sweeping rate of 5 °C min⁻¹ by heating from room temperature up to 80 °C and then cooling down to 40 °C.

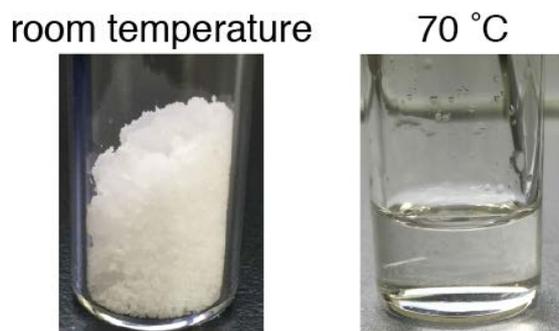


Figure 1. Photographs of the obtained complex at room temperature and 70 °C.

Results and discussion

TABLE I shows elemental analysis results for H, C, N, F, and S. The experimental value was in good agreement with the calculated value assuming that the complex was 18C₆:H₂O:HTf₂N = 1:1:1. The H₂O content of the complex was 3.29 wt% analyzed by Karl–Fischer titration, in good agreement with the calculated value (3.20 wt%). Therefore, it is concluded that the complex consists of equimolar amount of 18C₆, H₂O, and HTf₂N.

TABLE I. Elemental analysis results for the obtained sample.

The complex	H (%)	C (%)	N (%)	F (%)	S (%)
Calculated	4.80	29.84	2.49	20.25	11.37
Experimental	4.90	29.97	2.40	20.07	11.35

The presence of H_3O^+ readily established from the characteristic bands of the hydronium ion present in the high-wavenumber region from 1600 cm^{-1} to 4000 cm^{-1} of infrared spectra (Figure 2). The bands due to H_3O^+ are reported to be $2780\text{--}3250\text{ cm}^{-1}$ (ν_1), $1048\text{--}1182\text{ cm}^{-1}$ (ν_2), $2500\text{--}3100\text{ cm}^{-1}$ (ν_3), and $1477\text{--}1705\text{ cm}^{-1}$ (ν_4) (5–6). The ν_1 and ν_3 stretching modes of the complex gave the very broad band centered at 2920 cm^{-1} , which overlapped the sharper maximum arising from the C–H stretching motions of 18C6 at 2880 cm^{-1} . The band at 1650 cm^{-1} was attributable to the ν_4 bending mode. The characteristic band also appeared at 2200 cm^{-1} , attributable to the first harmonic of ν_2 , *i.e.* symmetric bending mode (4, 7). The ν_2 band at 1100 cm^{-1} was not clearly observed, where a strong band from 18C6 overlapped (7). When water was added to the complex, a broad band appeared at $3200\text{--}3600\text{ cm}^{-1}$ (not shown). Therefore, the broad band observed at 3480 cm^{-1} for pure 18C6 was attributable to unprotonated water (8). The water content of pure 18C6 was 0.14 wt% analyzed by Karl–Fischer titration. In the infrared spectra of the complex, the broad band at 3480 cm^{-1} due to unprotonated water disappeared and the sharp band appeared at 3570 cm^{-1} , which may be due to the formation of $[\text{H}_3\text{O}^+\cdot 18\text{C6}]$. Consequently, the complex hardly includes unprotonated water.

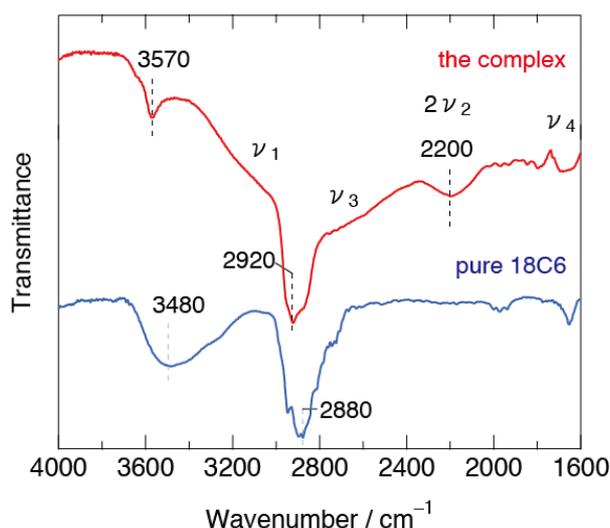


Figure 2. High-wavenumber region from 1600 cm^{-1} to 4000 cm^{-1} of the infrared spectrum of the complex (expected as $[\text{H}_3\text{O}^+\cdot 18\text{C6}][\text{Tf}_2\text{N}^-]$) and pure 18C6 mullied in hexachlorobutadiene.

Figure 3 shows the infrared spectra of the complex and pure 18C6 in the low-wavenumber region from 800 cm^{-1} to 1400 cm^{-1} . The broad band at 1125 cm^{-1} of pure 18C6 was the C–O–C stretching absorption of 18C6. In the infrared spectra of the complex, the broad band at 1125 cm^{-1} of 18C6 disappeared and split into sharp bands at 1138 cm^{-1} and 1091 cm^{-1} because of $[\text{H}_3\text{O}^+\cdot 18\text{C6}]$ formation (4). From these

experiments, the formulation of the complex was estimated to be as $[\text{H}_3\text{O}^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$. The schematic structure of which is shown in Figure 4.

Figure 5 shows differential scanning calorimeter (DSC) thermograms of $[\text{H}_3\text{O}^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$ sample. The melting point of $[\text{H}_3\text{O}^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$ was 68–70 °C. The melting point of pure 18C6 and of pure HTf_2N are 40 °C and 52–58 °C, but endothermal reaction below 60 °C were not observed in Figure 5. Therefore, it was concluded that $[\text{H}_3\text{O}^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$ neither included isolated 18C6 nor HTf_2N .

At 70 °C, the viscosity of $[\text{H}_3\text{O}^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$ was 39.5 mPa s, the conductivity was 1.9 mS cm^{-1} , and the density was about 1.32 g cm^{-3} . These bath properties of $[\text{H}_3\text{O}^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$ were similar to those of common ILs at room temperature. Therefore, $[\text{H}_3\text{O}^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$ was characterized as an IL.

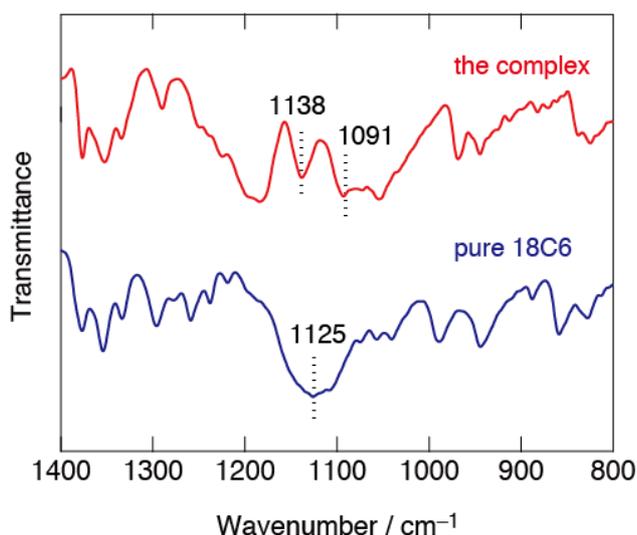


Figure 3. Low-wavenumber region from 800 cm^{-1} to 1400 cm^{-1} of the infrared spectra of the complex (expected as $[\text{H}_3\text{O}^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$) and pure 18C6 mullied in Nujol.

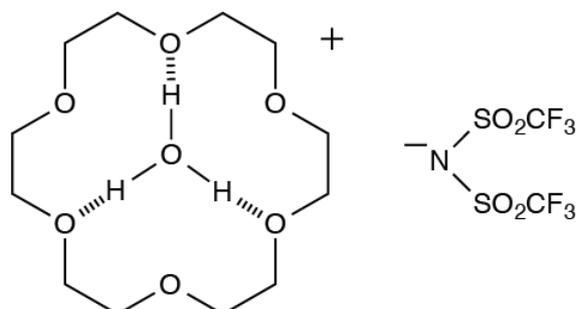


Figure 4. Schematic structure of $[\text{H}_3\text{O}^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$.

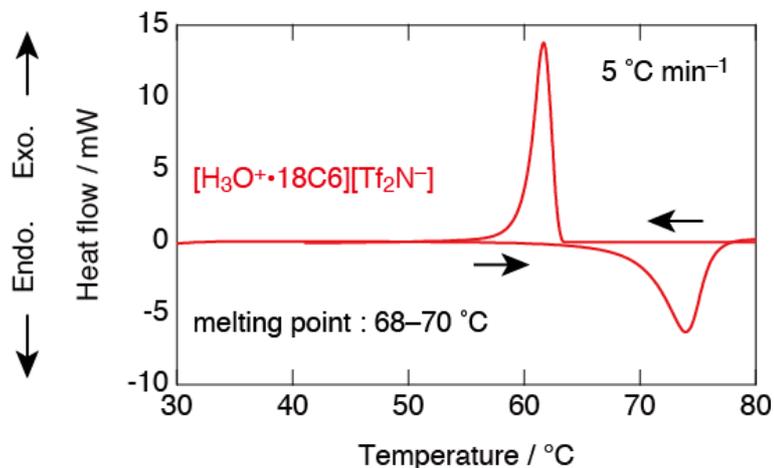


Figure 5. DSC thermograms of 24.6 mg of the $[\text{H}_3\text{O}^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$ placed in a hermetically sealed aluminum pan.

Conclusions

In conclusion, we synthesized a new IL consisting of H_3O^+ cation encapsulated by 18C6 and an amide anion, of which melting point was below 100 °C. The obtained complex was concluded as $[\text{H}_3\text{O}^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$. The bath properties of $[\text{H}_3\text{O}^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$ at 70 °C were similar to those of common ILs at room temperature. In the infrared spectra, it was revealed that H_3O^+ of the obtained complex was encapsulated by 18C6. In addition, $[\text{H}_3\text{O}^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$ hardly includes unprotonated water. Further study is needed to reveal other properties of $[\text{H}_3\text{O}^+\cdot 18\text{C}6][\text{Tf}_2\text{N}^-]$.

Acknowledgments

This work was financially by Grant-in-Aid for Scientific Research (A) (No. 25249106 and No. 16H02411), Grant-in-Aid for challenging Exploratory Research (No. 15K14193), and Grant-in-Aid for Young Scientists (B) (No. 15K18253) from the Japan Society for the Promotion of Science (JSPS). A.K also thanks Izumi Science and Technology Foundation for their financial support (No. H27-J-080).

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