doi:10.1246/cl.2010.1142

Preparation and Properties of Low Viscous Triazolate-based Ionic Liquids Containing Two Cyano Groups

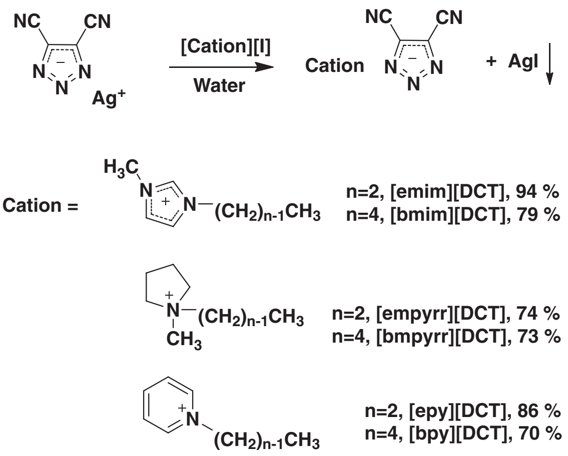
Satoshi Kitaoka, Kaoru Nobuoka, Naoki Yoshiiwa, Thomas Harran, and Yuichi Ishikawa*
Department of Applied Chemistry, Faculty of Engineering, Oita University, 700 Dannoharu, Oita 870-1192

(Received July 28, 2010; CL-100662; E-mail: ishichem@oita-u.ac.jp)

We synthesized novel triazolate-based ionic liquids containing two cyano groups. These liquids exhibit lower viscosity and glass transition temperatures than the ionic liquids without cyano groups. The present method of delocalizing anion charges in triazolate-based ionic liquids by means of cyano substitutions may be applicable to other ionic liquids to reduce their viscosity, thus making them promising reactive media and electrolytes.

Many aspects of ionic liquids (ILs) have been studied ranging from electrochemistry,[1] reaction solvent, and catalysis[2] due to their green properties such as nonvolatility, nonflammability, high thermal stability, and other valuable properties. However, ILs pose a serious problem because of their relatively high viscosity. In view of this problem, this research attempts to develop novel low viscous ILs. Regulating the viscosity of ILs is useful for application. There is evidence that the substitution of some electron-withdrawing groups into an anion reduces the viscosity of ILs. For instance, ILs comprising NTf_2^-,[3] BF_4^-,[3b,4] $F(HF)_{2.3}$,[5] $N(CN)_2^-$,[6] $C(CN)_3^-$,[7] and $B(CN)_4^-$[8] have been reported to be low viscous. In these ILs, their low viscosities are due to the anion charge delocalization over two or more electron-withdrawing groups. On the other hand, aromatic azolate anions, such as 1,2,4-triazolate and 1,2,3,4-tetrazolate, provide low viscous ILs, in spite of the non-fluorinated anion. The viscosities at 25 °C of [emim][1,2,4-triazolate] and [emim][1,2,3,4-tetrazolate] are 60.2 and 42.5 cP, respectively.[9] In order to further decrease the viscosity of the azole ILs, the anion charge should be further delocalized by introducing some electron-withdrawing groups. Azolate-based ILs and electrolytes containing substituents have been widely researched.[10] Herein, we explain the preparation and the properties of novel ILs including anions which are substituted with two cyano groups at 4,5-position of 1,2,3-triazolate.

4,5-Dicyano-1,2,3-triazolate salts have already been reported as a sodium, an ammonium, and a guanidinium salt.[10c] These salts are solid at room temperature. Thus, as cations, we select imidazolium, pyridinium, and pyrrolidinium, which are known to readily produce room-temperature ILs. 4,5-Dicyano-2*H*-1,2,3-triazole (**1**), sodium 4,5-dicyano-1,2,3-triazolate monohydrate (**2**), and silver 4,5-dicyano-1,2,3-triazolate (**3**) were synthesized according to the literature.[10c] 1-Ethyl-3-methylimidazolium 4,5-dicyano-1,2,3-triazolate, [emim][DCT] (94%) was obtained by anion exchange between [emim][I] and **3** in water. In addition, 1-butyl-3-methylimidazolium 4,5-dicyano-1,2,3-triazolate, [bmim][DCT] (79%), 1-ethyl-1-methylpyrrolidinium 4,5-dicyano-1,2,3-triazolate, [empyrr][DCT] (74%), 1-butyl-1-methylpyrrolidinium 4,5-dicyano-1,2,3-triazolate, [bmpyrr][DCT] (73%), 1-ethylpyridinium 4,5-dicyano-1,2,3-triazolate, [epy][DCT] (86%), and 1-butylpyridinium 4,5-dicyano-1,2,3-triazolate, [bpy][DCT] (70%) were obtained by the same method as shown in Scheme 1. The structures and purities of these air- and water-stable ILs were supported by data from ^1H and ^{13}C NMR spectra and ESI MS analyses (see the Supporting Information).[13]



Scheme 1. Preparation of triazolate ionic liquids containing double cyano groups, [Cation][DCT].

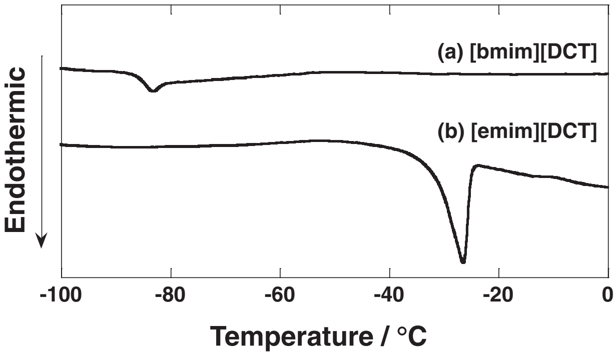


Figure 1. DSC thermograms of (a) [bmim][DCT] and (b) [emim][DCT].

All DCT-based ILs except [empyrr][DCT] and [epy][DCT] are liquids at room temperature. To examine their thermal properties, differential scanning calorimetry (DSC) measurement of all DCT-based ILs was carried out by an EXSTER 6100DSC (Seiko Instruments Inc.) at a heating rate of 2 °C min^{-1}. The glass transition temperature was observed for [bmim][DCT] (Figure 1a), [bmpyrr][DCT], and [bpy][DCT] while the melting endothermic peak is shown in [emim][DCT] (Figure 1b) and [epy][DCT] thermograms. Table 1 summarizes the melting point and the glass transition temperature of each IL. The melting point of [emim][DCT] ($T_m = -26$ °C) is lower than that

Table 1. Melting points and glass transition temperatures of DCT-based ILs

ILs	T_m/°C	T_g/°C
[emim][DCT]	−26	—[b]
[bmim][DCT]	—[a]	−87
[empyrr][DCT]	—[a]	—[b]
[bmpyrr][DCT]	—[a]	−88
[epy][DCT]	17	—[b]
[bpy][DCT]	—[a]	−83

[a]No melting transition observed. [b]No glass transition observed.

Table 2. Viscosities of DCT-based ILs, [emim][Tf_2N], and [emim][1,2,4-triazolate]

ILs	η/cP at 25 °C
[emim][DCT]	38
[bmim][DCT]	79
[bmpyrr][DCT]	68
[bpy][DCT]	151
[bpy][Tf_2N][a]	57
[emim][Tf_2N][b]	34
[emim][1,2,4-triazolate][c]	60

[a]Data from ref. 11. [b]Data from ref. 3a. [c]Data from ref. 9.

of fluorous [emim][Tf_2N] ($T_m = -3$ °C).[3a] Since the two ILs have the same cation, DCT anion has an effect on the melting point as well as the Tf_2N anion. The glass transition temperature of [bmim][DCT], [bmpyrr][DCT], and [bpy][DCT] are −87, −88, and −83 °C, respectively. These glass transition phenomena are similar to that of [emim][1,2,4-triazolate] ($T_g = -76$ °C) which is composed of an azole anion with no cyano groups.[9] 3,5-Dinitro-1,2,4-triazolate (DNT)-based ILs[10a] were reported previously. However, the report provides no data about viscosity because DNT-based ILs have melting points higher than 25 °C (the lowest melting point among DNT-based ILs is 35 °C). Nevertheless, the fact that four DCT-based ILs are liquids at room temperature is thought to provide solid evidence that effects of electron-withdrawing groups on the viscosity of ILs are appreciable for DCT-based ILs.

The viscosity was measured for four ILs in a liquid state at room temperature (Table 2). The [bpy][DCT] shows the highest viscosity (151 cP) at 25 °C among the DCT-based ILs. The viscosity is nearly triple that of [bpy][Tf_2N] (57 cP) composed of the same pyridinium cations.[11] On the other hand, [emim][DCT] has the lowest level of viscosity (38 cP) which has almost the same viscosity as [emim][Tf_2N] (34 cP). In addition, the viscosity level of [emim][DCT] with the cyano groups is lower by 22 cP than that of [emim][1,2,4-triazolate] (60 cP) without the cyano groups. In DCT anion, the anion charge of the triazole ring is delocalized over two cyano groups. The decrease in the anion charge density weakens the cation–anion interaction of ILs. As a result, the viscosity of the DCT-based ILs becomes lower.

In addition to viscosity, the solubility of saccharides is also an important property arising from ILs. The solubility of glucose was influenced much more by the nature of the anion than that of the cation. [bmim][$N(CN)_2$] dissolved 145 g L^{-1} of glucose at 25 °C, whereas [bmim][BF_4] and [bmim][PF_6] dissolved only <0.5 g L^{-1} of glucose.[12] The high solubility of carbohydrates is generally attributed to the H-bond acceptor properties of the $N(CN)_2$ anion. In addition to $N(CN)_2$-based ILs, the cyano groups of DCT-based ILs can act as an H-bond acceptor for dissolving glucose. The solubility of β-D-glucose in [emim][DCT] was measured. [emim][DCT] dissolved 15 g L^{-1} of β-D-glucose at 25 °C. Although the solubility is not higher than that of [bmim][$N(CN)_2$], DCT-based ILs with cyano groups as well as $N(CN)_2$-based ILs clearly have the ability to dissolve glucose. In addition, DCT anion has the possibility of metal coordination by using cyano groups and N atoms in the triazolate ring. The properties of DCT-based ILs such as low viscosity, carbohydrate solubility, and metal coordination offer promise for developing reactive solvents. In particular, the carbohydrate modification by means of metal–DCT-based ILs catalysts might be a useful strategy for the isolation, identification of sugar and the conversion into furan derivatives as fuels. Therefore, we are working on various applications of DCT-based ILs for reaction medium in our laboratory.

This research was supported by JSPS, Grant-in-Aid for Young Scientists (B) (No. 21710089, 2009), by JST, Research for Promoting Technological Seeds (No. 16-020, 2009), by Steel Industry Foundation for the Advancement of Environmental Protection Technology, by Iketani Science and Technology Foundation, and by Hayashi Memorial Foundation for Female Natural Scientists. ESI MS was measured by Ms. Seiko Oka at the Instrumental Analysis Division, Equipment Management Center, Creative Research Institution, Hokkaido University.

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13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.