

Synthesis of Multiester-appended and Multicarboxylic-appended Imidazolium Ionic Liquids

Wei Guo GENG, Xue Hui LI*, Le Fu WANG, Hong Li DUAN, Wei Ping PAN

Department of Chemical Engineering, School of Chemical and Energy Engineering,
South China University of Technology, Guangzhou 510640

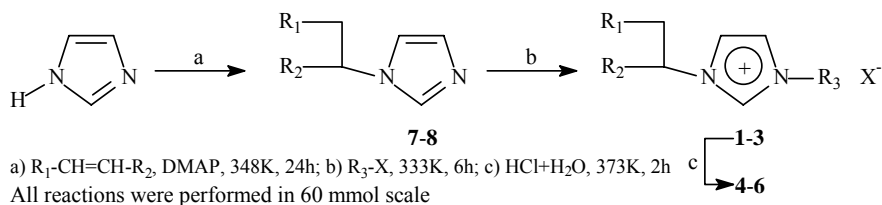
Abstract: Multiester-appended imidazolium ionic liquids were synthesized in a quaternization reaction between the imidazole derivatives carrying single or double esters and ethyl chloroacetate or bromoethane. Multicarboxylic-appended imidazolium ionic liquids were achieved from the hydrolysis of the corresponding ionic liquids. The influences of multifunctional groups on the transition temperatures and viscosity of these new ionic liquids were investigated.

Keywords: Ionic liquid, multiester group, multicarboxylic group, synthesis.

Currently ionic liquids (ILs) are attracting considerable interest as eco-friendly solvents for the replacement of volatile organic solvents in organic synthesis and catalysis¹. Low-melting ILs based on imidazolium cations have dominated this area over the last twenty years², and a variety of functional groups have been incorporated into the cations of ILs in order to modify their physico-chemical properties including carboxyl, nitrile, ester, amide, amine, ether and alcohol, vinyl, alkynyl, phenol, sulfonic acid, sulfonyl chloride, phosphine, 1, 4-cyclohexadiene, urea and thiourea, *etc*³. In virtue of these functional groups, ILs not only act as solvents but also are immobilized as catalysts and reactants in organic synthesis, separation and electrochemical applications⁴.

Researchers have been always trying to improve their understanding of structure-property relationships for ILs in the applications of ILs⁵. The properties of ILs are generally modified by altering the length of alkyl chains in the cations or incorporating a single functional group into the cations. We demonstrate our work of introducing multifunctional groups into one imidazolium cation as an extension of ionic liquids carrying a single functional group. Multifunctional imidazolium ILs exhibit low-melting which offer the opportunities for control over the reactivity of catalysts. This can not be obtained with molecular solvents. In the study of ILs' toxicity, the incorporation of an ester group was postulated to be a balance between reduced chemical stability and increased biodegradability⁶. As a new chance, multicarboxyl-appended imidazolium ILs, the hydrolyzate of multiester-appended imidazolium ILs, can be potentially applied as in catalysis and in immobilization of ILs.

* E-mail: cexhli@scut.edu.cn

Scheme 1 Synthesis of multiester-appended and multicarboxylic-appended imidazolium ILs **1-6****Table 1** Structures of multiester-appended and multicarboxylic-appended imidazolium ILs **1-6**

IL	R_1	R_2	R_3	X
1	$-\text{COOC}_2\text{H}_5$	$-\text{H}$	$-\text{CH}_2\text{COOC}_2\text{H}_5$	Cl
2	$-\text{COOC}_2\text{H}_5$	$-\text{COOC}_2\text{H}_5$	$-\text{C}_2\text{H}_5$	Br
3	$-\text{COOC}_2\text{H}_5$	$-\text{COOC}_2\text{H}_5$	$-\text{CH}_2\text{COOC}_2\text{H}_5$	Cl
4	$-\text{COOH}$	$-\text{H}$	$-\text{CH}_2\text{COOH}$	Cl
5	$-\text{COOH}$	$-\text{COOH}$	$-\text{C}_2\text{H}_5$	Br
6	$-\text{COOH}$	$-\text{COOH}$	$-\text{CH}_2\text{COOH}$	Cl

In this paper, we described the synthesis of new ionic liquids **1-6** with imidazolium cations carrying multiester and multicarboxylic groups and investigated the influences of multiester and multicarboxylic groups on the transition temperatures and viscosity of **1-6**. The synthesis of **1-6** described herein was shown in **Scheme 1**. The structures of **1-6** were displayed in **Table 1**.

Two precursors, 2-imidazol-1-yl-succinic acid diethyl ester **7** and 3-imidazol-1-yl-propionic acid ethyl ester **8**, were synthesized by the addition reactions of imidazole (Acros, 99%) with diethyl maleate (Aldrich, 97%) and ethyl acrylate (Aldrich, 99%), respectively, using DMAP (Acros, 99%) as the catalyst. Modifying the literature procedure for 1-alkyl-3-methylimidazolium bromides or chlorides, the precursor **8** was reacted with ethyl chloroacetate (Acros, 99%) giving **1**, and the precursor **7** was reacted with bromoethane (Acros, 98%) giving **2** and with ethyl chloroacetate giving **3**. The esters in ILs **1-3** hydrolyzed with hydrochloric acid to yield ILs **4-6** carrying with multicarboxylic acids. All salts **1-6** were analyzed by ^1H NMR, ^{13}C NMR, ESI-MS, FT-IR and elemental analysis⁷. Water contents of **1-6** after drying, measured by Karl Fischer titration, were 23-50 ppm.

The transition temperatures for **1-6** were determined by differential scanning calorimetry (Netzsch DSC 204F1 equipped with the liquid nitrogen cooling accessory, 10-20 mg samples, $10\text{ }^\circ\text{C min}^{-1}$ heating and cooling rates) and presented in **Table 2**. It was noticeable that liquid of ILs **1-6** were different from conventional imidazolium bromides or chlorides at room temperature. No melting points could be observed. Only glass transition points were observed for **1-6**, indicating that with our cooling conditions ILs **1-6** crystalized very slowly and became increasingly viscous and only turned into glasses, but not crystals. The effect of cation size was obvious: ILs **1-3** carrying esters groups present lower glass transition points than their corresponding hydrolyzate **4-6**. The cation symmetry effect on glass transition points determined that IL **1** and **4** take on higher glass transition points than **2** and **5**, respectively.

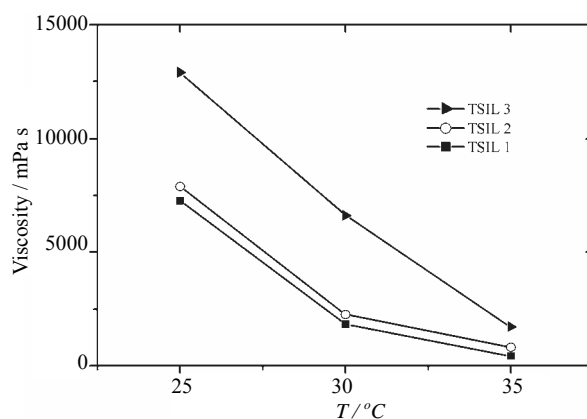
Table 2 Transition temperatures for **1-6** measured from transition midpoints for glass transitions from DSC; enthalpy (kJ mol⁻¹) given in parentheses

IL	Number of functional groups	Treatment	$T_g^a / ^\circ\text{C}$ ($\Delta H / \text{kJ mol}^{-1}$)
1	2	Cool	-44.6 (0.5)
		Heat	-42.3 (0.7)
2	2	Cool	-55.8 (2.8)
		Heat	-51.8 (1.0)
3	3	Cool	-42.9 (4.6)
		Heat	-39.5 (1.9)
4	2	Cool	-37.4 (0.6)
		Heat	-35.6 (0.7)
5	2	Cool	-46.5 (3.1)
		Heat	-43.7 (1.3)
6	3	Cool	-40.3 (4.2)
		Heat	-38.5 (2.2)

^a T_g = glass transition point.

The viscosity for **1-3** was shown in **Figure 1**. For these ILs, the viscosities decreased markedly as the temperature increased from 25 °C to 30, 35 °C. At 35 °C, the viscosity was only 6-13 % of that at 25 °C. The viscosities of the ILs with the same number of ester groups varied slightly at different temperature. The ILs with more ester groups appeared more viscous at each temperature presumably as a result of increased van der Waals interactions. In addition, ILs **4-6** with much more stronger COO-H \cdots X⁻ H bond appeared viscous beyond measurement limits, thus the data of their viscosity can not be collected under the above conditions.

Finally, anion metathesis can be used to prepare multilester-appended imidazolium ILs containing a wide variety of anions, such as [PF₆]⁻, [BF₄]⁻ and [CF₃SO₃]⁻, *etc.* We are carrying out the applications of multicarboxyl-appended imidazolium ILs in acidic catalysis and in immobilization of ionic liquids. Detailed reports of our ongoing work will be published in future.

Figure 1 Viscosity for ILs **1-3** measured with a Brookfield DV-II+ viscometer on 20 mL of samples at 25 °C, 30 °C and 35 °C respectively using an external temperature controller

In conclusion, we have reported the initial synthesis of new ionic liquids with imidazolium cations carrying multiester or multicarboxyl groups. It is available to change the properties of ionic liquids by controlling the number of functional groups incorporated into the cation. Multicarboxyl-appended imidazolium ILs will greatly extend the application of ionic liquids in acid-catalysis and will potentially provide a new type of immobilization for ionic liquids.

Acknowledgments

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7. ¹H NMR, ¹³C NMR, FT-IR, ESI-MS and elemental analysis data of typical compound **3**: ¹H NMR (DMSO-*d*₆, δ ppm): 9.34 (s, 1H, H-2), 7.92 (s, 1H, H-4), 7.80 (s, 1H, H-5), 5.95 (x (apparent t), 1H, *J* = 7.2 Hz, CH), 5.31 (s, 2H, CH₂), 4.19 (m, 4H, OCH₂), 4.06 (q, 2H, *J* = 7.1 Hz, OCH₂), 3.37 (m, 2H, CH₂), 1.20 (m, 9H, CH₃); ¹³C NMR (DMSO-*d*₆, δ ppm): 169.2 (CO), 167.1 (CO), 166.7 (CO), 138.6 (C2), 123.9 (C4), 122.2 (C5), 62.7 (CH₂), 62.1 (CH₂), 61.2 (CH₂), 57.8 (CH), 49.9 (CH₂), 35.8 (CH₂), 14.0 (CH₃), 13.9 (CH₃); IR (KBr, cm⁻¹): 3147, 3108, 2985, 2941, 2875, 1741, 1638, 1561, 1469, 1401, 1379, 1352, 1220, 1178, 1097, 1020; ESI-MS: 327 [M-Cl]⁺; Anal. Calcd. for C₁₅H₂₃ClN₂O₆ (%): C 49.66, H 6.39, N 7.72; Found: C 49.72, H 6.46, N 7.79.

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