

Microwave-Assisted Synthesis and Spectral Identification of [Rmim]PF₆ (R = p,b,c₆) Ionic Liquids

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By microwave irradiation, the intermediates of imidazolium ionic liquids: 1-Butyl-3-methylimidazolium bromide ([bmim]Br), 1-propyl-3-methylimidazolium bromide ([pmim]Br), 1-hexyl-3-methylimidazolium bromide ([c₆mim]Br) were synthesized, respectively from 1-methylimidazole and organic bromide (1-bromobutane, 1-bromopropane, 1-bromohexane). The optimal technological conditions were obtained by the crossed experiment, *i.e.*, 1-methylimidazole/organic halide (in mole): 1:1.1, temperature: 80 °C, time: 20 min. The product yield was 90 % and more. Each of them reacted with HPF₆ for 4 h at room temperature, respectively to get hydrophobic imidazolium ionic liquids, *i.e.*, 1-butyl-3-methyl-imidazolium hexafluorophosphate ([bmim]PF₆), 1-propyl-3-methyl-imidazolium hexafluorophosphate ([pmim]PF₆), 1-hexane-3-methyl-imidazolium hexafluorophosphate ([c₆mim]PF₆). The product yield was about 50 %. Their structures were analyzed and identified by UV-vis, IR and ¹H NMR spectra, respectively.

Key Words: Ionic liquid, Microwave, [bmim]PF₆, [pmim]PF₆, [c₆mim]PF₆, Spectroanalysis.

INTRODUCTION

Green chemistry is an important direction of chemical progress in this century. It is an important chemical research field to exploit substitutes for volatile organic solvents and high-effect nontoxic catalysts to reduce environmental pollution today. Ionic liquids as green solvents have become a hotspot of recent synthetic chemistry because of their particular characters¹. Ionic liquids mean the organic liquids completely composed of ions at room or near room temperature. They have particular characters such as environment- friendly, repetitious use, big electrochemical window, very low vapour tension and no volatile. They provide new chemical reaction surroundings for chemists² and have been used in chemical separation, electrochemistry and so on.

There are many kinds of ionic liquids. They are usually divided into two classes, *i.e.*, pyridine class and imidazole class³. It is difficult for ionic liquids with pyridine matrix to be decomposed⁴. However, it is very easy for ionic liquids with imidazole matrix to be decomposed by animalcules and their toxicity is very low⁵. The application of them can better reduce environmental pollution. Therefore, imidazole class of ionic liquid is very important in research and application of ionic liquids. The microwave-assisted synthesis of 1-butyl-3-methyl-imidazolium hexafluorophosphate ([bmim]PF₆), 1-propyl-3-methyl-imidazolium hexafluorophosphate

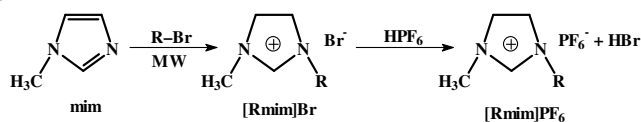
([pmim]PF₆) and 1-hexane-3-methyl-imidazolium hexafluorophosphate ([c₆mim]PF₆) [mim is for 1-methylimidazole; b is for butyl, p is for propyl, c₆ is for hexane] were studied in this paper because microwave irradiation (MW) was a new heating method and had some special properties in chemical reaction such as not changing the inner structure of molecule, fast temperature rising, short reaction time, good reaction selectivity, high reaction yield and so on. The crossed experimental method was also used to optimize productive conditions. The synthesized ionic liquids were analyzed and identified by UV-vis, IR and ¹H NMR spectra, respectively.

EXPERIMENTAL

Microwave-assisted syntheses of [pmim]PF₆, [bmim]PF₆ and [c₆mim]PF₆ ionic liquids

Principle of synthesis: 1-Methylimidazole (mim) was quaternized with alkyl bromide by microwave heating to synthesize [Rmim]Br intermediate compounds of imidazolium ionic liquids. Then [Rmim]Br reacted with HPF₆ at room temperature to get hexafluorophosphate ionic liquid [Rmim]PF₆. The synthetic route is given in Fig. 1.

Microwave-assisted synthesis of [Rmim]Br: Taking the synthesis of 1-butyl-3-methylimidazolium bromide ([bmim]Br) for example: 1-methylimidazole (AR grade, made in AlfaAesar Co. US) reacted with 1-bromine butane (AR grade,

Fig. 1. Synthetic route of [Rmim]PF₆ (R = p, b, c₆) ionic liquid

made in the National Combinational Chemicals Co., China) in different mole ratio (1.0:1.1, 1.0:1.2, 1.0:1.4) under microwave irradiating (MAS-I type microwave reactor, made in Sineo Co. China, Frequency 2450 MHz, Power 0-850 watta, temp control). Controlled different temperature (60, 70, 80 °C) and different reaction time (10, 20, 30 min) according to the L₉ (3³) cross experiment to prepare [bmim]Br intermediate of imidazolium ionic liquids. The optimal technological condition was chosen by calculating product yield. The same method was used to prepare 1-propyl-3-methylimidazolium bromide ([pmim]Br) and 1-hexyl-3-methylimidazolium bromide ([c₆mim]Br). The optimal technology was shown in Table-1.

TABLE-1

OPTIMAL TECHNOLOGY PREPARING
[pmim]Br, [bmim]Br AND [c₆mim]Br IONIC LIQUID
INTERMEDIATE BY MICROWAVE HEATING

Factor	[pmim]Br	[bmim]Br	[c ₆ mim]Br
Ratio of reactants*	mim/p 1.0-1.1	mim/b 1.0-1.1	mim/c ₆ 1.0-1.1
Temperature (°C)	80	80	70
Time (min)	20	20	10
Product yield (%)	93	96	97

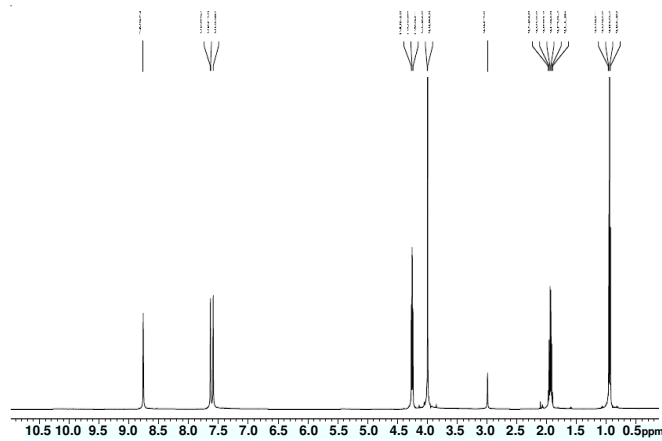
*mim is 0.05 mol.

Synthesis of [Rmim]PF₆ ionic liquid: The obtained [bmim]Br was dissolved in 50 mL water and 7.3 g HPF₆ was added in it subsequently. The mixed solution was stirred at room temperature for 4 h and was divided into two layers. The upper layer was water phase and rejected. The lower layer was ionic liquid phase and washed with distilled water repeatedly until it was neutral and the washing water had not deposit as AgNO₃ solution was dropped into it. The ionic liquid was washed again with 10 mL ether for three times and was then dried in vacuum desiccator at 70 °C for 24 h. The pale yellow oleaginous [bmim]PF₆ ionic liquid was obtained. The product yield was 52%. In same method, the yellow oleaginous [pmim]PF₆ ionic liquid and the pale yellow oleaginous [c₆mim]PF₆ ionic liquid were obtained. Their product yields were 48 and 50 %, respectively.

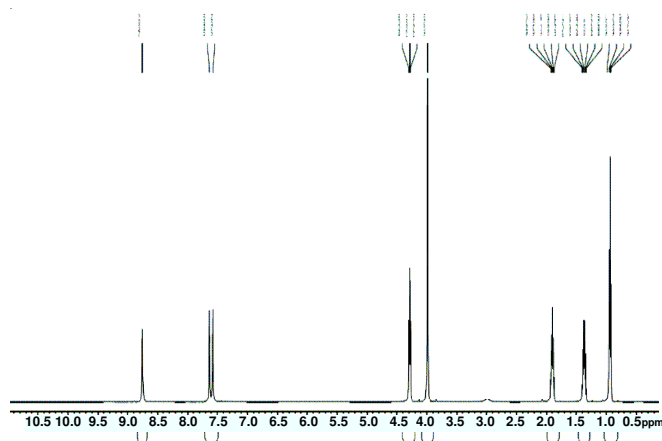
RESULTS AND DISCUSSION

The samples of [pmim]PF₆, [bmim]PF₆, [c₆mim]PF₆ ionic liquids were further purified and dried. The structure of them were analyzed and identified by UV-vis, IR and H¹ NMR spectrum separately.

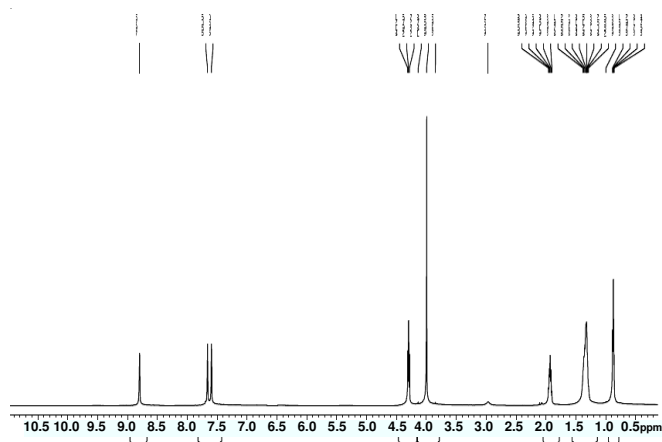
H¹ NMR spectral identification of [Rmim]PF₆: The H¹ NMR spectrum of [Rmim]PF₆ was obtained by the Varian INOVN-300 H¹ NMR spectrograph. The deuteroacetone was used as solvent. The sorts and content of hydrogen atoms in the compound molecule could be identified by the group amount of absorption peaks, the chemical displacement value and the integral curves of the peak areages. Then the construct of the ionic liquid could be identified. The H¹ NMR spectra of [pmim]PF₆, [bmim]PF₆, [c₆mim]PF₆ were shown in Figs. 2-4.



Chemical displacement data of hydrogen atom: 1H, s, NCHN 8.76 ppm 2H, m, CH₃NCHCHN 7.63 ppm, 2H, t, NCH₂CH₂CH₃ 4.25 ppm, 3H, s, NCH₃ 4.00 ppm, 2H, m, NCH₂CH₂CH₃ 1.94 ppm 3H, t, N(CH₂)₂CH₃ 0.95 ppm

Fig. 2. ¹H NMR spectrum of [pmim]PF₆

Chemical displacement data of hydrogen atom: 1H, s, NCHN 8.75 ppm 2H, m, CH₃NCHCH 7.60 ppm, 2H, t, NCH₂(CH₂)₂CH₃ 4.28 ppm 3H, s, NCH₃ 3.99 ppm, 2H NCH₂CH₂CH₂CH₃ 1.90 ppm, 2H N(CH₂)₂CH₂CH₃ 1.38 ppm, 3H N(CH₂)₂CH₃ 0.94 ppm

Fig. 3. ¹H NMR spectrum of [bmim]PF₆

Chemical displacement data of hydrogen atom: 1H, s, NCHN 8.80 ppm, 2H, m, CH₃NCHCHN 7.63 ppm, 2H, t, NCH₂(CH₂)₂CH₃ 4.29 ppm, 3H, s, NCH₃ 3.40 ppm, 2H NCH₂CH₂(CH₂)₂CH₃ 1.92 ppm, 7H N(CH₂)₂(CH₂)₂CH₃ 1.32 ppm, 3H N(CH₂)₂CH₃ 0.87 ppm

Fig. 4. ¹H NMR spectrum of [c₆mim]PF₆

IR spectral analysis and identification of [Rmim]PF₆:

The IR spectra of [Rmim]PF₆ were obtained by IR spectrograph (sepectrum one B-type, made in PE Co.). The samples were prepared by KBr press slice method. The bound of metrical wavenumber was 4000-400 cm⁻¹. In C-H retracting vibration absorption spectral band of 3500-2000 cm⁻¹ wavenumber, higher than 3000 cm⁻¹ was caused by the aromatic C-H retracting vibration, the 3000-2700 cm⁻¹ was the retracting vibration frequency section of saturation C-H, the 1675-1600 cm⁻¹ was the vibration frequency section of aromatic framework, the 838 cm⁻¹ was the absorption peak of PF₆⁻, the 751-753 cm⁻¹ was the C-H absorption peak in CH₂ long chain. It could be seen that there was no hydrogen bond absorption spectral band. It testified that PF₆⁻ was a weak ligand anion and it was difficult to form strong hydrogen bond with other ion. It meant that Coulombian force between the anion and cation would affect whole structure. The partial space orientation affected the final orientation of ion. This made the orientation of PF₆⁻ be the reason which ionic liquids had hydrophobic property.

UV-Vis spectral analysis and identification of [Rmim]PF₆: The UV-vis spectrum of [Rmim]PF₆ was measured by UV-vis spectrometer (UV-vis-2010, made in Hitachi Co., Japan). The sample was placed in 1 cm quartz colorimetric vessel to be measured after it was dissolved in methanol. The scan wavelength is in 200-700 nm.

In the measure of UV-vis spectrum, the solvent was used to not only dissolve ionic liquid but also decrease polymerization of high viscous and strong conducting ions. Methanol was used as solvent in these experiments and the sample concentration is 2.5×10^{-4} mol L⁻¹. The UV-vis absorption spectra of [pmim]PF₆, [bmim]PF₆ and [c₆mim]PF₆ measured at room temperature were shown in Fig. 5.

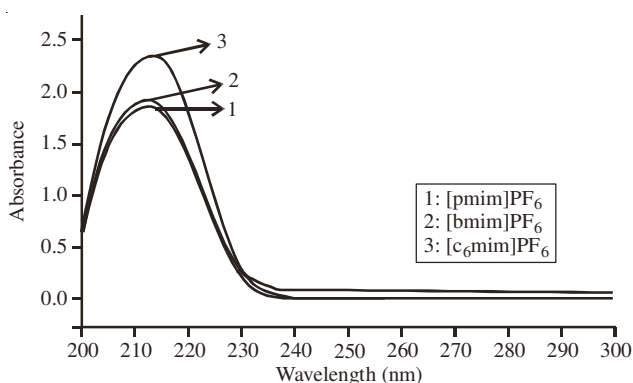


Fig. 5. UV-Vis spectra of [bmim]PF₆ [pmim]PF₆ and [c₆mim]PF₆

Obviously, the light transmittances of three ionic liquids increased at 240 nm and there were obvious inflexions. The inflexions had trend to move in shortwave direction. This was because the interaction between anion and cation decreased while ionic liquid formed.

Conclusion

The optimal technological condition preparing the intermediate of imidazolium ionic liquids under microwave irradiation by the crossed experiment methods was that for 1-butyl-3-methylimidazolium bromide ([bmim]Br), the mole ratio of 1-methylimidazolium to 1-brominebutane was 1:1.1, temperature was 80 °C, reaction time was 20 min. For 1-propyl-3-methylimidazolium bromide ([pmim]Br), the mole ratio of 1-methylimidazolium to 1-bromopropane was 1:1.1, temperature was 80 °C, reaction time was 20 min; for 1-hexyl-3-methylimidazolium bromide ([c₆mim]Br), the mole ratio of 1-methylimidazolium to 1-bromohexane was 1:1.1, temperature was 70 °C, reaction time was 10 min. The yields were above 90 %.

The intermediate [bmim]Br, [pmim]Br, [c₆mim]Br of ionic liquids reacted with HPF₆, respectively to get corresponding hydrophobic imidazolium ionic liquids [bmim]PF₆, [pmim]PF₆ and [c₆mim]PF₆. The react yields are 52, 48 and 50 %, respectively. The structures of [bmim]PF₆, [pmim]PF₆ and [c₆mim]PF₆ were analyzed and identified by UV-vis, IR and ¹H NMR spectra.

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