



Synthesis of some imidazolium based ionic liquids and influence of some factors on reaction yields

Ha T. N. Uong^{1,2,3}, Ngoc C. Pham⁴, Hoang Thị Kim Dung^{1,2}, Tang Ngoc Thanh Van⁵, Thuy T. L. Bui⁶

¹*Institute of Chemistry, Vietnam Academy of Sciences and Technology, 18-Hoang Quoc Viet, Nghia Do, Cau Giay, Hanoi*

²*Institute of Chemical Technology, Vietnam Academy of Sciences and Technology, 1-Mac Dinh Chi Street, Ho Chi Minh City*

³*Chemistry Department, Ho Chi Minh University of Medicine and Pharmacy, 227 Hong Bang, Ho Chi Minh City*

⁴*Earlham College, 801 National Rd W, Richmond, IN 47374, United State*

⁵*Tan Binh High School, 19 Hoa Bang, Tan Son Nhi Ward, Tan Phu District, Ho Chi Minh City*

⁶*Oil Refining and Petrochemistry Department, Hanoi University of Mining and Geology, 18-Vien, Duc Thang, Bac Tu Liem, Hanoi*

Email: Thuykhai2001@gmail.com

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ABSTRACT

In this paper, three imidazolium ionic liquids 1-methyl -3-n-tetradecylimidazolium chloride ([C₁₄MIM]Cl), 1-n-butyl -3-n-butylimidazolium chloride ([C₄BIM]Cl), and 1-n-butyl-3-n-tetradecylimidazolium chloride ([C₁₄BIM]Cl) with different alkyl chain lengths were synthesized and characterized by infrared, ¹H-NMR and ¹³C-NMR NMR and nuclear magnetic resonance, and mass spectra. The effect of structure of alkyl chloride and imidazole compounds on the synthesis yield was evaluated. In addition, the effects of reaction conditions such as temperature, time, and molar ratio of reactants on the synthesis yield were also investigated to find out suitable conditions for the synthesis processes.

Introduction

Ionic liquids (ILs) were found in 1914, when the first paper about the salts that melt at room temperature was published by Walden [1]. After that, many ILs were synthesized and studied for different applications [2 - 7]. Due to many special properties such as very low vapor pressure, high thermal and electrical conductivity, the highly compatibility with many different substances and possibility of adjustment of properties such as acidity, solubility [8-10] by changing their cation and anion structures, their application is increasing in many

different fields [11-14], especially imidazolium ionic liquids which are very common and have many applications. However, one of the limitations for industrial application is that they are quite expensive, so the study of synthesizing them in simple conditions should be concerned. In this study, synthesis of three imidazolium-type ionic liquids with different lengths of alkyl chains attached to the imidazolium ring was performed.

Materials and methods

Chemicals

Butylimidazole (99%), methylimidazole (99%), 1-chlorobutane (99%), 1-chlorotetradecane (99,5 were purchased from Merck, German. Diethyl ether purchased from Guangdong company, China.

Synthesis of ionic liquids

Ionic liquids are synthesized according to the following general procedure: a mixture of two reactants including of 1-methylimidazole (or 1-n-butylimidazole) and alkylchloride was introduced in a two neck round bottom flask which was installed a reflux condenser and immersed in an oil bath with magnetic stirrer. The mixture was stirred and heated to a suitable temperature for the suitable duration. The mixture was cooled and washed it with diethyl ether to remove any excess reactant. Examples of specific reaction procedures are presented below:

Synthesis of 1-methyl -3-n-tetradecylimidazolium chloride ([C₁₄MIM]Cl)

Put 1,231 g 1-methylimidazole (0.015 mol) and 4.203 g 1-Chlorotetradecane (0.018 mol) with a molar ratio of Chlorotetradecane/1-methylimidazole = 1:1.2 was introduced in a two neck round bottom flask which was installed a reflux condenser and immersed in an oil bath with magnetic stirrer. The reaction was carried out at 90°C for 120 h. After the reaction, the reaction mixture is yellow and thick. Clean the product by washing with diethyl ether, the product is a white waxy solid.

Synthesis of 1-n-butyl -3-n-butylimidazolium chloride ([C₄BIM]Cl)

3,725 g of 1-n-butylimidazole (0.03 mol) and 3,330 g of 1-chlorobutane (0.036 mol) with a ratio of 1-chlorobutane/butylimidazole = 1:1.2 was introduced in a two neck round bottom flask which was installed a reflux condenser and immersed in an oil bath with magnetic stirrer. The mixture was stirred and heated at 90°C for 120 hours. The reaction mixture was washed with diethyl ether to obtain a pure product with a mass of 5.985 g. The obtained product is pale yellow viscous.

Synthesis of 1-n-butyl-3-n-tetradecylimidazolium chloride ([C₁₄BIM]Cl)

3.725 g of butyl imidazole (0.03 mol) and 8,370 g of 1-chlorotetradecan (0.036 mol with a molar ratio of 1-

chlorotetradecan/ butyl imidazole = 1:1.2 was introduced in a two neck round bottom flask which was installed a reflux condenser and immersed in an oil bath with magnetic stirrer. The mixture was stirred and heated at 90°C for 120 hours. The product was cleaned with diethyl ether. The obtained product is yellow, waxy, with weight of 11,020 g.

Product characterization methods

The infrared spectroscopy of ionic liquids was performed on an IR Tensor 37 - Bruker - Germany machine at the Institute of Chemical Technology, Vietnam Academy of Science and Technology. The structures of the ionic liquids were characterized by ¹H-NMR and ¹³C-NMR spectra using a Bruker AM0 FT-NMR Spectrometer (at 500 MHz for the proton spectrum and at 125 MHz for the ¹³C spectrum) in solvents CDCl₃ and mass spectrometry with ionization technique (MS-ESI) on a high resolution 6500 series Q-TOF mass spectrometer system (Agilent), at the Central Analysis Department of the University of Natural Sciences, Ho Chi Minh City.

Results and Discussion

The results of structural characterization of ionic liquids

The FT-IR, HRMS (ESI) and NMR spectra of synthesized ionic liquids synthesized were measured and the results are presented in Table 1-3.

Table 1: FT-IR, HRMS, and NMR spectroscopy results of [C₁₄MIM]Cl (108 h, mol ratio of alkyl chloride /imidazole=1:1.2; 95°C)

HRMS (ESI)	Spectral data FT-IR $\nu(\text{cm}^{-1})$	Spectral data ¹ H-NMR (500 MHz, J(Hz), CDCl ₃); ¹³ C-NMR (125 MHz, CDCl ₃)
m/z: [M - Cl] ⁺ = 279,281 6 (theoretical: 279,27 95)	3477(N-H), 2917(C-H), 2850 (C-H), 1619, 1565, 1466 (C-N), 1162 (C-N), 762 (C-Cl)	H-NMR $\delta(\text{ppm})$: 0,86 (t, J = 6,5 Hz, 3H, H ¹⁴); 1,23-1,31 (m, 22H, H ³ -H ¹³); 1,87 (m, 2H, H ²); 4,08 (s, 3H, NCH ₃); 4,28 (t, J = 7,5 Hz, 2H, H ¹); 7,27 (s, 1H, H ⁵); 7,41 (s, 1H, H ⁴); 10,24 (s, 1H, H ²). ¹³C-NMR $\delta(\text{ppm})$: 14,22 (C ¹⁴), 22,80 (C ¹³), 30,42 (C ²), 36,82 (NCH ₃), 50,34 (C ¹), 123,19 (C ⁴), 121,50 (C ⁵), 138,70 (C ²).

Table 2: FT-IR, HRMS, and NMR spectroscopy results of [C₄BIM]Cl (72 h, mol ratio of alkyl chloride /imidazole=1:1.2; 95°C)

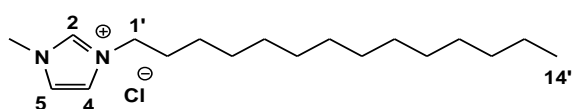
HRMS (ESI)	Spectral data FT-IR $\nu(\text{cm}^{-1})$	Spectral data ¹ H-NMR (500 MHz, <i>J</i> (Hz), CDCl ₃); ¹³ C-NMR (125 MHz, CDCl ₃)
m/z: [M - Cl] ⁺ = 181,1705 (theoretical : 181,1699)	3245(N-H), 2961(C-H), 2872(C-H), 1630, 1563, 1463 (C-N), 1165(C-N), 755(C-Cl)	¹H NMR $\delta(\text{ppm})$: 0,94 (<i>t</i> , <i>J</i> = 7,5 Hz, 6H, H ^{4'}); 1,36 (<i>m</i> , 4H, H ^{3'}); 1,87 (<i>m</i> , 4H, H ^{2'}); 4,33 (<i>t</i> , <i>J</i> = 7 Hz, 4H, H ^{1'}); 7,36 (<i>s</i> , 2H, H ⁴ và H ⁵); 10,56 (<i>s</i> , 1H, H ²). ¹³C-NMR $\delta(\text{ppm})$: 13,51 (C ^{4'}), 19,57 (C ^{3'}), 32,26 (C ^{2'}), 49,91 (C ^{1'}), 121,92 (C ⁴ , C ⁵), 137,94 (C ²).

Table 3: FT-IR, HRMS, NMR spectroscopy results of [C₁₄BIM]Cl (120 h, mol ratio of alkyl chloride /imidazole=1:1.2; 100°C)

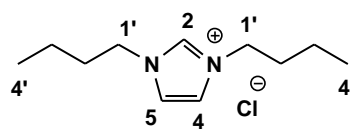
HRMS (ESI)	Spectral data FT-IR $\nu(\text{cm}^{-1})$	Spectral data ¹ H-NMR (500 MHz, <i>J</i> (Hz), CDCl ₃); ¹³ C-NMR (125 MHz, CDCl ₃)
m/z: [M - Cl] ⁺ = 321,3252 (theoretical : 321,3264)	3424(N-H), 2957(C-H), 2854(C-H), 1630, 1563, 1463(C-N), 1165(C-N), 763(C-Cl)	¹H NMR $\delta(\text{ppm})$: 0,85 (<i>t</i> , <i>J</i> = 5 Hz, 3H, H ^{14'}); 0,96 (<i>t</i> , <i>J</i> = 5 Hz, 3H, H ^{4'}); 1,32 -1,24 (<i>m</i> , 24H, (H ^{3''} - H ^{12''})); 1,90 (<i>m</i> , 4H, H ^{2''} và H ^{2'}); 4,36 (<i>m</i> , 4H, H ^{1''} và H ^{1'}); 7,21 (<i>s</i> , 2H, H ⁴ và H ⁵); 10,86 (<i>s</i> , 1 H, H ²). ¹³C NMR $\delta(\text{ppm})$: 13,58 (C ^{14''}), 14,23 (C ⁴), 19,66 (C ^{13''}), 29,80-22,82, (10C, (C ^{3''} - C ^{12''})), 30,45 (C ^{3'}), 32,05 (C ^{2''}), 50,09 (C ^{1''}), 50,37 (C ^{1'}), 121,32 (C ⁴), 121,36, C ⁵), 138,93 (C ²).

From the results of infrared spectroscopy, HRMS (ESI) and nuclear magnetic resonance spectroscopy in Table 1-3 and reference combination [15,16] the products are structurally determined as follows:

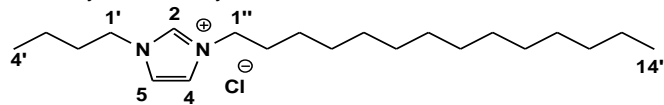
Figure 1: Structure of three synthesized ionic liquids



1-methyl-3-n-tetradecylimidazolium chloride.



1-n-butyl-3-n-butylimidazolium chloride



1-n-butyl-3-n-tetradecylimidazolium chloride

Influence of some factors on the ionic liquid synthesis yield

Influence of reaction time

Experiments were carried out at 95°C with the molar ratio of reactants [C₁₄H₂₉Cl]/[MIM], [C₄H₉Cl]/[BIM], [C₁₄H₂₉Cl]/[BIM] being 1:1.2 and performed at different time intervals from 24 to 132 h. Synthesis results of [C₄BIM]Cl are shown in Figure 1. The results show that, when increasing the time from 24 to 72 hours, the yield rapidly increases from 54.1% to 90.8%. However, when increasing the time from 72 hours to 96 hours, the reaction yield increased insignificantly. Similarly, the yields of [C₁₄MIM]Cl and [C₁₄BIM]Cl increased rapidly from 80 hours to 108 hours and from 96 hours to 120 hours, respectively. After the above time periods, the synthesis yield is stable. It can be observed that the synthesis reaction time of ionic liquids increases with the following order: [C₄BIM]Cl < [C₁₄MIM]Cl < [C₁₄BIM]Cl, that means, reaction time is increased with increasing the length of alkyl substituents attached to the imidazole ring. Specifically, to obtain the similar synthesis efficiency (about 90%) of [C₄BIM]Cl and [C₁₄MIM]Cl it is necessary to perform the reaction from 96 hours and 108 hours while [C₁₄BIM]Cl requires 120 hours. This could be explained by the fact the longer alkyl chain leads to reactants move slower and reaction center is highly spatially hindered, therefore, the collision between the reaction centers on the reagents is reduced. When methylimidazole or butylimidazole approaches C₁₄H₂₉Cl for a reaction to take place, methylimidazole reacts more readily than butylimidazole because the methyl group attached to methylimidazole ring is smaller than butyl group. Therefore, the synthesis of [C₁₄BIM]Cl takes more time than [C₁₄MIM]Cl.

Similarly, when butylimidazole reacts with C₁₄H₂₉Cl and C₄H₉Cl, the results show that the synthesis time of [C₁₄BIM]Cl is longer than the that of [C₄BIM]Cl.

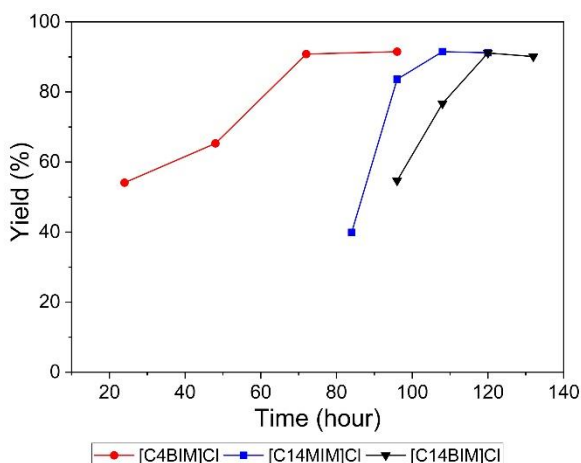


Figure 2: Influence of reaction time on synthesis yield of [C₄BIM]Cl, [C₁₄MIM]Cl and [C₁₄BIM]Cl (mol ratio alkyl chloride /imidazole = 1:1.2; 95 °C)

Influence of reaction temperature

The series of experiments were performed at 95-100 °C, molar ratio is 1:1.2, reaction time of 72 hours, 108 hours and 120 hours for [C₄BIM]Cl, [C₁₄MIM]Cl and [C₁₄BIM]Cl. The results are recorded in Figure 3.

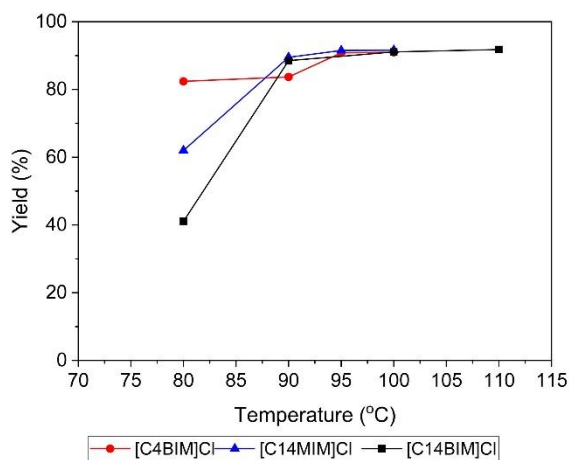


Figure 3: Influence of reaction temperature on synthesis yield of [C₄BIM]Cl, [C₁₄MIM]Cl and [C₁₄BIM]Cl (mol ratio alkyl chloride /imidazole = 1.2; 95 °C)

Figure 3 shows that the reaction yields of [C₄BIM]Cl, [C₁₄MIM]Cl and [C₁₄BIM]Cl increase rapidly from 82.4%, 62.0%; and 41.1%, respectively to about 83.7% when increasing the temperature from 80°C to 90°C and increase more slowly when increasing temperature from 90°C to 95°C. The synthesis yields of [C₁₄MIM]Cl and [C₄BIM]Cl at 100°C and 95°C achieved 91.4% and 90.8%, respectively. When the reaction temperature increases to 100 °C, the yield of both reactions did not change significantly. The C₁₄BIM]Cl is synthesized from

the reactants has a more bulky structure, so that the reaction time is longer and the reaction temperature is higher. When the reaction temperature increases to 100°C, the yield reaches 91.1% and if temperature continue to increase to 110°C, the yield does not change. Therefore, the most suitable temperatures for the synthesis reactions of [C₄BIM]Cl and [C₁₄MIM]Cl are 95°C and of [C₁₄BIM]Cl is 100°C.

Influence of mol ratio of reactants

Based on the above survey, a series of experiments were conducted with reaction time and temperature of ILs were fixed ([C₄BIM]Cl : 72 hours and 95°C, [C₁₄MIM]Cl : 108 hours and 95°C) and [C₁₄BIM]Cl : 120 hours and 100°C); molar ratios of alkyl chloride /imidazole are in range 1÷1.4. The results are presented in Figure 4.

It can be seen from the results of Figure 4 that, when the molar ratio of alkyl chloride /imidazole increasing from 1 to 1.2, the synthesis yields of [C₄BIM]Cl, [C₁₄MIM]Cl and [C₁₄BIM]Cl increased from 86.7%; 83.2% and 64.5% to 90-91% and remained steady when the molar ratio further increasing to 1.4. If the molar ratio of alkyl chloride /imidazole is 1.0, [C₁₄BIM]Cl were formed with the lowest yield (64.5%) and [C₄BIM]Cl with the highest yield. This shows that the structure of the reactants strongly influences on the ionic liquid synthesis reaction. At a molar ratio of alkyl chloride /imidazole 1.2, the synthesis yields of [C₁₄MIM]Cl, [C₁₄BIM]Cl, and [C₄BIM]Cl were 91.4%, 91.1%, and 90.8%, respectively. The higher the molar ratio of alkyl chloride /imidazole, the less significant change in yield.

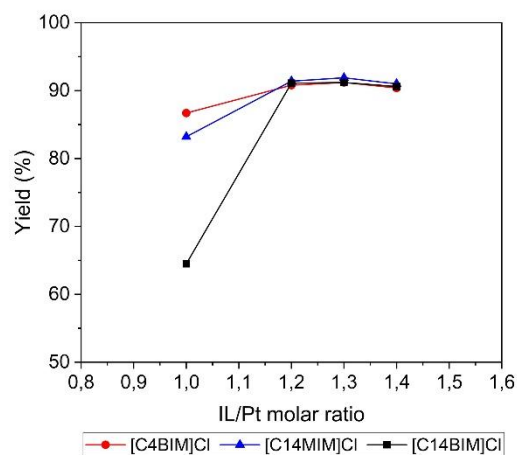


Figure 4 : Influence of mol ratio alkyl chloride /imidazole on synthesis yield of [C₄BIM]Cl, [C₁₄MIM]Cl and [C₁₄BIM]Cl

In summary, the reaction time ranges from 72 to 120 hours depending on the length of the alkyl groups of the imidazole and of alkyl chlorides. In which [C₄BIM]Cl is synthesized from alkyl chloride with a shorter alkyl chain (–C₄H₉), therefore, the reaction time is the shortest (72 hours). Reaction of C₁₄H₂₉Cl with the methylimidazole (to prepare [C₁₄MIM]Cl) takes more time and need high temperature than with butylimidazole (to prepare [C₁₄BIM]Cl), because butyl substituent of butylimidazole is larger than the methyl group of methylimidazole. Similarly, the reaction of butylimidazole with C₁₄H₂₉Cl requires a longer time and higher temperature compared to reaction with C₄H₉Cl. This also proves that the synthesis of [C₁₄MIM]Cl requires longer time and higher temperature than [C₄BIM]Cl. From the results of synthetic surveys of 3 ionic liquids, it can be concluded that the stereochemistry of the alkyl group in the alkyl chloride is stronger than that in the imidazole ring ; [C₁₄BIM]Cl needs the highest temperature and the longest time, while [C₄BIM]Cl needs the lowest time and temperature ([C₄BIM]Cl < [C₁₄MIM]Cl < [C₁₄BIM]Cl).

It is possible to recommend suitable conditions in the survey area to synthesize 3 ionic liquids in Table 4.

Table 4 : The suitable conditions for the synthesis of ionic liquids [C₄BIM]Cl, [C₁₄MIM]Cl and [C₁₄BIM]Cl

Factors	Ionic liquid		
	[C ₄ BIM]Cl	[C ₁₄ MIM]Cl	[C ₁₄ BIM]Cl
Time (h)	72	108	120
Temperature (°C)	95	95	100
Mol ratio	1.2	1.2	1.2
Yield (%)	90.8	91.4	91.1

Conclusion

Three ionic liquids [C₁₄MIM]Cl, [C₄BIM]Cl and [C₁₄BIM]Cl were prepared from imidazole and alkyl halide compounds in high yields using conversional method with magnetic stirrer. The conditions for the synthesis of ionic liquids depend on their structure, the alkyl length of imidazole and alkyl halide compounds. [C₁₄BIM]Cl is made up of 2 substances which both have the longest alkyl group, therefore, it need to be synthesized at highest temperature and longest time among three ionic liquids [C₁₄MIM]Cl, [C₄BIM]Cl, [C₁₄BIM]Cl. Under the temperature (95°C-100°C) and fixed molar ratio of alkyl chloride /imidazole (1.0/1.2), the synthesis yields of [C₁₄MIM]Cl, [C₄BIM]Cl, [C₁₄BIM]Cl reach 91.4%, 90.8%, and 91.1% after 120, 72 and 120 hours, respectively.

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