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A comparison study on the properties of 1,3-dialkylimidazolium tetrafluoroborate salts prepared by halogen-free and traditional method☆

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ABSTRACT

A series of 1,3-dialkylimidazolium tetrafluoroborate salts had been prepared *via* one-step alkylation of N-alkylimidazole with trialkyloxonium salts and traditional two-step method, respectively. The possible impurities in these ionic liquids (ILs) such as Cl^-, Br^-, Na^+ and alkyl imidazoles were measured. Detailed characterizations of two approaches in the ILs properties and performances such as spectroscopic properties, phase behavior, viscosity, refractive index, and electrochemical properties were systemically conducted. The obtained results showed that the variety of synthesized methods resulted in the distinct changes in physicochemical properties for the same IL. Therein, the comparison of spectroscopic properties and phase behaviors for the employed ILs were emphasized. Furthermore, in most cases, the ILs prepared by traditional two-step possessed the higher viscosity, lower refractive index as well as lower ionic conductivity than that of ILs prepared by one-step. It was worth noting that the 1-decyl-3-ethylimidazolium tetrafluoroborate ($[DEIm]BF_4$) prepared with the traditional and trialkyloxonium methods respectively exhibited distinctly different phase and fluorescence behaviors. The reason might be attributed to the significant improvement on the purities of ILs by the one-step strategy.

1. Introduction

Ionic liquids (ILs) have received extensive attention due to their unique properties (*e.g.* negligible vapor pressure, high thermal, chemical and electrochemical stability, and high ionic conductivity) as well as increasing applications that spread in both academia and industry fields as diverse as electrochemistry [1], synthesis [2], catalysis [3], material [4], separation [5], biotechnology [6], and so on. Up to now, ILs can be prepared through several methods. The first efficient method involves acid–base reactions from a suitable precursor compound and an acid. For example, Wasserscheid's group reported a highly promising approach to hydroxide-based precursors used for the synthesis of ILs [7]. The second method concerns one-step alkylation of N- or P-containing compounds using alkyl sulfates [8], carbonates [9], or phosphates [10] *etc.* as alkylating agent, which is considered as a very efficient protocol to produce halogen-free ILs. The third method, and also, the most extensively used strategy, is a two-step method, *i.e.*, a quaternization reaction with the aim to form an IL precursor containing a target cation, and followed by a metathesis process leading to the desired product. Therefore, to synthesize a target IL, the reaction routes should be taken into account as required.

However, the different synthetic methods may result in the distinction in the purity, and further effect on the properties and performances for the same IL. According to the previous literatures [11,12], the possible impurities in conventional 1,3-dialkylimidazolium BF_4^- salts were unreacted alkylimidazoles, alkyl halide, halogen anions (Br^-, Cl^-), inorganic cations (Na^+, K^+, NH_4^+) and water *etc.*, which have remarkable influence on the physicochemical properties and performance of ILs. Halides are known to coordinate to the transition-metal centers of catalysts, and thus affecting the rate of reaction such as hydrogenations [13,14] and Heck-type reactions [15]. It has also been reported [11b] that residual chloride ions, even at a very low level of concentration, increase the viscosity and decrease the density of ILs. The presence of water and organic solvents was proven to decrease the viscosity of ILs [11]. As an important contamination in 1,3-dialkylimidazolium based ILs, the unreacted alkylimidzole has been ignored in the past long time. Of late, it has been reported that the presence of *ca.* 0.18 mol% 1-methylimidazole in ILs led to a sharp decline in turn-over frequency in

☆ Electronic supporting information available: Experimental details with ^1H NMR as well as characterizations of physicochemical properties with DSC, Infrared and Raman, X-Ray Photoelectron Spectroscopy, UV–vis, etc. are available free of charge.

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the metathesis of 1-octene to 7-tetradecene [16]. Noticeably, the impurities make the reported physicochemical data of ILs be omnifarious in the previous literatures. Moreover, in the presence of impurities in ILs, especially for halogen ions, catalytic results and physicochemical data reported would be not repeatable, unless the purity of the ILs was determined.

Currently, the most widely used 1,3-dialkylimidazolium tetrafluoroborate (BF_4^-) salts were mainly prepared by traditional two-step approach. Recently, another efficient method was reported by Egashira et al. for the one-step synthesis of dialkylimidazolium BF_4^- ILs *via* the alkylation of N-alkylimidazole using $Me_3O^+ BF_4^-$ as an alkylating agent [17a]. Since there are two different methods for the syntheses of dialkylimidazolium BF_4^- based ILs, which are very important in the fields of ILs' research and application, it is worthy of studying the influence of different synthetic methods on the properties and performances of ILs. In this view, some earlier research had been undertaken in our laboratory [17b], wherein an attempt was made to systematically synthesize a series of dialkylimidazolium BF_4^- salts according to both the one-step method and traditional two-step approach as shown in Scheme 1. Here, the possible impurity contents such as halogen ions, inorganic metal ions, and unreacted alkylimidazoles were measured in detail. Between the ILs generated by new approach and two-step method, respectively, a scientific comparison of properties and performances such as spectroscopic properties, phase behavior, viscosity, refractive index, and electrochemical properties were carried on.

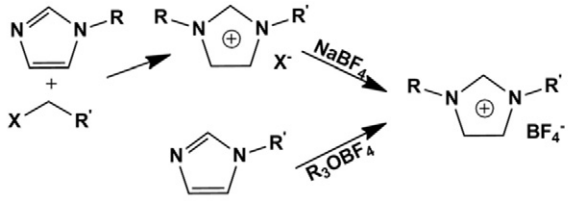
2. Experimental

2.1. Materials

Sodium (AR) was obtained from Kermel. Imidazole (AR) and 1-bromooctane (AR) were obtained from Beijing Chemical Reagent Corporation Ltd. Trimethyloxonium tetrafluoroborate (>98%) and triethyloxonium tetrafluoroborate (95%, stab. with 3–5% diethyl ether) were obtained from Alfa Aesar. Trimethyloxonium tetrafluoroborate was washed with dichloromethane three times and triethyloxonium tetrafluoroborate was recrystallized from dichloromethane by diethyl ether before using. High purity $[BMIm]BF_4$ was obtained from Merck for the purpose of comparison. The other reagents used in this study were obtained from Tianjin Chemical Reagent Corporation Ltd. and were used without further purification.

2.2. Synthesis and measurement

All the ILs prepared by new method were washed twice by diethyl ether and dried at 90 °C under 1–5 mm Hg for 1 h. For the purpose of comparison, the counterparts of above ILs were synthesized by traditional two-step method reported previously [18]. Then these counterparts were dissolved in dichloromethane, respectively, and washed by a small quantity of distilled water three times ($V_{IL}/V_{dichloromethane}/V_{distilled\ water} = 1/10/0.05$). The dichloromethane phase was collected and followed by distillation. The products were further dried at 90 °C under 1–5 mm Hg for 1 h. The detailed information on preparation of ILs was given in Supporting Information.



Scheme 1. Two different synthesis methods of dialkylimidazolium BF_4^- salts.

All ILs were dried at 90 °C under 1–5 mm Hg for 1 h before measured. ^1H NMR spectrum was recorded on a Bruker AMX FT 400-MHz NMR spectrometer. Chemical shifts were reported in parts per million (ppm, δ). The halogen and Na^+ contents were measured using METTER TOLEDO SevenMulti meter with Cl^-, Br^- and Na^+ ion selective electrodes at 25 °C. The alkylimidazole content was measured by assisting of Agilent 6820 Gas Chromatography. The detailed procedure of measurement was given in supporting information. The viscosity was measured by BROOKFIELD DV-III ULTRA Programmable Rheometer at 25 °C. Ultra-Vis spectra were conducted on an Agilent 8453 UV–vis spectrophotometer. Infrared spectra were recorded by Thermo Nicolet 5700 FT-IR spectrometer as a thin film on sodium bromide and absorptions were reported in wavenumbers (cm^{-1}). Raman spectra were recorded by Thermo Nicolet 5700 FT-Raman spectrometer and absorptions were reported in Raman Shift (cm^{-1}). The fluorescence spectra were recorded at room temperature on a Hitachi model F-7000 FL spectrophotometer at a scan speed of 1200 nm min^{-1}. X-Ray Photoelectron Spectroscopy (XPS) analyses were performed on a VG ESCALAB 210 instrument with Mg Kα source (1253.6 eV) and calibrated *versus* C 1s peak at 285.0 eV. A thin layer of IL was deposited on a polycrystalline gold substrate, and was kept under moderate vacuum for at least 12 h before introducing them into the analytical chamber of the XPS instrument. Spectrometer pass energies of 100 eV for the survey spectra and 30 eV for high resolution spectra were used for all elemental spectral regions. The pressure in the analytical chamber was 10^{-9} Torr. Thermal analysis and temperature-dependent phase behavior were examined in the circular range of −100 to 100 °C by using a METTER TOLEDO DSC822^e Differential Scanning Calorimeter with scan rate of 10 °C min^{-1} under N_2 atmosphere. The samples for DSC measurements were tightly sealed in Al pans. The glass transition temperature (T_g) was recorded as the midpoint of the glass transition. Melting point (T_m) and crystal-crystal transition temperature (T_c) were recorded as the onset of the melting transition and the onset of crystal-crystal transition of the DSC curve, respectively. Electrospray ionization mass spectra were recorded on a Bruker Daltonics APEX II 47e FTMS. The samples were dissolved in acetonitrile. Ion conductivity was measured by METTER TOLEDO SevenMulti meter with InLab 710 conductivity electrode at 25 °C. Electrochemical measurements for cyclic voltammetry were performed using a CHI660A electrochemical workstation (CH instruments, USA).

3. Results and discussion

Nine ILs synthesized by new method (*i.e.* $[EMIm]BF_4$, $[BMIm]BF_4$, $[HMIm]BF_4$, $[OMIm]BF_4$, $[DMIm]BF_4$, $[BEIm]BF_4$, $[HEIm]BF_4$, $[OEIm]BF_4$ and $[DEIm]BF_4$) were colorless liquids at room temperature. The detail preparation procedure and ^1H NMR data were shown in supporting information. Except that $[OMIm]BF_4$, $[DMIm]BF_4$, $[OEIm]BF_4$ and $[DEIm]BF_4$ exhibited the colour of pale yellow, the rest ILs synthesized by two-step method were colorless liquids.

3.1. Measurement of possible impurity contents in ILs

The possible impurities in ILs, including unreacted alkylimidazole, Br^-, Cl^-, Na^+, and water were taken into account. The measurement of alkylimidazoles and halogen ions would be particularly emphasized, since both of them were dominating contaminations.

3.1.1. Halogen ions and inorganic metal ions

From Table 1, it could be seen that the residual Br^-, Cl^- and Na^+ were found in all ILs by two-step method. Among these studied ILs, $[BMIm]BF_4$, $[HMIm]BF_4$, $[BEIm]BF_4$ and $[HEIm]BF_4$ were prepared from the chloride precursors, while other ILs (*i.e.* $[EMIm]BF_4$, $[OMIm]BF_4$, $[DMIm]BF_4$, $[OEIm]BF_4$ and $[DEIm]BF_4$) derived from the anion-exchange reactions of the corresponding bromide precursors. The residual Cl^- contents were ranged from 0.12 to 1.03 wt%, while the Br^- contents were determined as 0.69–2.12 wt%, in which $[HMIm]BF_4$ and