Liquid imidazole–borane complex

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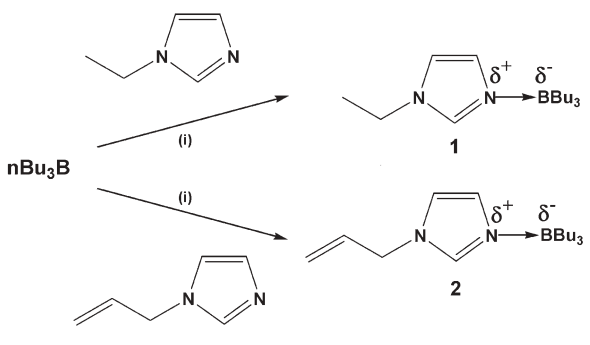
Physical properties of liquid imidazole–borane complex were investigated to demonstrate their utility as aprotic polar solvents or liquid electrolytes appropriate for selective ion transport.

Due to the recent remarkable development of ionics devices, preparation of excellent electrolyte material is a research subject of a great deal of importance. Among electrolytes, polyether derivatives[1] have been widely studied for several decades. However, strong coordination of ether oxygen toward cation generally prevents efficient target cation transport. On the other hand, these days, room temperature molten salts termed ionic liquids (ILs)[2] have been intensely studied world wide because of their intriguing features such as non volatility and non flammability. They are attracting much attention as a new generation of electrolytes as well as reaction media. At the same time, in spite of their high ionic conductivity, selective ion transport in ILs[3–5] is not facilely achieved, because ILs themselves are composed of ions.

In the present work, as a further approach to provide non polyether type ion transporting media appropriate for selective ion transport, the physical properties of liquid alkylborane–imidazole complexes (Scheme 1) such as thermal properties, viscosity, polarity, ionic conductivity and so forth were investigated. Due to the strong coordination of nitrogen to boron, amine–borane complexes should pose a considerable amount of charge on them to act as a aprotic polar solvent which are capable of dissolving various substrates or salts. Since amine–borane complexes do not include mobile ion originating from matrix, these materials should be suitable for the purpose of target ion transport, and might have a profound potential as a new class of reaction media or electrolytes.



Scheme 1 Preparation of imidazole—borane complex. *Reagents*: (i) THF/ at r.t./ 12 h/ quant.

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Amine–borane adducts are widely known materials.[6] Since boron atom possess the vacant p-orbital, it readily accepts the lone pair electrons of Lewis bases to form amine–borane complexes as reported in the early study by H. C. Brown *et al.*[7] Some amine–borane complexes are known as reducing reagents[8] for ketones and aldehydes, initiators for polymerization[9] and precursors for ceramics.[10] Among conventional borane reagents, amine–borane complexes such as pyridine–borane[11] and butylamine–borane[12] are considered to be the most stable and can be used in air. Especially, the latter compound is known to be soluble in water without decomposition.

In spite of the reasonable stability and utility of amine–borane complexes, there is no example of the application of these materials as electrolyte or solvent to the best of our knowledge.

In the present study, the amine–borane complexes *N*-ethylimidazole–tributylborane and *N*-allylimidazole–tributylborane were investigated in detail. Both amine–borane complexes were prepared by the treatment of a THF solution of tributylborane with an equimolar amount of the imidazole under inert atmosphere. These compounds were obtained as non viscous transparent liquids at room temperature. From the ^{11}B-NMR spectra of the imidazole–borane complex in CDCl$_3$, peaks due to the coordinated boron atom were observed at −11.9 and −11.6 ppm for **1** and **2**, respectively. The ^{11}B-NMR spectra were not significantly changed after addition of LiTFSI (0.5 M). After sufficient drying under reduced pressure, their physical properties were studied as listed in Table 1. First, the glass transition temperature (T_g) and melting point (T_m) were measured by differential scanning calorimetry measurement. The observed T_g for the borane–imidazole complexes was $-77.5 \sim -80.5$ °C, which was comparable to those for conventional ILs. T_m was far below room temperature ($9.1 \sim -3.5$ °C). After exposure to air for 4 weeks, the thermal properties of the imidazole–alkylborane complexes had not been changed significantly.

The viscosity of these borane–amine complexes was found to be $36 \sim 28$ cP at 298K (Fig. 1). These values are similar to that for 1-ethyl-3-methylimidazolium TFSI (34 cP).

The solvent polarity of the amine–borane complexes was evaluated using Reichardt's betaine dye (2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate),[13] which is a well known solvatochromic dye frequently used to determine the polarity of a medium

Table 1 Physical properties of imidazole–borane complexes

Complex	T_g/°C^a	T_m/°C^a	η/cP (at 25 °C)	$E_T(30)$
1	−78	9.1	36	44
2	−81	−3.5	28	43
acetone	—	—	0.3	42
ethanol	—	—	1.0	52

^{a} At the heating rate of 10 °C min^{-1}.

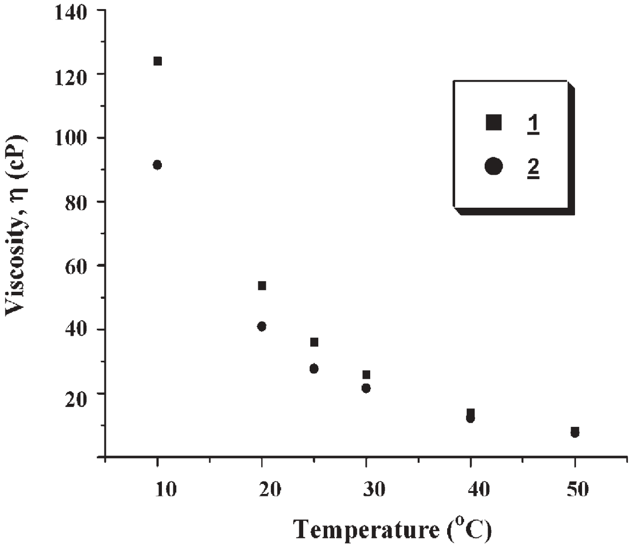

Fig. 1 Temperature dependence of viscosity for **1** and **2**.

experimentally. The UV-vis spectra of Reichardt's dye were measured in imidazole–borane complexes at room temperature. The absorption maximum wavelength due to intramolecular charge transfer was observed at 667 ~ 657 nm. The solvent polarity parameter $E_T(30)$ for imidazole–borane complex were 44 ~ 43, respectively, which are similar to that for acetone (42) or acetonitrile (46).

Ion conductive properties of the imidazole–borane complexes were studied by ac impedance method after addition of LiTFSI (Fig. 2). LiTFSI was facilely soluble up to 1.0 M at room temperature. The ionic conductivity observed was $2.23 \times 10^{-4} \sim 1.32 \times 10^{-4}$ S cm^{-1} at 323 K (Table 2). Dependence of salt concentration on ionic conductivity was also studied. In the case of imidazole–borane complex **2**, the maximum ionic conductivity of 2.23×10^{-4} S cm^{-1} at 323 K was observed at a higher salt concentration region (0.5 M) compared with **1**. This should be due to lower viscosity of **2** in comparison with that of **1**. These values are not so high as those for conventional ILs in spite of their low viscosity, possibly because these systems do not contain mobile ions originating from the matrix itself.

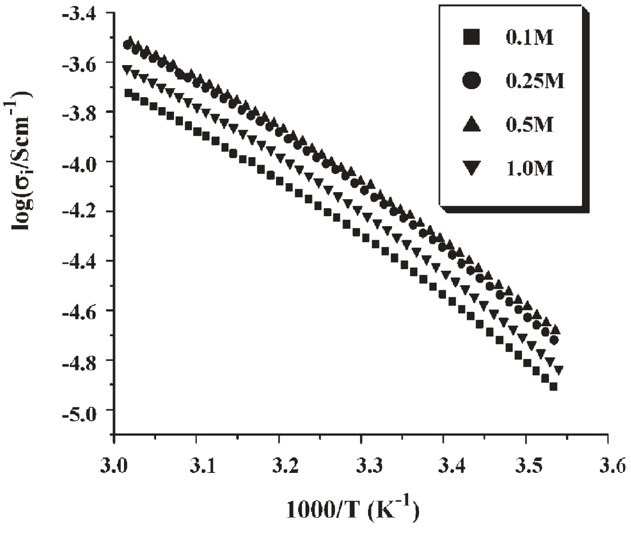

Fig. 2 Temperature dependence of ionic conductivity for **2** in the presence of LiTFSI.

Table 2 Ionic conductivity of **1** and **2** in the presence of LiTFSI

Imidazole-borane	[Li$^+$](M)	σ_i/S cm^{-1} at 303K^a	σ_i/S cm^{-1} at 323K^a
1	0.1	5.01×10^{-5}	1.58×10^{-4}
1	0.25	9.09×10^{-5}	2.22×10^{-4}
1	0.5	6.27×10^{-5}	1.76×10^{-4}
1	1.0	6.07×10^{-5}	1.73×10^{-4}
2	0.1	5.21×10^{-5}	1.32×10^{-4}
2	0.25	8.17×10^{-5}	2.07×10^{-4}
2	0.5	8.32×10^{-5}	2.23×10^{-4}
2	1.0	6.41×10^{-5}	1.66×10^{-4}

^{a} Determined by ac impedance method.

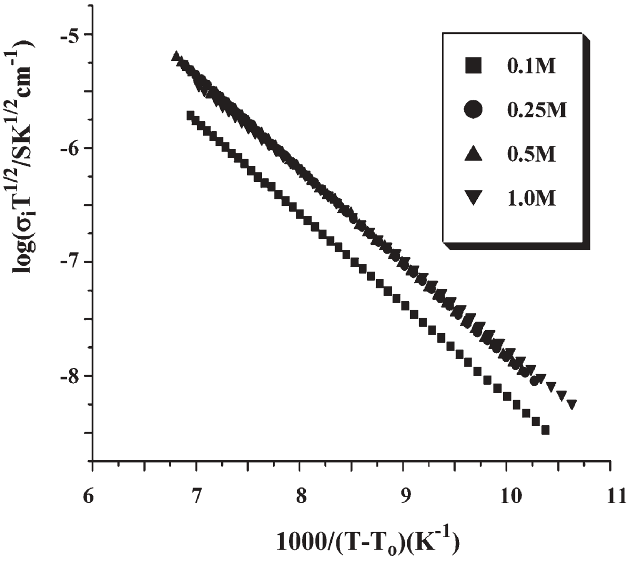

Fig. 3 VFT plots for **2** in the presence of LiTFSI.

The ionic conductivity of imidazole–borane complexes obeyed the VFT (Vogel–Fulcher–Tamman) equation[14] quite well (Fig. 3). VFT parameters for both systems are summarized in Tables 3 and 4. In the case of **1**, the VFT parameter corresponding to activation energy (*B*) monotonically decreased with increasing the salt concentration. Although carrier ion number was highest at the salt concentration [Li$^+$] of 0.1 M, the maximum ionic conductivity was observed when [Li$^+$] was 0.25 because of the lower activation energy of this system. On the other hand, activation energy did not significantly vary in the case of **2** possibly due to lower viscosity. Therefore, ionic conductivity was simply governed by the number of carrier ions to exhibit the maximum ionic conductivity at the

Table 3 VFT parameters for **1**/LiTFSI

[Li$^+$](M)	T_g(°C)^a	T_0(°C)^a	A/S cm^{-1} K$^{1/2}$	B/K	RMS
0.1	−75	−138	12.18	1581	0.9999
0.25	−72	−115	4.607	1158	0.9999
0.5	−70	−82	1.704	823.5	0.9999
1.0	−69	−79	1.659	809.3	0.9999

^{a} At the heating rate of 10 °C min^{-1}.

Table 4 VFT Parameters for **2**/LiTFSI

$[\mathrm{Li}^+]$(M)	T_g/°C[a]	T_o/°C[a]	A/S cm^{-1} K$^{1/2}$	B/K	RMS
0.1	−80	−86	0.8622	796.3	0.9999
0.25	−78	−87	1.461	812.2	0.9999
0.5	−76	−89	1.545	827.9	0.9998
1.0	−72	−84	1.018	777.2	0.9999

[a] At the heating rate of 10 °C min^{-1}.

salt concentration of 0.5 M where the number of carrier ions (A) was the largest.

In conclusion, physical properties of liquid imidazole–borane complexes were investigated in detail with respect to thermal property, viscosity, polarity and ionic conductivity. The observed low viscosity, high polarity, and moderate ionic conductivity demonstrate that imidazole–borane complexes should be useful as electrolyte materials appropriate for target ion transport. These materials should also have utility as designer solvents for a variety of organic reactions whose physical properties are tunable by changing the combination of the amine–borane complex or incorporating various substituents on imidazole or boron atom. Synthesis and evaluation of solid polymer electrolytes based on imidazole–borane complexes is also currently underway.

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