Synthesis and Characterization of Brønsted Acidic Ionic Liquids

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***Abstract*—Five kinds of Brønsted-acidic ionic liquids with different nitrogen-contained chemical groups and different anions were synthesized, and were respectively characterized by nuclear magnetic resonance(NMR), infrared spectrum (IR), electrospray ionization mass spectrum (ESI-MS) and thermogravimetry(TG.). It was found that ten kinds of ionic liquids were synthesized, whose structures were consistent with the designed ones. And all of their purities were more than 95 %. These ionic liquids possess high thermal stability and wide liquid range,and their decomposition temperatures are higher than 300℃ except that the tempetature of [MPy]NO_3 is 199℃by analyzing TG .**

Keywords-ionic liquids; infrared spectrum; nuclear magnetic resonance; electrospray ionization mass spectrum; thermogravimetry

I. INTRODUCTION

Ionic liquid is generally a substance in liquid state at or near room temperature, which consists of specific organic cations with a big volume and an asymmetric structure and inorganic anions with a small volume. In comparison with traditional catalysts such as solid acid and liquid acid, acidic ionic catalyst has many advantages such as high density reactive site, nonvolatility, wide liquid range, high thermal stability and acidity and structure adjustability [1-3]. At present, using ionic structure designability to prepare high efficiency catalyst according to the characteristics of different reaction systems has become a research hotspot[4-5]. For this reason, in the present study, we discussed some common combinations of cations and anions in acidic ionic liquids, designed and synthesized five types of Brønsted acidic ionic liquids for preparation of biodiesel and characterized their structures and physical properties by NMR, FT-IR, ESI-MS and TG-DTA characterization methods to provide basis for further research of high efficiency catalyst.

II. EXPERIMENTS

A. Instruments and Reagents

Varianmercury-plus 400 MHz pulse Fourier transform nuclear magnetic resonance spectrometer, using TMS as the internal standard and D_2O as the solvent, manufactured by America Varian company; Nexus670 infrared spectrometer, manufactured by America Nicolet company; FINNIGAN LTQ ion trap electrospray mass spectrometer, manufactured by America Thermo Electron company. TRT-1 thermogravimetric analyzer, manufactured by China Beijing Buoyn Smelting Technology Ltd.

Pyridine, 2-methylpyridine, triethylamine, concentrated H_2SO_4, concentrated H_3PO_4, concentrated HNO_3, anhydrous ether, ethyl acetate and ethanol, which are analytical reagents; N-methylimidazole, with a purity of≥98%；pyridine propane sulfonic ylide, with a purity of≥99%.

B. Preparation of Ionic Liquids

1) Synthesis of pyridine ionic liquid

At room temperature, put a certain amount of reactant pyridine into a 250mL three-neck flask equipped with motor stirrer, reflux condenser and thermometer, add equal moles of phosphoric acid or sulfuric acid dropwise slowly (to prevent violent heat release, the adding speed is controlled to 3-5s/drop). After the dropwise addition, the mixture with sulfuric acid condenses into a white crystal, while the mixture with phosphoric acid becomes a transparent liquid. Heat up slowly to 80℃ and stir for 0.5 days, the crystal melts and the mixture turns from colorless and transparent to a light yellow transparent solution. Continue to heat up slowly to 120℃ and carry out reflux stirring for 2-3 days near the boiling point of pyridine, a brown transparent viscous liquid is obtained. Carry out equal-amount washing for 3 times respectively with ethyl acetate and ether to remove the unreacted materials and organic solvent. During washing, the ionic liquid may condense into solid state, so heating up with air dry oven and washing with solvent shall be carried out alternately. Then, carry out forced air drying for 1 day at 100℃, heat up slowly to 100℃ and carry out vacuum drying for 1 day, a pyridine ionic liquid is obtained.

2) Synthesis of the Other Four Types of Ionic Liquids

The synthesis of quaternary ammonium ionic liquid is carried out in accordance with literature[6], the synthesis of methylimidazole ionic liquid is carried out in accordance with literatures[7-8], and the synthesis of 2-methylpyridine ionic liquid is carried out in accordance with literatures[9-10]. The synthesis of pyridine propane sulfonic ionic liquid is carried out in accordance with literature[11].

Five types of ten protonated ionic liquids having different nitrogen-containing functional groups are prepared by the above methods, which are expressed as 1#-10#.

Their structures are shown in Figure 1.

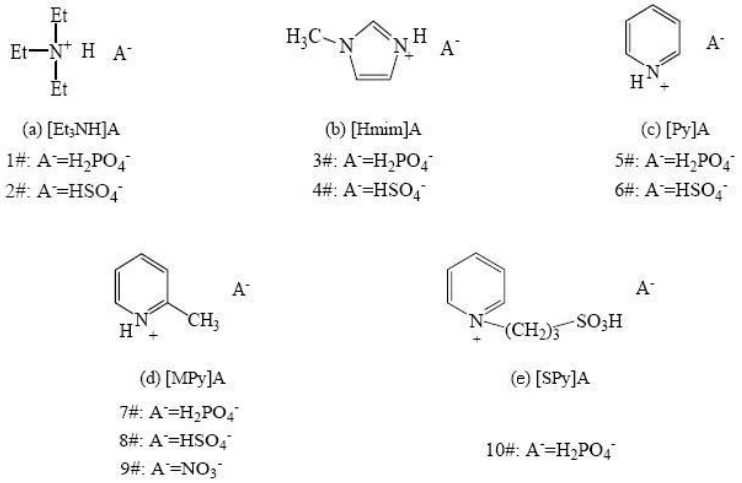


Figure 1. Structures of ionic liquids

III. RESULTS AND DISCUSSION

A. Nuclear Magnetic Resonance Analysis

The ^{1}HNMR and ^{13}CNMR results of the ten ionic liquids measured with the nuclear magnetic resonance spectrometer are given in Table I:

TABLE I. ^{1}H-NMR AND ^{13}C-NMR SPECTRA DATA OF IONIC LIQUIDS

The sample	^{1}HNMR(D_2O)	^{13}CNMR(D_2O)
1#	δ0.997(t,3H), 2.906(m,2H)	δ8.347, 46.723
2#	δ1.004(t,3H), 2.926(m,2H)	δ8.439, 46.822
3#	δ3.557(t,3H), 7.072(d,2H), 8.291(s,1H)	δ35.336, 119.359, 122.803, 134.807
4#	δ3.825(d,2H), 7.342(d,2H), 8.566(s,1H)	δ35.564, 119.587, 123.066, 135.112
5#	δ7.931(t,2H), 8.482(m,1H), 8.647(t,2H)	δ127.578, 141.242, 147.370
6#	δ7.752(t,2H), 8.291(m,1H), 8.465(t,2H)	δ127.311, 141.006, 146.969
7#	δ2.372(s,3H), 7.442(m,2H), 8.031(t,1H), 8.180(d,1H)	δ19.986, 124.308, 127.959, 140.236, 146.474, 153.760
8#	δ2.468(s,3H), 7.543(m,2H), 8.392(t,1H), 8.287(d,1H)	δ19.089, 124.427, 128.077, 140.343, 146.626, 153.855
9#	δ2.729(s,3H), 7.800(m,2H), 8.392(t,1H), 8.541(d,1H)	δ19.089, 124.488, 128.134, 140.415, 146.710, 153.985
10#	δ2.395(m,2H), 2.915(t,2H), 4.703(t,2H), 8.018(t,2H), 8.493(m,1H), 8.814(d,2H)	δ26.291, 47.214, 60.060, 128.584, 144.561, 146.097

From the above nuclear magnetic data and spectrograms, we can see that the ten ionic liquids are the target products and that they are consistent with the structural formulas of ionic liquids shown in Figure 1. In addition, the peak intensity of the impurity peak of the ^{1}HNMR spectrum is very small and almost invisible. This shows that the purity of the ionic liquid prepared is greater than 95% and that the synthesis and purification methods of the ionic liquids are reliable and can prepare high purity ionic liquids.

B. Infrared Spectrum Analysis

The infrared spectrum determination results of the ten ionic liquids classified by the cation are shown in Figure 2. From the figure, we can see that in ammonium ionic liquids 1# and 2#, the deformation vibration absorption peaks of $-CH_2-$ and $-CH_3$ in $N-CH_2CH_3$ appear respectively near 1480cm^{-1} and 1391cm^{-1} and the stretching vibration absorption peak of C-H in $-CH_2$ appears near 2990cm^{-1}, and that in tertiary amine salt, the stretching vibration absorption peak of N-H radical appears at 2680cm^{-1}.

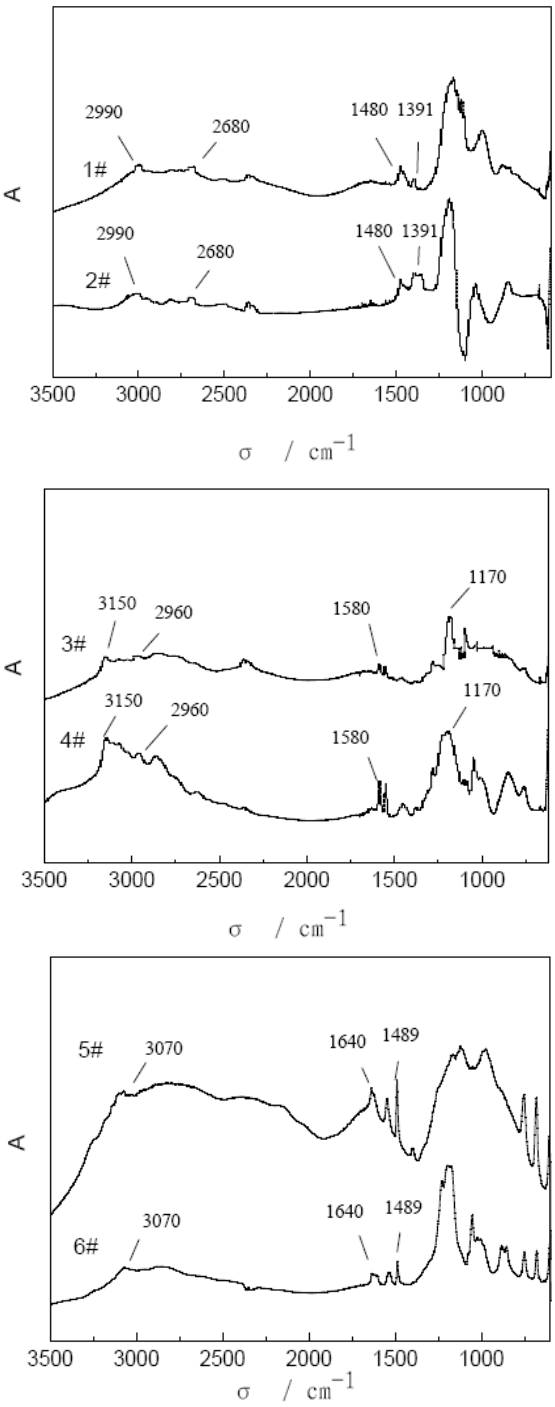
In the spectrograms of imidazole ionic liquids 3# and 4#, the stretching vibration peak of C-H in the imidazole ring appears at 3156cm^{-1}, the bending vibration appears at 1170cm^{-1}, the stretching vibration of C=N in the imidazole ring appears at 1575cm^{-1}, the asymmetrical stretching vibration absorption peak of C-H in the substituent $-CH_3$ in the imidazole ring appears at 2960cm^{-1}.

From the infrared spectrograms of pyridine ionic liquids 5# and 6#, we can see that the stretching vibrations of C=N and C=C in the pyridine ring appear respectively near 1640cm^{-1} and 1489cm^{-1} and the stretching vibration of C-H in the pyridine ring appears near 3070cm^{-1}.

Similar to pyridine ionic liquids, in 2-methylpyridine ionic liquids 7#, 8# and 9#, the stretching vibrations of C=N and C=C in the pyridine ring appear respectively near 1640cm^{-1} and 1490cm^{-1} and the stretching vibration of C-H in the pyridine ring appears near 3070cm^{-1}.

In pyridine propane sulfonic ionic liquid 10#, the stretching vibration of C-H in the pyridine ring also appears near 3070cm^{-1}, the stretching vibrations of C=N and C=C in the pyridine ring appear respectively near 1640cm^{-1} and 1490cm^{-1} and the antisymmetric and symmetric stretching

vibration absorption peaks of S=O in $-SO_3H$ appear near 1345cm^{-1} and 1155cm^{-1}. Therefore, this further proves that the structures of the ten ionic liquids conform to the structural formulas shown in Figure 1.



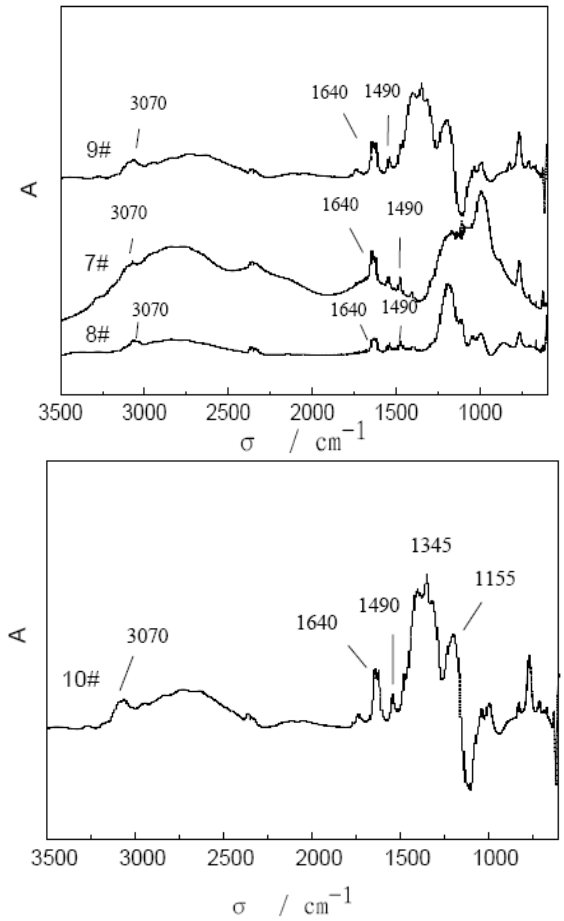


Figure 2. IR spectra of ionic liquids

C. *Electrospray Mass Spectrum Analysis*

The electrospray mass spectrums in cation and anion modes of the ten ionic liquids, arranged in the order of 1#-10#, are shown in Figure 3. The upper one is the mass spectrum in cation mode, and the lower one is the mass spectrum in anion mode. From the structural formulas shown in Figure 1, we can see that the cations of the ten ionic liquids are $[Et_3NH]^+$, $[HMIm]^+$, $[Py]^+$, $[MPy]^+$ and $[SPy]^+$, and their relative molecular masses are 102.19, 83.08, 80.01, 94.13 and 202.03; the anions are $H_2PO_4^-$, HSO_4^- and NO_3-, and their relative molecular masses are 97.10, 97.8 and 62.03. Therefore, the relative molecular masses of the ten ionic liquids are 199.27, 199.19, 180.10, 180.08, 177.20, 177.18, 191.13, 191.21, 156.14 and 359.03.

From the cation mode spectrums shown in Figure 3, we can see that in quaternary ammonium ionic liquids 1# and 2#, the polymeric cation peaks 301.10 and 301.12 of the whole molecule and the cation exist. In addition, in ionic liquid 2#, the polymeric cation peak 499.75 of two molecules and the cation exists. From the anion mode spectrums, the dimeric anion peak 194.96 and trimeric anion peaks 292.78 and 292.93 of the two anions H_2PO_4- and HSO_4- can be observed.

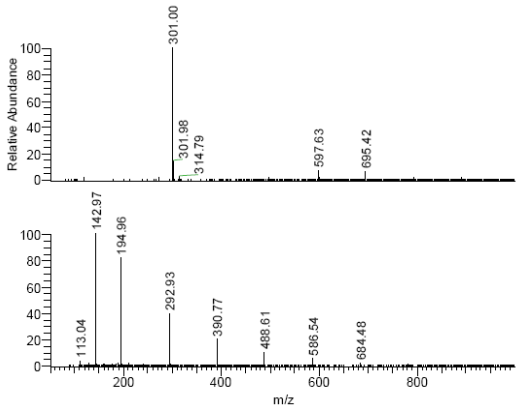
In methylimidazole ionic liquids 3# and 4#, the dimeric cation peaks 164.89 and 164.90 of the cation $[HMIm]^+$ exist. In ionic liquid 4#, the polymeric cation peak 262.84 of the whole molecule and the cation and the low-abundance polymeric cation peak 442.67 of two molecules and the cation also exist. From the anion mode spectrums, the dimeric and trimeric anion peaks 194.96 and 292.93 of the two anions $H_2PO_4^-$ and HSO_4^- can be observed. In ionic liquid 3#, the tetrameric and pentameric anion peaks of $H_2PO_4^-$ also exist.

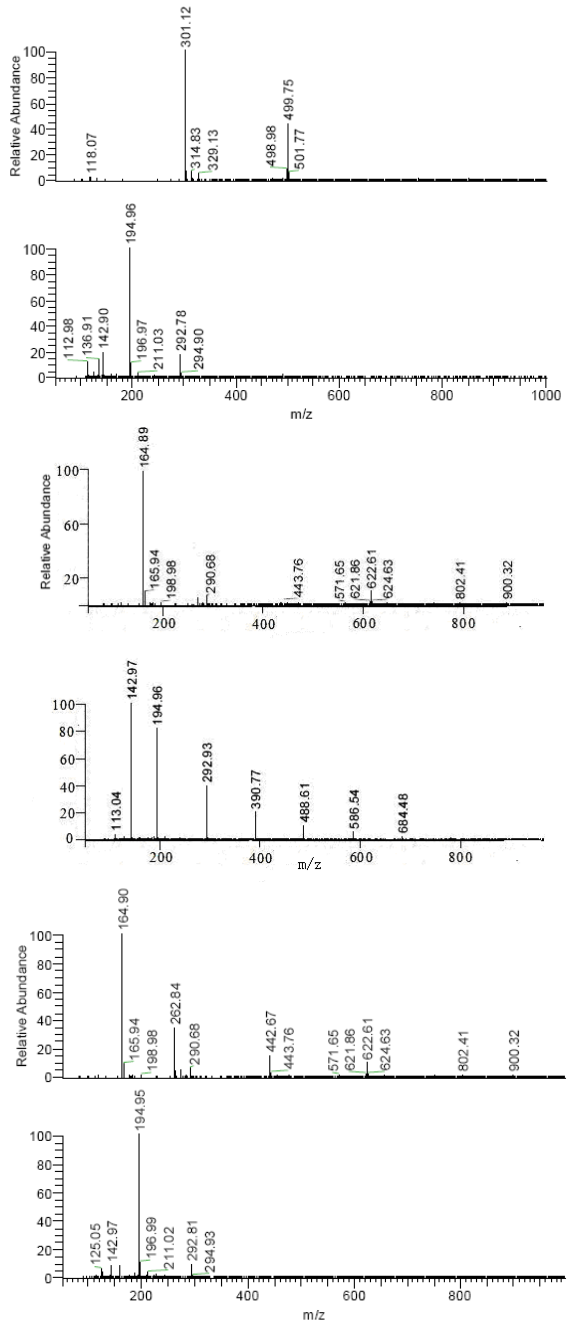
In pyridine ionic liquids 5# and 6#, the cation peak 80.03 and the dimeric cation peak 160.04 exist. In ionic liquid 6#, the polymeric cation peak 256.97 of the whole molecule and the cation also exists. From the anion mode spectrums, the anion peak, dimeric and trimeric anion peaks 96.99, 194.96 and 292.93 of the two anions $H_2PO_4^-$ and HSO_4^- can be observed. In ionic liquid 5#, the tetrameric and pentameric anion peaks of $H_2PO_4^-$ also exists.

From the cation mode spectrums shown in Figure 3, we can see that in 2-methylpyridine ionic liquids 7#, 8# and 9#, the polymeric cation peaks 284.83, 285.00 and 249.80 of the whole molecule and the cation exist. In ionic liquid 8#, the low-abundance polymeric cation peak 475.57 of two molecules and the cation also exists. From the anion mode spectrums, the dimeric anion peaks 194.96, 194.95 and 124.89 of the three anions $H_2PO_4^-$, HSO_4^- and NO_3^- can be observed. In ionic liquid 7#, the trimeric, tetrameric and pentameric anion peaks of $H_2PO_4^-$ also exists.

For ionic liquid 10#, pyridine propane sulfonic sulfate, from Figure 3, we can see that the dimers of the cation and the cation corresponding to the peak values of 202.03 and 403.10 and the dimeric anion peak 195.05 of the anion $H_2PO_4^-$ exist in the product.

Through the above comparative analysis, we know that the results of the cation and anion electrospray mass spectrums of the ten ionic liquids conform to the expected composite molecular weight of the ionic liquid. This further proves the structural formulas shown in Figure 1.





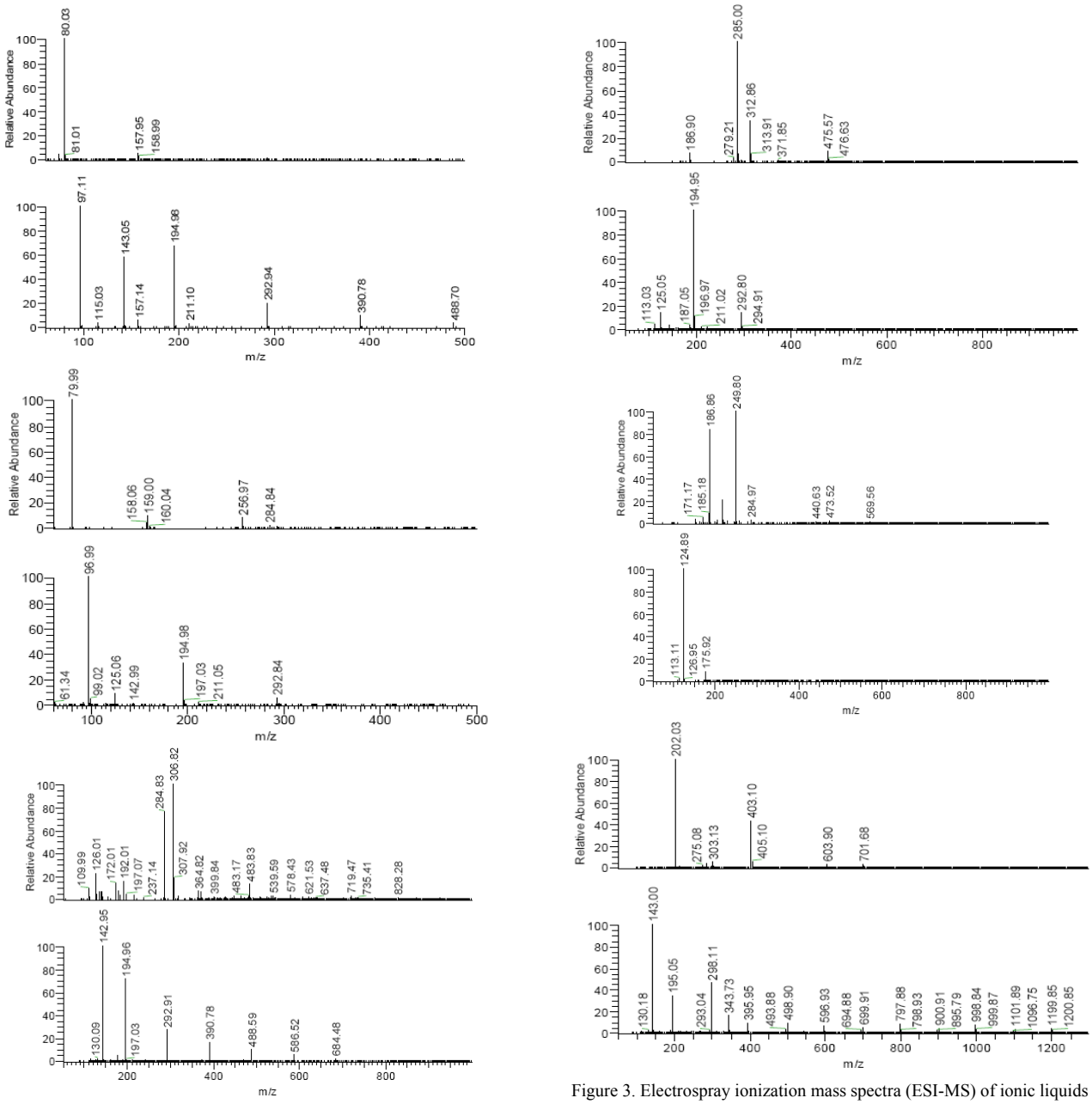


Figure 3. Electrospray ionization mass spectra (ESI-MS) of ionic liquids

D. Thermogravimetric Anlysis

The measured thermogravimetric temperature (decomposition temperature) of the ionic liquids [HMIm]HSO_4, [Py]HSO_4, [MPy]HSO_4, [MPy]NO_3 are respectively 364, 311, 317 and 199℃ This shows that the imidazole, pyridine and methylpyridine ionic liquids containing HSO_4^- have a high thermal stability and a wide liquid range of greater than 300℃. The ionic liquid containing $H_2PO_4^-$ has a similar structure to the above ionic liquids, and therefore has a similar thermogravimetric temperature, a high thermal stability and a wide liquid range. However, the ionic liquid containing NO_3^- has a low

thermogravimetric temperature and a liquid range of about 200℃.

IV. CONCLUSION

This paper studies the preparation methods for nine protonated ionic liquids having different nitrogen-containing functional groups and one B acidic ionic liquid having $-SO_3H$ functional group and characterizes them by NMR, IR and ESI-MS characterization methods. It is found that the ionic liquids prepared in this paper conform to the expected structure and have a purity of greater than 95%. This shows that the preparation and purification methods of the ionic liquids are reliable. All the electrospray mass spectrums indicate the cation and anion peaks or polymeric peaks of the ionic liquid and conform to the expected composite molecular weight of the ionic liquid. This shows that the structure of the synthesized ionic liquid conforms to the expected structural formula. Furthermore, no visible impurity peak is observed, which shows that the ionic liquids have a high purity. Thermogravimetric analysis shows that, the ionic liquids prepared have a high decomposition temperature of above 300℃, except for $[MPy]NO_3$ which has a decomposition temperature of 199℃, and have a high thermal stability and a wide liquid range. The present study is a basic study. It will provide a theoretical basis for the research of the catalytic performance of ionic liquids.

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