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Novel Lewis-base ionic liquids replacing typical anions

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Abstract—We have synthesized two kinds of new Lewis-base ionic liquids (ILs); one is based on the relatively strong Lewis basic acetate anion, and the other is a salt composed of a mono-alkylated diamine such that the Lewis base site is incorporated in the cation. 1-Octyl-4-aza-1-azonia-bicyclo[2.2.2]octane bis(trifluoromethanesulfonyl)amide, [C_8dabco]TFSA, and *N*-butyl-*N*-methylpyrrolidinium acetate, [$p_{1,4}$]OAc, melted into fluid liquids at 26 and 81 °C, respectively. The thermal decomposition of [$p_{1,4}$]OAc started at around 150 °C, whereas the thermal stability of [C_8dabco]TFSA was almost equal to that of typical TFSA-based ILs in spite of the Lewis base site. This suggests that if the Lewis base site is incorporated into the cation the IL can maintain higher thermal stability. In addition, as a further result of the presence of the basic nitrogen, [C_8dabco]TFSA can dissolve hydrated $Cu(NO_3)_2$ whereas the other TFSA-based ILs cannot.

In the past decade, there has been a great interest in the development of new ionic liquids (ILs) as green solvents because ILs have fascinating properties such as negligible vapor pressure, nonflammability, etc.[1] In addition, we can design-in the function of the IL through the design of the component ions, to produce so-called task-specific ILs.[2] Nucleophilicity of the component ions[3] is a key feature currently being explored since it is one of the most important factors in determining the ability of the IL to dissolve many kinds of materials, for instance, carbohydrates,[4] biopolymers,[5] synthetic polymers,[6] and so on. Thus far, it seems that the solubility of these materials is affected more by the nature of the anion than that of the cation, that is, ILs involving, for example, the chloride anion or the dicyanamide anion (DCA^-) can dissolve those materials in high concentrations. According to these results, the hydrogen bond acceptor ability of the anion is a key to dissolution of those materials.[7]

Strong nucleophilicity, that is, strong Lewis basicity of the anion, however, also tends to induce thermal decomposition of the ILs at a lower temperature compared with typical ILs having tetrafluoroborate or triflate anions.[8,9] In other words, thermal stability of ILs, which is one of their very useful properties, is sacrificed.

In this letter, in order to combine strong Lewis basicity with high thermal stability, we describe the synthesis and properties of a new IL based on a diamine structure. We have previously reported that the salt based on 1,4-diazabicyclo[2.2.2]octane (dabco) coupled with the bis(trifluoromethanesulfonyl)amide (TFSA) anion is water-soluble when the N-substituted alkyl chain length is 2, [C_2dabco]TFSA.[10] In general, it is well-known that organic cations combined with $TFSA^-$ are water-immiscible.[11] This hydrophilic behavior of [C_2dabco]TFSA most likely results from the hydrogen bonding between the tertiary amine nitrogen and a water molecule. Hence, we hypothesize that the mono-charged dabco salts should work as Lewis-base ILs if the melting point can be lowered sufficiently to render these salts useful as ILs. In this letter, the *n*-octyl derivative, [C_8dabco]TFSA,[12] as shown in Figure 1, has been found to reduce the melting point of the dabco salt below room temperature.

We have also synthesized a pyrrolidinium salt of the acetate anion (OAc^-) as a new Lewis base IL for

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Keywords: Ionic liquids; Lewis base; Nucleophilicity; Pyrrolidinium salts.

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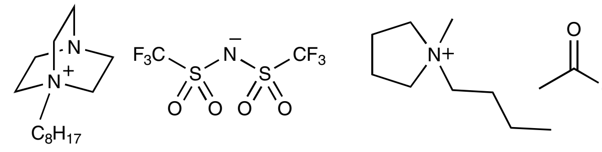

$[C_8dabco]TFSA$ $[p_{1,4}]OAc$

Figure 1. Structures of novel Lewis base ILs.

comparison.[13] Of course, although we cannot expect high thermal stability, it is expected that the acetate anion will show (comparatively) strong Lewis basicity, which can be equal to or stronger than the chloride. The ILs with OAc^- cannot only be categorized as Lewis base ILs, but can also be produced as halogen-free ILs. This is desirable in the drive towards inexpensive, environmentally benign solvents. In addition, preparing acetate-based ILs can be a challenging issue because there are only a few reports on ILs containing OAc^-.[11,14,15] To prepare this IL with an *N*-*n*-butyl-*N*-methylpyrrolidinium cation ($[p_{1,4}]^+$), an ion exchange resin method was developed and is described here.

The octyl derivative is a colorless oil at room temperature and is water-immiscible in the same way as typical TFSA-based ILs. The hydrophobicity of $[C_8dabco]TFSA$ as compared to the C_2 analogue is a result of the longer *N*-alkyl chain. On the other hand, $[p_{1,4}]OAc$ is a solid, which melts at 81 °C (Fig. 2c). In general, small, less charge delocalized anions tend to produce higher T_m's than other anions due to strong electrostatic interaction with the cation. However, the T_m of $[p_{1,4}]OAc$ is substantially lower than that of halogen analogues although it is expected that anion nucleophilicity is almost the same. This type of behavior is one of the merits of ILs. The synthesis of other ILs possessing OAc^- is in progress and will be reported elsewhere.

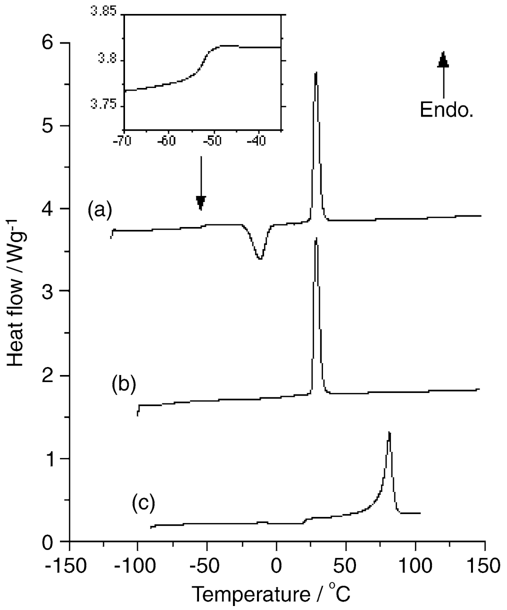

Figure 2. DSC traces of $[C_8dabco]TFSA$ (a, b) and $[p_{1,4}]OAc$ (c). (a) Aluminum pan was cooled from room temperature to −120 °C at a cooling rate of 10 °C min^{-1}, then was heated to 150 °C. (b) After annealing at −20 °C for 10 min, the measurement was carried out between −100 and 150 °C at a cooling/heating rate of 10 °C min^{-1}.

The thermal behavior of $[C_8dabco]TFSA$ was investigated in detail as shown in Figure 2. When the sample pan was directly cooled to −120 °C with a cooling rate of 10 °C, the differential scanning calorimetry (DSC) trace (Fig. 2a) showed a glass transition temperature (T_g), a crystallization temperature (T_c), and a melting point (T_m) at −54, −22, and 26 °C, respectively, during the heating process. The octyl derivative forms a supercooled state with ease. In addition, its T_m was reduced to 50 °C from that of the ethyl dabco salt as anticipated. Although $[C_8dabco]TFSA$ is a viscous liquid at room temperature, it was considered a possibility that it might be in a metastable phase, therefore, the sample pan was annealed at −20 °C for 10 min before performing a second DSC run. The DSC trace (Fig. 2b) showed only a T_m at 26 °C. Thus, this IL will solidify with ease depending on the conditions.

The thermal stability of $[C_8dabco]TFSA$ was investigated by means of thermogravimetric analysis (TGA). Figure 3 shows TGA traces of $[C_8dabco]TFSA$ and $[p_{1,4}]OAc$ along with those of other ILs ($[p_{1,4}]TFSA$; *N*-*n*-butyl-*N*-methylpyrrolidinium TFSA,[16] $[p_{1,4}]DCA$; *N*-*n*-butyl-*N*-methylpyrrolidinium dicyanamide,[17] $[C_2mim]SCN$; 1-ethyl-3-methylimidazolium thiocyanate[18]) in order to compare the effect of Lewis basicity on the thermal stability. As expected, the decomposition temperature of the ILs reduces in the following order, $TFSA^- > DCA^- \sim SCN^- > OAc^-$. The thermal decomposition of $[p_{1,4}]OAc$ starts at around 150 °C, while that of the TFSA analogue starts at over 400 °C. The difference of thermal stability of the two materials amounts to over 200 °C. Acetate based ILs are thus not as stable as many ILs, but it is expected that they may be used as solvents, being equal to the halogen analogues in dissolving many materials. The instability is very likely to involve a Hoffman elimination reaction in which the

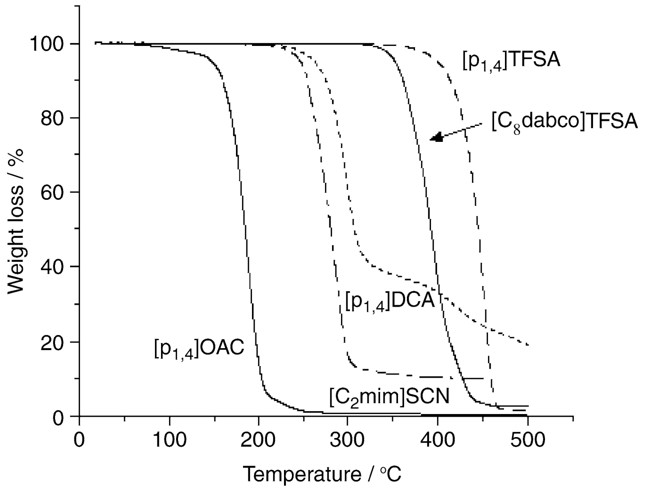

Figure 3. Thermal gravimetric analysis (TGA) traces of various ILs. The thermal stability of ILs is considerably affected by the nature of the anion.

nucleophile abstracts a proton on a carbon to the nitrogen in the butyl chain. This releases acetic acid, methyl pyrrolidine, and butene, all of which are sufficiently volatile to rapidly escape the liquid and thereby drive the reaction.

On the other hand, the thermal stability of [C_8dabco]TFSA is slightly reduced as compared to [$p_{1,4}$]TFSA, which is a typical TFSA-based IL. This difference reflects the effect of the Lewis basicity of the mono-charged dabco cation because the thermal stability of ILs tends to depend on the nucleophilicity of the ions. For example, ILs containing halogen anions, which show strong Lewis basicity, are thermally unstable as compared with other anion systems.[9] However, the dabco system is only slightly less thermally stable than [$p_{1,4}$]TFSA in spite of the Lewis base site, suggesting that if the Lewis base site is associated with the cation, the ILs maintain higher thermal stability. We have thus succeeded in overcoming the thermal instability of Lewis base ILs.

Since the [C_8dabco] cation can interact weakly with a metal cation through a tertiary amine nitrogen, it is expected that the mono-charged dabco system could dissolve many kinds of metal salts. In fact, [C_8dabco]TFSA can dissolve hydrated $Cu(NO_3)_2$ without any ligand molecules whereas other TFSA-based ILs cannot. This result most likely arises due to the interaction between the cupric ion and the Lewis base site. Figure 4 shows the UV–vis spectrum of [C_8dabco]TFSA in which hydrated $Cu(NO_3)_2$ is dissolved. The UV–vis data for the cupric salt dissolved in water is included for comparison. The dabco system shows a maximum absorption wavelength at 352 nm and displays a red shift of 50 nm as compared with the aqueous solution as is typical of tertiary amine ligands with Cu^{II}. It therefore appears that the mono-charged dabco behaves as a good ligand for Cu^{II}.[19] Certainly, the dabco salts also offer interesting coordination chemistry, especially in the context of immobilizing metal catalysts.[20]

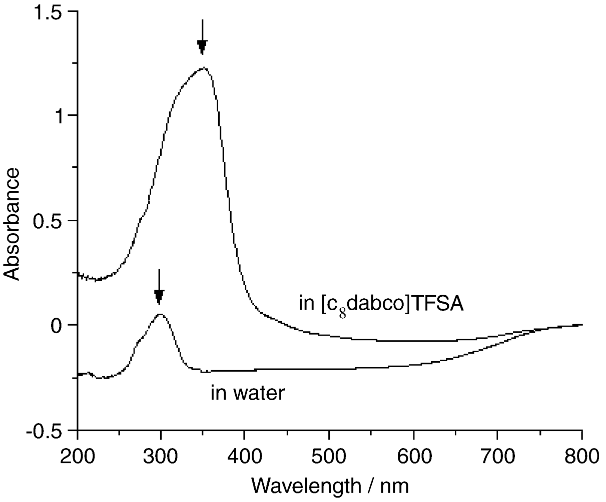

Figure 4. UV–vis spectra of hydrated $Cu(NO_3)_2$ dissolved in [C_8dabco]TFSA and water.

In this letter, the synthesis of two kinds of new Lewis base ILs is reported; one is based on a strong Lewis base anion as a typical system, and the other one is a mono-charged dabco salt in which the Lewis base site is incorporated in the cation. [C_8dabco]TFSA and [$p_{1,4}$]OAc showed T_m at 26 and 81 °C, respectively. The [$p_{1,4}$]OAc was not stable over 200 °C, whereas the thermal stability of [C_8dabco]TFSA was almost equal to that of typical TFSA-based ILs, in spite of the Lewis base site. This suggests that if the Lewis base site is incorporated in the cation, higher thermal stability can be maintained. In addition, [C_8dabco]TFSA can dissolve hydrated $Cu(NO_3)_2$ although other TFSA-based ILs cannot. This result most likely arises due to the interaction between the cupric ion and the Lewis base site.

Acknowledgements

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12. [C_8dabco]TFSA was synthesized according to the literature method.[10] The bromide salt (10.0 g, 32.8 mmol) and LiTFSA (11.3 g, 39.4 mmol) yielded [C_8dabco]TFSA (14.1 g, yield 85%) as a colorless oil. δ_H (300 MHz, DMSO-d_6) 0.83 (3H, t, $J = 6.8$ Hz, CH_3), 1.24 (10H, br s, $5 \times CH_2$), 1.61 (2H, br s, CH_2), 2.98 (6H, t, $J = 7.4$ Hz, $3 \times CH_2$), 3.12 (2H, m, CH_2) and 3.21 (6H, t, $J = 7.4$ Hz, $3 \times CH_2$). MS (ESI): ES^+ m/z 225.1 ([C_8dabco]$^+$, 100%), ES^- m/z 280.0 ($TFSA^-$, 100%).
13. The first step in the use of the ion exchange resin (Dowex MSA-1 macroporous resin) involves loading with the desired anion. A 20 wt % NaOAc solution was flushed through a column containing 1 kg of resin. The above solution (2.5 L) was required to achieve complete substitution of the chloride ions. Then, flushing the column with an aqueous solution of the iodide salt of the desired cation resulted in rapid displacement of the target anion by the iodide. After the reaction was complete, the aqueous solution containing the new IL was concentrated and the IL isolated and dried. Residual iodide and chloride were concerns in this process and these were determined using an ion selective electrode. Ionode S16 was used for iodide determination and Ionode S10 for chloride determination. Calibrations curves for both ions were made from 1 to 1000 ppm. The ionic concentrations were determined by dissolving 0.97 g of [$p_{1,4}$]OAc in 5 mL of water.

    N-*n*-Butyl-*N*-methylpyrrolidinium iodide ([$p_{1,4}$]I)[21] (5.0 g, 18.7 mmol) was dissolved in 50 mL of distilled water and added to a column loaded with acetate anions. The material was eluted through with 400 mL of water where the last 250 mL was collected. The water was evaporated and the residual material was dried under vacuum at 60 °C (yield ~85%). δ_H (300 MHz, D_2O) 0.89 (3H, t, $J = 7.4$ Hz, CH_3), 1.33 (2H, m, CH_2), 1.71 (2H, m, CH_2), 1.84 (3H, s, CH_3), 2.14 (4H, m, $2 \times CH_2$), 2.97 (3H, s, CH_3), 3.25 (2H, m, CH_2), 3.44 (4H, m, $2 \times CH_2$). MS (ESI): ES^+ m/z 142 ([$p_{1,4}$]$^+$, 100%), ES^- m/z 59 (OAc^-, 100%). Ion selective electrodes: 0.02% iodide and 0.2% chloride.
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