Allylimidazolium Halides as Novel Room Temperature Ionic Liquids

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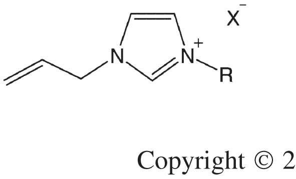
Liquid state halide salts composed of imidazolium cations having allyl groups were prepared. Their ionic conductivity, viscosity, and thermal properties were investigated. Introduction of allyl group on *N*-position effectively suppressed the crystallization of the corresponding salts. 1,3-diallyl imidazolium halides therefore showed considerably lower viscosity and higher ionic conductivity than other halide salts.

Room temperature ionic liquids (RTIL) are collecting increasing attention as a new class of ion conductive matrices for electrochemical devices[1] as well as reaction media for organic synthesis.[2] Most RTILs are composed of 1,3-dialkylimidazolium cations and large anions such as BF_4^-, $CF_3SO_3^-$, PF_6^-, and $(CF_3SO_2)_2N^-$. On the other hand, 1,3-dialkylimidazolium halides were not used as RTIL because of their relatively high melting points (T_m). Recently, 1,3-dialkylimidazolium halides having relatively low T_m, such as 1-butyl-3-methylimidazolium chloride ($T_m = 67\,°C$), have received attentions as a novel solvent for bio- or bio-related materials. For example, cellulose,[3] cyclodextrin,[4] and DNA[5] were found to be soluble in 1,3-dialkylimidazolium halides at temperature above T_m. These halide-based ionic liquids can readily dissolve biomaterials because of their high polarity, and proton accepting nature. Furthermore, Kimizuka and Nakashima reported the preparation of fibers, bilayer membranes, and vesicles through self-assembly of component molecules in ether containing 1,3-dialkylimidazolium halides with a small amount of water (≈ 2.5 wt %).[6]

However, due to relatively high T_m, 1,3-dialkylimidazolium halide salts are rarely used as solvents at room temperature. For the improvement of this drawback, advanced molecular design is required for lowering their T_m and viscosity.[7] Although some imidazolium halide salts having long alkyl chains (C5–C10) are known to form super-cooled liquid, they usually show high viscosity. In the present work, we analyzed the effect of allyl group(s) on imidazolium ring to lower T_m of these halide salts. The chemical structure of the examined compounds is summarized in Table 1. Among a series of allylimidazolium halide, 1-allyl-3-methylimidazolium halides [AMIm]X (X = Cl, Br, and I), and 1,3-diallylimidazolium bromide [AAIm]Br were reported by Chan et al.,[8] and Jones et al.,[9] respectively about 30 years ago. Very recently, Wu et al. used [AMIm]Cl as a solvent for cellulose.[10] These previous papers have only mentioned that some allylimidazolium halides could be obtained as liquid. However, in spite of potential utility of this type of ionic liquid, there has been no systematic study on the structure-physical property relationship for allylimidazolium halide salts. Hence, we have prepared a series of allylimidazolium type RTIL including several novel salts, and clarified their physical properties for the first time in detail.

Table 1. Chemical structure of 1-allyl-3-*R*-imidazolium halide salts; *R* represents for alkyl or allyl group

Ionic Liquid	R	X^-
[AAIm]Cl	Allyl	Cl^-
[AMIm]Br	Me	Br^-
[AEIm]Br	Et	Br^-
[APIm]Br	*n*-Propyl	Br^-
[AAIm]Br	Allyl	Br^-
[APenIm]Br	*n*-Pentyl	Br^-
[AOIm]Br	*n*-Octyl	Br^-
[AAIm]I	Allyl	I^-
[AAIm][TFSI]	Allyl	$(CF_3SO_2)_2N^-$



As a typical example of a series of allylimidazolium salts, preparation of 1-allyl-3-ethylimidazolium bromide [AEIm]Br was carried out as follows. To a solution of *N*-allylimidazole (5.0 mL, Acros Organics) in 20 mL toluene, excess amount of 1-ethylbromide (10 mL, Kanto Chemical) was added dropwise at 0 °C. The solution was gradually wormed up to room temperature. The reaction mixture was stirred for several hours. During the stirring, an oily phase was separated from the reaction mixture. This binary solution was further stirred for 24 h. After removing the solvent and unreacted 1-ethylbromide, oily product was washed with toluene for several times. Then, the product was dried in vacuo at 80 °C for more than 48 h. Water content was found to be below 0.1 wt %. In the case of chloride salt, the reaction was carried out at 80 °C. The water content of chloride salts was confirmed to be lower than 0.2 wt % by Karl–Fischer titration. Water content of chloride-containing salts was higher than that of other salts even after drying. This should be due to larger charge density of chloride anion.

All the allylimidazolium halide salts were obtained as viscous, slightly yellowish liquid at room temperature. These salts kept liquid state by storing at 5 °C for over one year. When these salts were kept at −18 °C, [AAIm]Cl, [AMIm]Br, [APIm]Br, and [APeIm]Br were slowly crystallized within a few weeks. However, in any case, they could not be recrystallized from supersaturated solutions by simple cooling. Under the same condition, [AEIm]Br, [AAIm]Br, [AOIm] Br, and [AAIm]I remained liquid for over 6 months. These results show very strong supercooling nature of allylimidazolium halide salts.

Table 2 shows physical properties of the obtained salts. In the DSC measurement, each sample showed glass transition temperature (T_g) at around −60 °C. The decomposition temperature (T_d) was higher than 250 °C. The viscosity (η) of the series of allylimidazolium halide salts was lower than 1000 cP at ambient temperature except for [AAIm]Cl and [APIm]Br. [AEIm]Br showed the lowest viscosity among these salts.

Among a series of salts, it is noteworthy that [AAIm]X were obtained as liquid under ambient temperature in spite of sym-

Table 2. Physical properties of a series of 1-allyl-3-*R*-imidazolium halide salts; *R* represents alkyl or allyl group

Ionic Liquid	σ_i/mS cm^{-1} (25 °C)	T_g /°C	T_m /°C^a	T_d /°C^b	η/cP (25 °C)
[AAIm]Cl	0.58	−68.3	21.5	234	1198
[AMIm] Br	1.55	−65.5	53.1	264	852
[AEIm] Br	1.05	−69.0	—	270	723
[APIm] Br	0.48	−67.0	29.5	256	1665
[AAIm] Br	0.74	−67.9	—	252	827
[APenIm]Br	0.17	−61.3	21.0	260	
[AOIm]Br	0.06	−64.5	—	253	
[AAIm]I	1.21	−72.1	—	249	
[AAIm][TFSI]	2.48	−91.6	—	389	31

[a] Temperature at signal peak.
[b] Temperature for 10% weight loss under N_2 atmosphere.

metrical structure. Generally, salts with such symmetrical imidazolium cations are easily crystallized. For example, 1,3-dipropylimidazolium bromide was reported to show T_m at 134 °C.[11] More interestingly, [AAIm]Br has considerably lower viscosity (827 cP at 25 °C) than that of [APIm]Br as shown in Table 2. These results demonstrated strong plasticizing effect of *N*-allyl group related to extremely slow crystallization and low viscosity of these salts.

As a reference, we also prepared 1,3-dipropargylimidazolium bromide in order to investigate the effect of unsaturated groups on the imidazolium cation ring. This salt was obtained as white crystal showing T_m at 142 °C. Such high crystallinity of this salt is attributable to the absence of rotation of propargyl groups to increase free volume.

Figure 1 shows the temperature dependence of the ionic conductivity for a series of allylimidazolium salts in the cooling scan. The ionic conductivity was 10^{-4}–10^{-3} S cm^{-1} at ambient temperature. Temperature dependence of the ionic conductivity obeyed the Vogel–Fulcher–Tamman (VFT) equation that expresses the temperature dependence of the viscosity of amorphous materials.[12] As seen in the series of bromide salts, the conductivity decreased with the increase of the alkyl chain length at the *N*-position, except for [AAIm]Br. [AAIm]Xs showed relatively high ionic conductivity among those systems reflecting lower T_g.

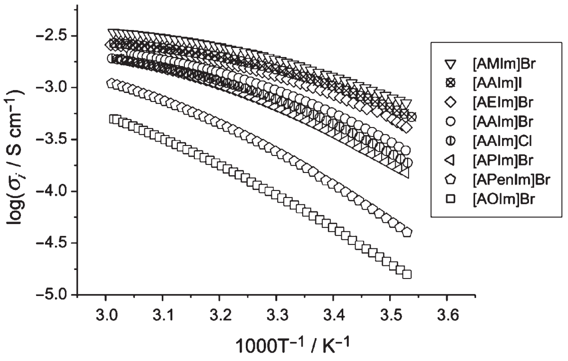


Figure 1. Temperature dependence of the ionic conductivity for 1-allyl-3-*R*-imidazolium halide salts.

We also prepared [AAIm][TFSI] salt. The salt was obtained as less viscous but hydrophobic RTIL with a water content of 24 ppm. Similarly to other halide salts, [AAIm][TFSI] did not show T_m in spite of symmetric structure of the cation. The viscosity was 31 cP at 25 °C, showing that this salt can be categorized as one of the least viscous RTILs.[13] These data also demonstrated the advantage of introducing allyl group to prepare excellent RTIL.

In conclusion, all the *N*-allyl substituted imidazolium salts obtained were RTIL showing moderate viscosity. *N*-allyl group has a strong plasticizing effect to introduce amorphous nature of the ionic liquids. From the comparison of bromide salts, 1-allyl-3-ethylimidazolium cation was confirmed to be better for the preparation of RTIL having low viscosity and amorphous nature.

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