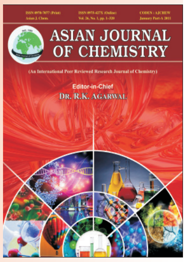
Asian Journal of Chemistry;   Vol. 26, No. 8 (2014), 2369-2372

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16005



Synthesis of Ionic Liquid [BMIM]Br in Micro-Channel Reactor

J. ZHANG[1], Y.J. WANG[1] and S.Z. HU[2,*]

[1]Liaoning Key Laboratory of Petroleum and Chemical Industry, Liaoning Shihua University, Fushun 113001, P.R. China
[2]Institute of Eco-environmental Sciences, Liaoning Shihua University, Fushun 113001, P.R. China

*Corresponding author: Tel: +86 24 23847473; E-mail: hushaozheng001@163.com

Received: 5 July 2013;   *Accepted*: 21 August 2013;   *Published online*: 15 April 2014;   AJC-15028

A microchannel reaction system, mainly consisting of a micromixer and a tubular reactor was used to investigate the synthesis of the ionic liquid 1-butyl-3-methylimidazolium bromide ([BMIM]Br). The influence factors, such as residence time, molar ratio of reactants and reaction temperature to the conversion rate were investigated. The results showed that the optimal synthesis condition was molar ratio of 1:1.05 (1-bromo butane to methyl imidazole), residence time of 3.2 min and reaction temperature of 110 °C.

Keywords: 1-Butyl-3-methylimidazolium bromide, Exothermic reaction, Ionic liquid, Micro-structured reactor.

INTRODUCTION

Ionic liquids are compounds that are completely composed of ions and are liquid at or close to room temperature. With the continuous efforts of some chemists, ionic liquids have not only become increasingly popular as reaction and extraction media in research and development, they have also widely been promoted as "green solvents". Moreover, for the economical and ecological reasons, ionic liquids nowadays are very fascinating to the researchers from a wide variety of fields, especially the area of organic synthesis[1], environmentally benign solvents[2,3], reaction media[4,5], catalysts[6], electrolytes[7], lubricants and others. This is due to the unique properties of ionic liquids, such as negligible vapor pressure, relatively high conductivity, high thermal and chemical stability, non-flammability and reduced friction. However, no large scale commercial application of ionic liquids has been reported, probably due to the high costs and the unavailability of ionic liquids in large volume.

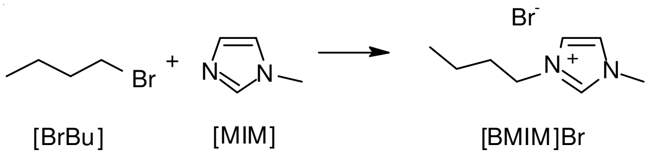
Currently, ionic liquids are mainly produced in batch reactors. The synthesis of ionic liquids, such as 1-butyl-3-methylimidazolium bromide, is highly exothermic in the alkylation and the alkylation kinetics is often dramatically fast[8]. It is reported that high temperature had a detrimental effect on the quality of the obtained ionic liquids[9]. Therefore, an efficient removal of released reaction heat is crucial in order to improve the purity of ionic liquids. Since heat generation rate is the product of reaction rate and intrinsic reaction heat, one way to control the temperature in a highly exothermic reaction is to slow it down. The decrease of reaction rate can be achieved by diluting the reactants with solvents and/or slowly adding one of the reactants to the reaction mixture. For the production of ionic liquids in a batch reactor, large quantity of organic solvents, such as 1,1,1-trichloromethane, ethanol and THF, are often used to dilute the reactants. Nevertheless, it is often necessary to add the reactants slowly to avoid hot-spot formation and to ensure a narrow operational temperature window. The use of large solvent volumes gives a rise of costs and possibly pollution and a slow addition of reactants lead to very long processing times (hours or even days). Therefore, a solvent-free synthesis system with enhanced heat transfer is highly desirable.

The application of microsystems for chemical and biological reactions was discussed at a workshop in 1995 in Mainz (Germany), which can be seen as the starting point for worldwide development[10]. Recently, several groups reported the syntheses of ionic liquids in micro-channeled reactor systems[11,12]. Microstructured reactors are reactors with three-dimensional structures, the inner dimensions of which are under a millimeter in size and more specifically between ten and a hundred micrometers. Therefore, it follows that the main feature of these reactors, in comparison to conventional chemical reactors, is the high surface-area-to-volume ratio. Specific surface areas of micro-structures lie between 10000 and 50000 m^2m^{-3}, while those of traditional reactors are generally about 100 m^2m^{-3} and in rare cases reach 1000 m^2m^{-3} [13]. Since the heat-transfer coefficient is inversely proportional to the channel diameter, a value on the order of 10 kW m^2 K^{-1} is obtained[14], which is significantly higher than for traditional heat exchangers. This high heat-exchanging efficiency allows for fast heating and cooling in reaction mixtures within the microstructures whereby reactions under isothermal conditions with exactly defined residence times can be carried out[15]. The development of hot spots or the accumulation of reaction heat within microstructures is suppressed so that undesirable side reactions and fragmentations are hindered. The outcome in many cases is higher selectivity, yield and product quality. Thus, micro-structured reactors can be used to great effect for fast and/or strongly exothermic or endothermic chemical reactions[16].

In the present paper, we report a convenient method to synthesis ionic liquid 1-butyl-3-methylimidazolium bromide ([BMIM]Br) by micro-reactor system. The influence factors, such as residence time, molar ratio of reactants and reaction temperature to the conversion rate were investigated.

EXPERIMENTAL

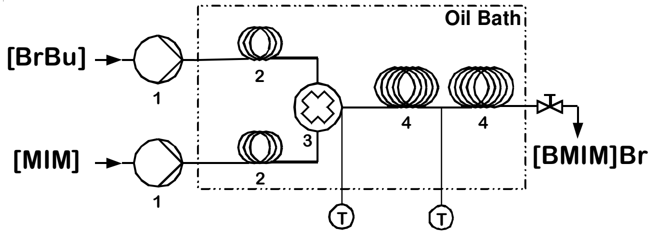
As a representative reaction in the synthesis of ionic liquids, the butylation of methylimidazole [MIM] with 1-bromobutane [BrBu] to yield [BMIM]Br, was chosen as an instructive example for the kinetic study. The reaction equation is as follows:



[MIM] and [BrBu] are of AR grade and used without further purification. As reference substance, [BMIM]Br was obtained from Shanghai Meisibei Co.

The setup of the microchannel reactor is shown in Fig. 1. It consists of two pumps, two preheating tube coils, one SIMM-V2 micro-mixer (IMM Mainz, Germany) with a standard mixing channel of 45 × 200 μm^2 and a total inner volume of 8 μL (Fig. 2)[17], and a loop tubular reactor (1.80 mm in inner diameter and 1.13 m in length). The preheating tube coils, the mixer and the reactor were emerged in a circulating oil bath (volume: 40 L). The temperature of the oil bath was kept constant during the reaction. The advantage of our set-up lies in the fact that the reactants are preheated separately and thus the reaction is triggered at the desired temperature when they meet in the micro-mixer. Because the retention time in the mixer is in the milliseconds range, the reaction proceeds mainly in the tubular reactor. We measured the temperatures at the outlet of the micro-mixer and in the middle of the tubular reactor. The measurement at nearly complete conversion indicated that only 0.8 °C temperature difference was observed. It is therefore assumed that the reaction takes place at nearly isothermal conditions, which is in accordance with the prediction of the modeling from Waterkamp *et al.*[18].

Because the butylation reaction continues slowly at room temperature, a long delay until analysis will cause a falsification of the experimental results. Therefore, a sample treatment and a fast analysis is essential to ensure valid kinetic data. Since [MIM] and [BrBu] are non-ionic whereas [BMIM]Br is ionic, we developed a fast method of determining the conversion. The procedure is based on the titration of Br- in the reaction mixture, which indicates the conversion of [BrBu] by the Volhard titration method. A series of "standard" solutions at given [MIM] conversions ($x_{[MIM]}$) were prepared by mixing [MIM], [BrBu] and [BMIM]Br. The product containing [BMIM]Br was collected at the outlet of the tubular reactor. 1 mL of the product was immediately dissolved in 1 mL ethanol and then Br- concentration in the solution was determined as follows: 0.1 mL of the solution, 10 mL $AgNO_3$ aqueous solution (0.053 M), 10 mL $NH_4Fe(SO_4)_2$ aqueous solution (0.2 M) and 10 mL HNO_3 aqueous solution (3.2 M) were added to 70 mL de-ionized water giving a white suspension. 0.0353 M NH_4SCN was used to titrate the above suspension until the $Fe(SCN)_3$ precipitate (red colour) was formed. Our preliminary investigation showed that no byproduct was detected, implying that one mole Br- is formed when one mole [MIM] is converted in the synthesis. Thus, $x_{[MIM]}$ can be determined from the titration volume (V):



1. Syringe pump; 2. preheating coil; 3. micromixer; 4. delay pipe

Fig. 1. Schematic diagram of the micro-structured reactor system

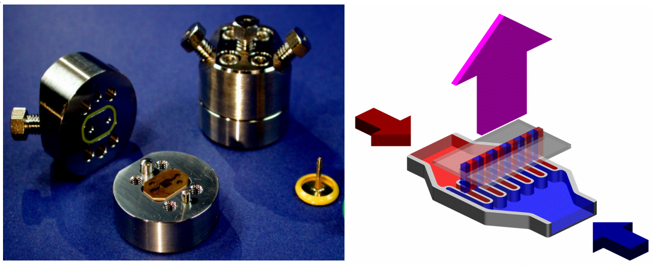


Fig. 2. Photo (left) and the schematic diagram (right) of SIMM-V2 micro-mixer (source IMM)

$$x_{[MIM]} = \frac{(0.053\times10-0.0353V)\times M_{[MIM]}\times10^{-3}}{\rho_{[MIM]}\times0.1v_{[MIM]}/[2(v_{[MIM]}+v_{[BrBu]})]} \tag{1}$$

where $v_{[MIM]}$ and $v_{[BrBr]}$ are the volumetric flow rates of [MIM] and [BrBu], respectively; $M_{[MIM]}$ is the molar mass of [MIM] (82.1) and $\rho_{[MIM]}$ is the density of [MIM].

RESULTS AND DISCUSSION

Fig. 3 shows the variation of methyl imidazole conversion with molar ratio of 1-bromo butane to methyl imidazole. When the molar ratio was 1, the methyl imidazole conversion was approximately 90 %. When the molar ratio icreased to 1.05, the methyl imidazole conversion increased to more than 98 %. With further increase the molar ratio, the conversion showed no obvious increase, indicating the optimal molar ratio was 1.05 for this micro-reactor system.

Fig. 4 shows the variation of methyl imidazole conversion with reaction temperature. When the reaction occurred at 100 °C, the methyl imidazole conversion was 94 %. When the reaction temperature increased to 105 °C, the methyl imidazole conversion increased to the maximum, more than 98 %. However,

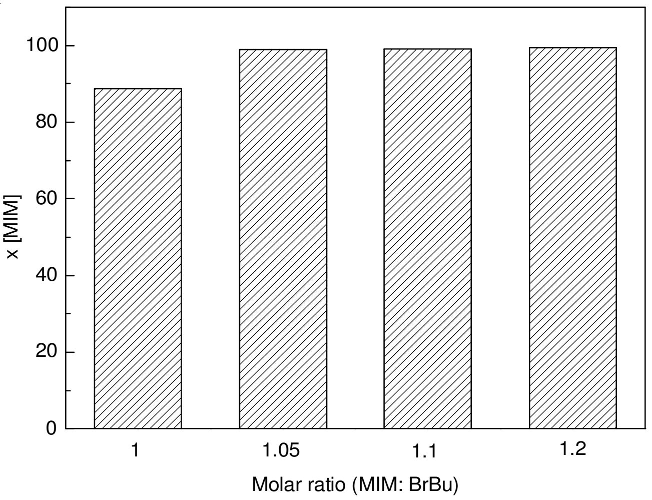


Fig. 3. Variation of methyl imidazole conversion with molar ratio of 1-bromo butane to methyl imidazole (temperature :105 °C, residence time: 3.2 min)

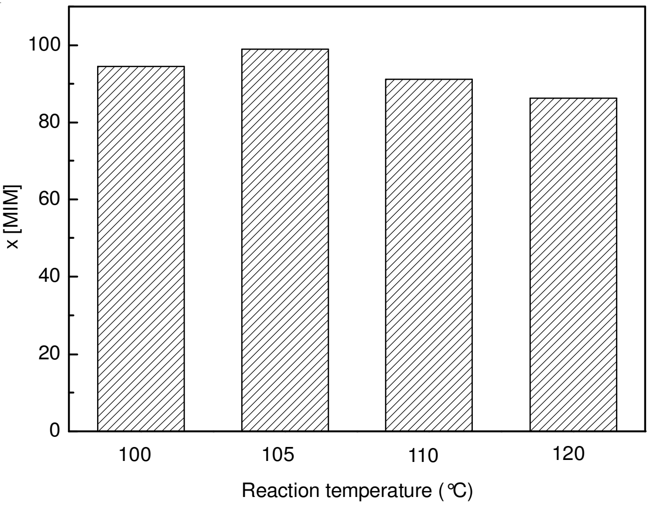


Fig. 4. Variation of methyl imidazole conversion with reaction temperature (molar ratio: 1.05, residence time: 3.2 min)

with further increase the reaction temperature, the conversion decreased obviously. The conversion was lower than 90 % when the temperature was 120 °C. This may be due to the low boiling point of 1-bromo butane, 102 °C. In this reaction system, due to the especial structure of reactor, two liquid reactants mixed quickly and then form the ionic liquid [BMIM]Br. However, when the reaction temperature was much higher than the boiling point of 1-bromo butane, the 1-bromo butane bubbled up in the preheating tube and became the gas phase. Therefore, when the gaseous 1-bromo butane mixed with liquid methyl imidazole in the reactor, the mixing effect was much poor than that of liquid-liquid mixing. Thus, the methyl imidazole conversion decreased obviously.

Fig. 5 shows the variation of methyl imidazole conversion with residence time. The residence time was calculated according to the corresponding residence tube length, molar ratio and feed rate. It is shown that when the residence time was 1.9 min, the conversion was more than 90%, indicating the high mixing effect of SIMM-V2. Because in the conventional method, it will take more than 10 h to convert more than 90 % methyl imidazole[9]. With further increase the residence time, the conversion further increased. When the residence time prolong to more than 3.2 min, the conversion showed no further increase. This indicated that the optimal residence time was 3.2 min.

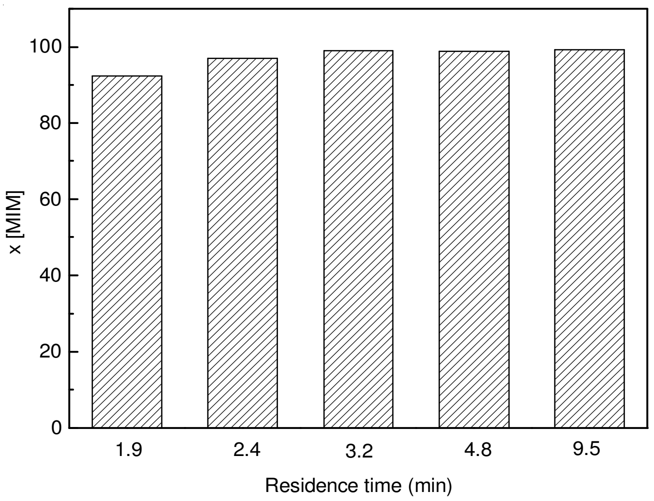


Fig. 5. Variation of methyl imidazole conversion with residence time (molar ratio: 1.05, reaction temperature: 105 °C)

Based on the above result, the optimal reaction condition was molar ratio of 1:1.05 (1-bromo butane to methyl imidazole), residence time of 3.2 min and reaction temperature of 110 °C. Therefore, the ionic liquid [BMIM]Br was synthesized under optimal condition. The obtained product was distilled under vacuum. The H^1 NMR result of obtained ionic liquid [BMIM]Br was shown in Fig. 6. Nine peaks were shown in the result of H^1 NMR. The peak located at 7.282 was attributed to the solvent Chloroform-d ($CDCl_3$). The other eight peaks belonged to the product [BMIM]Br. No reactant was detected in the H^1 NMR. Fig. 7 shows the photo of obtained ionic liquid [BMIM]Br under optimal reaction condition. The obtained product was white crystal, indicating the purity was extremely high. Therefore, based on the above conclusion, this is a convenient and fast method to synthesis ionic liquid [BMIM]Br using micro-channel reactor.

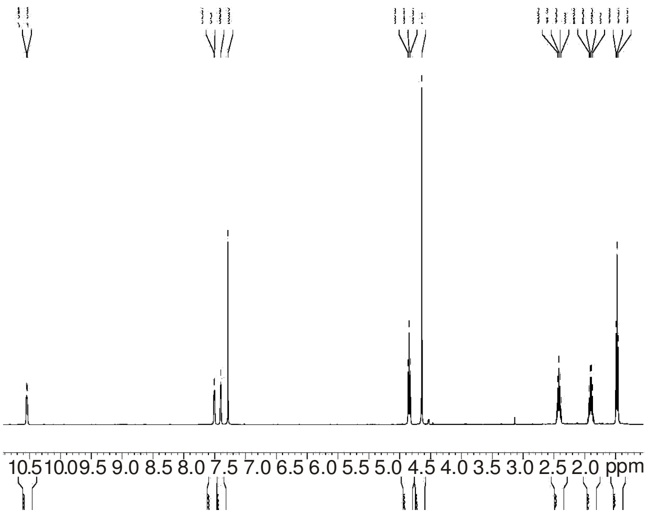


Fig. 6. H^1 NMR of obtained ionic liquid [BMIM]Br (synthesis condition: 1:1.05, 105 °C, and 3.2 min)

Fig. 7. Photo of obtained ionic liquid [BMIM]Br (synthesis condition: 1:1.05, 105 °C, and 3.2 min)

Conclusion

A microchannel reaction system, mainly consisting of a micromixer and a tubular reactor was used to investigate the synthesis of the ionic liquid 1-butyl-3-methylimidazolium bromide ([BMIM]Br). The investigation results showed that the optimal synthesis condition was molar ratio of 1:1.05 (1-bromo butane to methyl imidazole), residence time of 3.2 min and reaction temperature of 110 °C. Compared with the conventional method, this method decreased the reaction time greatly. Besides, the H^1 NMR result indicated that the purity of obtained product was extremely high.

REFERENCES

1. T.L.T. Bui, W. Korth, S. Aschauer and A. Jess, *Green Chem*., **11**, 1961 (2009).
2. F. Endres, *Chem. Phys. Chem*., **3**, 144 (2002).
3. H. Zhao, S.Q. Xia and P.S. Ma, *J. Chem. Technol. Biotechnol*. **80**, 1089 (2005).
4. P. Wasserscheid and W. Keim, *Angew. Chem. Int. Ed*., **39**, 3772 (2000).
5. C. Chiappe and D. Pieraccini, *J. Phys. Org. Chem.,* **18**, 275 (2005).
6. T. Welton, *Coord. Chem. Rev*., **248**, 2459 (2004).
7. M. Galinski, A. Lewandowski and I. Stepniak, *Electrochim. Acta*., **51**, 5567 (2006).
8. A. Renken, V. Hessel, P. Löb, R. Miszczuk, M. Uerdingen and L. Kiwi-Minsker, *Chem. Eng. Process*. **46**, 840 (2007).
9. A.G. Böwing and A. Jess, *Green Chem*., **7**, 230 (2005).
10. W. Ehrfeld, DECHEMA-Monographs, *DECHEMA,Frankfurt*, **132** (1995).
11. D. Wilms, J. Klos, A.F.M. Kilbinger, H. Löwe and H. Frey, *Org. Proc. Res. Dev*. **13**, 961 (2009).
12. F. Benaskar, V. Hessel, U. Krtschil, P. Löb and A. Stark, *Org. Proc. Res. Dev*. **13**, 970 (2009).
13. K.P. JNckel, *DECHEMA Monographs, VCH, Weinheim*, **132**, 29 (1996).
14. K. Schubert, J. Brandner, M. Fichtner, G. Linder, U. Schygulla and A. Wenka, *Microscale Thermophys. Eng*. **5**, 17 (2001).
15. J.J. Lerou, M.P. Harold, J. Ryley, J. Ashmead, T.C. O'Brien, M. Johnson, J. Perrotto, C.T. Blaisdell and T.A. Rensi, J. Nyquist, *DECHEMA Monographs, VCH, Weinheim*, **132**, 51 (1996).
16. O. Wörz, K.P. Jäckel, T. Richter and A.Wolf, *Chem. Eng. Technol*. **24**, 138 (2001).
17. S. Hardt and F. Schönfeld, *AIChE J*. **3**, 578 (2003).
18. D.A. Waterkamp, M. Heiland, M. Schlüter, J.C. Sauvageau, T. Beyersdorff and J. Thöming, *Green Chem*., **9**, 1084 (2007).