



Microwave-Assisted Synthesis and Spectral Identification of 1-Butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide [Bmim]NTf₂ Ionic Liquid

PING WANG, MINGDI YANG, YONGQING SU* and CONG LI

Faculty of Chemistry & Chemical Engineering, Yunnan Normal University, Kunming City 650092, P.R. China

*Corresponding author: E-mail: su_yongqing@yahoo.com

(Received: 12 October 2010;

Accepted: 15 June 2011)

AJC-10046

In this work, 1-butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide ([Bmim]NTf₂), a room-temperature ionic liquid, was synthesized by two-step method. Firstly, the ionic liquid intermediate, alkylimidazolium containing bromo anion ([Bmim]Br) was synthesized from 1-methylimidazole (C₄H₆N₂) and 1-butyl bromide under microwave irradiation. Then [Bmim]Br reacted with lithium *bis*(trifluoromethanesulfonyl)imide (Li(CF₃SO₂)₂N) to be [Bmim]NTf₂. The structure of [Bmim]NTf₂ was characterized and analyzed by ¹H NMR, infrared spectrum and UV-VIS spectrum.

Key Words: Ionic liquids, [Bmim]NTf₂, Microwave irradiation, Synthesis, Spectral identification.

INTRODUCTION

Ionic liquids are kinds of liquid ionic compounds at room temperature or near room temperature. They are also called room temperature ionic liquids, room temperature molten salts, organic ionic liquids, *etc.* They are liquid organic compounds which are completely composed of cations of heterocyclic compounds and other anions at room temperature or near room temperature without any molecule¹.

Compared with water and common organic solvents, ionic liquids have many particular characters, such as low melting point and wide temperature range in liquid state, thermostability and chemical stability at relative high temperature, very low vapour tension and viscosity, good conductivity and big decomposition voltage, strong polarity and can dissolve many organic and inorganic materials^{2,3}. Therefore, ionic liquids show good applied foreground in the fields of electrochemistry^{4,5}, chemical separation⁶, organic synthesis⁷⁻¹⁰, catalytic reaction¹¹⁻¹³, instrumental analysis¹⁴⁻¹⁶, preparation of nano-particulate materials¹⁷⁻²¹, media for preparing biological products²², *etc.*

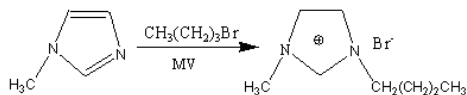
The sorts of ionic liquids are large. Different ionic liquid can be designed and synthesized by changing the combination of different anion and different cation according to practical requirement²³. There are two methods to synthesize ionic liquids, *i.e.*, one-step synthetic method and two-step synthetic method. One-step synthetic method includes the nucleophilic addition reaction of nucleophilic reagents - tertiary amine (such as imidazole, pyridine and pyrrole) with halohydrocarbon or esters

(such as carboxylic ester, sulfuric ester) and the neutralization reaction of basic tertiary amine with acid to form target ionic liquids by one-step²⁴. Two-step method must be used if the target ionic liquids could not be prepared by one-step²⁵. The synthesis of ionic liquids is organic reaction and it needs long time and some special condition in general method. Microwave irradiation (MW) is a new heating method and has 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. It was successful in synthesis of [Bmim]PF₆, [Rmim]PF₆ (R = p, b, c₆) ionic liquids²⁰⁻²⁶. In this paper, microwave-assisted synthetic method was adopted to synthesize 1-butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide ([Bmim]NTf₂) ionic liquid by two-step method. The structure of [Bmim]NTf₂ was identified by ¹H NMR, infrared spectrum and UV-VIS spectrum.

EXPERIMENTAL

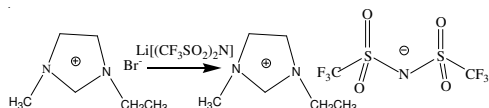
Microwave-assisted syntheses of [Bmim]NTf₂ ionic liquid: Ionic liquid intermediate, alkylimidazolium containing bromic anion ([Bmim]Br) was synthesized from 1-methylimidazole (C₄H₆N₂, mim. AR grade, made in AlfaAesar Co. US) and 1-butylbromide (C₄H₉Br, AR grade, made in the National Combinational Chemicals Co, China) under microwave irradiation. Then [Bmim]Br reacted with lithium *bis*(trifluoromethanesulfonyl)imide (Li(CF₃SO₂)₂N, AR grade, Japan Chemical Industry Co., Ltd.) to be the aimed product [Bmim]NTf₂.

First step: synthesis of the intermediate, as follow:



6.8 mL 1-methylimidazole ($C_4H_6N_2$) and 10 mL 1-butylbromide (C_4H_9Br) were put into 100 mL round-bottom flask and then be moved into the microwave reactor (MAS-I type microwave reactor, frequency 2450 MHz, power 0-850 wate, temperature control, made in Sineo Co. China). The primrose intermediate of the ionic liquid intermediate, [Bmim]Br, was obtained after the reaction continued for 20 minutes at 80 °C under magnetic stirring and microwave irradiation.

The second step: exchange of anions, as follow:

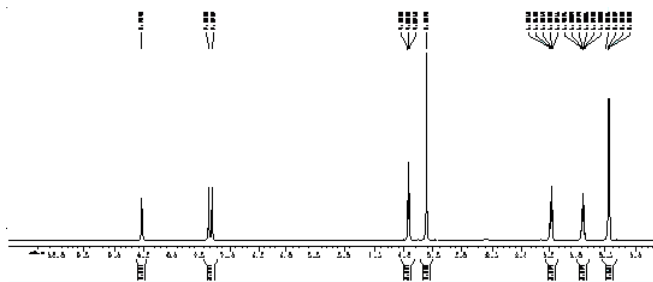


24.5 g lithium *bis*(trifluoromethanesulfony) imide $[Li(CF_3SO_2)_2N]$ was dissolved in 50 mL water and the [Bmim]Br prepared in step one was added in this solution. The solution was stirred for 3 h. The solution rested and separated two layers. The up layer was water phase and was poured out. The down layer was ionic liquid and was washed again and again by deionized water till the washing water was neutral and no precipitate occurred in it when a drop of $AgNO_3$ solution was added in. The ionic liquid was then washed three times with 30 mL of ether. Finally, the ionic liquid was reduced-pressure distilled at 0.8 atm and 70 °C for 5 h. A colourless, transparent and oily [Bmim]NTf₂ was obtained (yield 59.6 wt %).

RESULTS AND DISCUSSION

After being further purified and dried, [Bmim]NTf₂ sample was analyzed and identified by UV-VIS, IR and ¹H NMR spectra separately.

¹H NMR spectral identification of [Bmim]NTf₂: The ¹H NMR spectrum of [Bmim]NTf₂ was obtained by the Swiss Bruker DRX-500 H ¹H 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 ¹H NMR spectra of [Bmim]NTf₂ was shown in Fig. 1.



Chemical displacement data of hydrogen atom (black H was identified): 1H, s, NCHN 9.03 ppm; 2H, d, NCHCHN 7.82 ppm; 2H, t, $NCH_2(CH_2)_2CH_3$ 4.41 ppm; 3H, s, NCH_3 4.14 ppm; 2H, m, $NCH_2CH_2CH_2CH_3$ 1.94 ppm; 2H, m, $N(CH_2)_2CH_2CH_3$ 1.38 ppm; 3H, t, $N(CH_2)_3CH_3$ 0.96 ppm.

Fig. 1. ¹H NMR spectra of [Bmim]NTf₂

IR spectral analysis and identification of [Bmim]NTf₂:

The IR spectrum of [Bmim]NTf₂ was drawn by IR spectrograph (Ten Sor27, Germany Bruker). The sample was prepared by KBr press slice method. The bound of metrical wavenumber was 4000-400 cm^{-1} . The IR spectra were given in Fig. 2.

The 3500-3400 cm^{-1} wavenumber was due to the N-H retracting vibration absorption spectral band in the imidazole ring. The band in 3200-3000 cm^{-1} region was assigned for C-H retracting vibration absorption spectral band in the imidazole ring. The 3000-2900 cm^{-1} was C-H unsymmetrical and symmetrical retracting vibration absorption peak of the methyl and methylene. The 2900-2600 cm^{-1} was the N-CH retracting vibration absorption peak. There was no peak in 2600-1700 cm^{-1} region. The 1700-1400 cm^{-1} was the frequency section of imidazole ring. The 1400-1300 cm^{-1} and the 1200-1150 cm^{-1} were the unsymmetrical and symmetrical retracting vibration absorption peaks of O = S = O respectively. The 1150-1000 cm^{-1} was retracting vibration absorption peaks of C-F. The 1000-500 cm^{-1} was C-C, C-N dactylogram sections and C-H out-of-plane bending vibration absorption peaks.

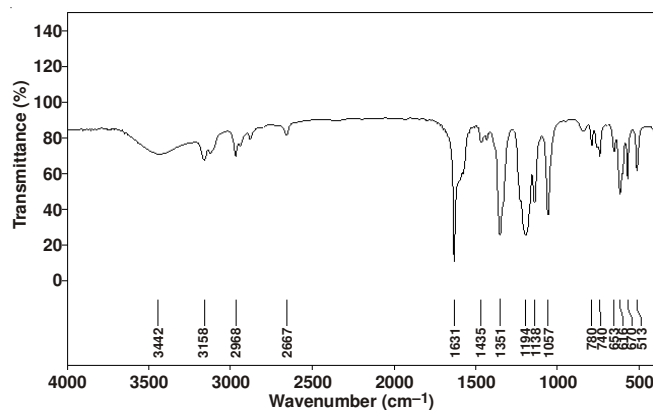


Fig. 2. IR spectra of [Bmim]NTf₂

UV-VIS spectral analysis and identification of [Bmim]NTf₂:

The sample of [Bmim]NTf₂ was dissolved in methanol and the concentration was 3.0×10^{-4} mol L⁻¹. The UV-VIS absorption spectrum of [Bmim]NTf₂ solution was measured by UV-VIS spectrometer (TU-1901, Beijing Purkinje general instrument Co., Ltd.). The sample of [Bmim]NTf₂ solution was placed in 1-cm quartz colourimetric vessel to be measured after [Bmim]NTf₂ was dissolved in methanol to be 3.0×10^{-4} mol L⁻¹ solution. The scan wavelength is in 200-700 nm. The spectrum was shown in Fig. 3. It showed that [Bmim]NTf₂ had conjugate structure because of a strong absorption peak in 296 nm. Moreover, -NR₁R₂ group was jointed with an end of the conjugate bond to bring p- π conjugate effect and made the spectrum be red shift.

Conclusion

The ionic liquid intermediate [Bmim]Br was firstly synthesized from 1-methylimidazole ($C_4H_6N_2$, mim) and 1-butylbromide (C_4H_9Br) under microwave irradiation and magnetic stirring at 80 °C for 20 min. Then [Bmim]Br and lithium *bis*(trifluoromethanesulfony) imide ($Li(CF_3SO_2)_2N$) were dissolved in water and was mixed well by stirring for 3 h to form the aimed product [Bmim]NTf₂. This synthetic method

was sample, short time and there was no outgrowth. The yield of [Bmim]NTf₂ was 59.6 % and higher than that by other ordinary method. The structure of [Bmim]NTf₂ was characterized and analyzed by ¹H NMR, Infrared spectrum and UV-VIS spectrum.

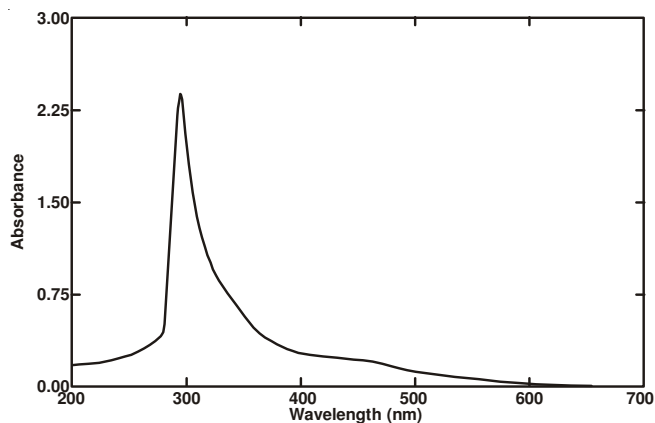


Fig. 3. UV-VIS spectrum of [Bmim]NTf₂

ACKNOWLEDGEMENTS

The authors would like to acknowledge the support provided by the Yunnan Province Science and Technology Department for the Program of Yunnan Province's Training Young-middle-aged Reserve of Scientific and Technological Principal (Grant No. 2006PY01-50) and the fund of Yunnan Province's Applied Basic Research Plan (Grant No. 2006E0032M). The authors also acknowledged the support from Department of Yunnan Province Education for the fund of Science Research (Grant no. ZD2010003).

REFERENCES

1. T. Well, *Chem. Rev.* **99**, 2071 (1999).
2. R. Li, *Green Solvents: Synthesis and Application of Ionic Liquids*, Beijing: Chemical Industry Press, 6 (2004).
3. X. Li, D. Zhao, Z. Fei and L. Wang, *Science in China (Series B)*, **36**, 181 (2006).
4. P. Hapiot and C. Lagrost., *Chem. Rev.*, **108**, 2238 (2008).
5. Y. He, Y. Su, C. Li, Y. Zhong and L. Liu, *Chin. Eng. Sci.*, **10**, 92 (2008).
6. L. Liu, Y. Su, C. Li, F. He, Y. He and Y. Zhong, *Chin. Eng. Sci.*, **9**, 187 (2007).
7. C.W. Lee., *Tetrahedron Lett.*, **40**, 2461 (1999).
8. M.J. Earle, K.R. Seddon, C.J. Adams and G. Robert, *Chem. Commun.*, **19**, 2097 (1998).
9. J. Ross and J. Xiao, *Green Chem.*, **4**, 129 (2002).
10. M.A.P. Martins, C.P. Frizzo, D.N. Moreira, N. Zanatta and H.G. Bonacorso, *Chem. Rev.*, **108**, 2015 (2008).
11. A.J. Carmichael, M.J. Earle, J.D. Holbrey, P.B. McCormac and K.R. Seddon, *Org. Lett.*, **1**, 997 (1999).
12. Y. Deng, F. Shi, J. Beng and K. Qiao, *J. Mol. Catal. A: Chem.*, **165**, 33 (2001).
13. M. Haumann and A. Riisager, *Chem. Rev.*, **108**, 1474 (2008).
14. J. Ding, T. Welton and D.W. Armstrong, *Anal. Chem.*, **76**, 6819 (2004).
15. J.F. Liu, J.A. Jonsson and G.B. Jiang, *Trends Anal. Chem.*, **24**, 20 (2005).
16. E. Aguilera-Herrador, R. Lucena, S. Cardenas and M. Valcarcet, *Anal. Chem.*, **80**, 793 (2008).
17. M. Antonietti, D. Kuang, B. Smarsly and Y. Zhou, *Angew. Chem. Int. Ed.*, **48**, 4988 (2004).
18. Y. Zhou and M. Antonietti, *Am. Chem. Soc.*, **125**, 14960 (2003).
19. K. Yoo, H. Choi and D.D. Dionysiou, *Chem. Commun.*, **5**, 2000 (2004).
20. Y. Su, M. Yang, C. Li, H. Wang, N. Ren and Y. Cai, *Nonferrous Metal (Extractive Metallurgy)*, **1**, 50 (2010).
21. Y. Su, C. Li, M. Yang, Y. Cai and N. Ren, *Eng. Sci.*, **8**, 20 (2010).
22. J.C. Plaquevent, J. Levillain, F. Guillen, C. Malhiac and A.C. Gaumont, *Chem. Rev.*, **108**, 5035 (2008).
23. J. Ranke, S. Stolte, R. Stormann, J. Arning and B. Jastorff, *Chem. Rev.*, **107**, 2183 (2007).
24. J. Xu, *Technol. Develop. Chem. Ind.*, **33**, 15 (2004).
25. A.S. Larsen, J.D. Holbrey, F.S. Tham and C.A. Reed, *J. Am. Chem. Soc.*, **122**, 7264 (2000).
26. Y. Su, Y. He, C. Li, P. Wang, Y. Zhong, L. Liu and F. He, *Asian J. Chem.*, **23**, 97 (2011).