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

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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

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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 alkyl chloride 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 with diethyl ether to remove any excess reactant. Examples of specific reaction procedures are presented below:

Synthesis of 1-methyl-3-n-tetradecylimidazolium chloride ([C4MIM]Cl)

Put 1,231 g 1-methylimidazole (0.015 mol) and 4.203 g 1-chlorotetradecane (0.018 mol) with a molar ratio of 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 h. 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 ([C4BIM]Cl)

3.725 g of butyl imidazole (0.03 mol) and 8,370 g of 1-chlorotetradecane (0.036 mol with a molar ratio of 1-chlorotetradecane/ 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 [C4MIM]Cl (108 h, molar ratio of alkyl chloride /imidazole=1:1.2; 95°C)

<table>
<thead>
<tr>
<th>HRMS (ESI)</th>
<th>Spectral data FT-IR ν(cm⁻¹)</th>
<th>Spectral data ¹H-NMR (500 MHz, δ(Hz), CDCl₃); ¹³C-NMR (125 MHz, CDCl₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/z: [M - Cl]⁺ = 279,281</td>
<td>3477(N-H), 2917(C-H), 2850(C-H), 1619, 1565, 1466(C-N), 1162(C-N), 762(C-Cl)</td>
<td>H-NMR δ(ppm): 0.86 (t, J = 6.5 Hz, 3H, H14); 1.23-1.31 (m, 22H, H2-H13); 1.87 (m, 2H, H2); 4.08 (s, 3H, NCH3); 4.28 (t, J = 7.5 Hz, 2H, H1); 7.27 (s, 1H, H3); 7.41 (s, 1H, H4); 9.24 (s, 1H, H2). ¹³C-NMR δ(ppm): 14.22 (C14), 22.80 (C13), 30.42 (C2), 36.01 (NCH3), 50.34 (C), 123.19 (C2), 121.50 (C3), 138.70 (C2).</td>
</tr>
</tbody>
</table>

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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)

<table>
<thead>
<tr>
<th>HRMS (ESI)</th>
<th>Spectral data FT-IR (λ)</th>
<th>Spectral data ( ^1 )H-NMR (500 MHz, J(Hz), CDCl(_3)); ( ^13 )C-NMR (125 MHz, CDCl(_3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/z: [M – Cl(^+)] = 181,1705 (theoretical: 181,1699)</td>
<td>3245(N-H), 2961(C-H), 2872(C-H), 1563, 1463(C-N), 1165(C-N), 765(C-Cl)</td>
<td>( ^1 )H NMR δ(ppm): 0.94 (t, J = 7.5 Hz, 6H, H(^4)), 1.36 (m, 4H, H(^3)), 1.87 (m, 4H, H(^2)), 4.33 (t, J = 7 Hz, 4H, H(^1)); 7.36 (s, 2H, H(^4) v(a) H(^5)), 10.56 (s, 1H, H(^2)). ( ^13 )C-NMR δ(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(^3)).</td>
</tr>
</tbody>
</table>

Table 3: FT-IR, HRMS, NMR spectroscopy results of [C4BIM]Cl (120 h, mol ratio of alkyl chloride /imidazole=1:1.2; 100°C)

<table>
<thead>
<tr>
<th>HRMS (ESI)</th>
<th>Spectral data FT-IR (λ)</th>
<th>Spectral data ( ^1 )H-NMR (500 MHz, J(Hz), CDCl(_3)); ( ^13 )C-NMR (125 MHz, CDCl(_3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/z: [M – Cl(^+)] = 321,3252 (theoretical: 321,3264)</td>
<td>3424(N-H), 2957(C-H), 2854(C-H), 1630, 1563, 1463(C-N), 1165(C-N), 763(C-Cl)</td>
<td>( ^1 )H NMR δ(ppm): 0.85 (t, J = 5 Hz, 3H, H(^14)), 0.96 (t, J = 5 Hz, 3H, H(^4)), 1.32 -1,24 (m, 24H, (H(^3)= H(^12))). 1.90 (m, 4H, H(^2) v(a) H(^5))); 4.36 (m, 4H, H(^1) v(a) H(^1))), 7.21 (s, 2H, H(^4) v(a) H(^5)); 10.86 (s, 1H, H(^2)). ( ^13 )C-NMR δ(ppm): 13,58 (C(^14)), 14,23 (C(^2)), 19,66 (C(^13))), 29,80-22,82, (10C, (C(^3)= C(^12))), 30,45 (C(^1)), 32,05 (C(^2)), 50,09 (C(^1)), 50,37 (C(^2)), 121,32 (C(^4), C(^5)), 138,93 (C(^3)).</td>
</tr>
</tbody>
</table>

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.

Influence of some factors on the ionic liquid synthesis yield

Experiments were carried out at 95°C with the molar ratio of reactants [C4H29Cl]/[MIM], [C4H5Cl]/BIM, [C4H23Cl]/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 [C4MIM]Cl and [C4BIM]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 < [C4MIM]Cl < [C4Cl]Cl, that means, reaction time is increased with increasing the length of alkyl substituents attached to the imidazole ring. Specifically, to obtain the same reaction yield, [C4BIM]Cl requires 120 hours, whereas [C4MIM]Cl requires 110 hours. This can be explained by the fact that 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 methylimidazolide or butylimidazole approaches C4H29Cl for a reaction to take place, methylimidazolide reacts more readily than butylimidazole because the methyl group attached to methylimidazolide ring is smaller than butyl group. Therefore, the synthesis of [C4BIM]Cl takes more time than [C4MIM]Cl.

Similarly, when butylimidazole reacts with C4H29Cl and C4H5Cl, the results show that the synthesis time of [C4BIM]Cl is longer than that of [C4MIM]Cl.

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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 shows that the reaction yields of [C4BIM]Cl, [C14MIM]Cl and [C14BIM]Cl (mol ratio alkyl chloride /imidazole = 1:1.2; 95 °C) 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 changed. 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 [C4BIM]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 alkyl chloride /imidazole increasing from 1 to 1.2, the synthesis yields of [C4BIM]Cl, [C14MIM]Cl and [C4BIM]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, [C4BIM]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.
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 C4H9Cl with the methylimidazolide (to prepare [C4MIM]Cl) takes more time and need high temperature than with butylimidazolide (to prepare [C4BIM]Cl), because butyl substituent of butylimidazolide is larger than the methyl group of methylimidazolide. Similarly, the reaction of butylimidazolide with C4H9Cl requires a longer time and higher temperature compared to reaction with C4H9Cl. This also proves that the synthesis of [C4MIM]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; [C4BIM]Cl needs the highest temperature and the longest time, while [C4BIM]Cl needs the lowest time and temperature ([C4BIM]Cl < [C4MIM]Cl < [C4BIM]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, [C4MIM]Cl and [C4BIM]Cl

<table>
<thead>
<tr>
<th>Factors</th>
<th>[C4BIM]Cl</th>
<th>[C4MIM]Cl</th>
<th>[C4BIM]Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (h)</td>
<td>72</td>
<td>108</td>
<td>120</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>95</td>
<td>95</td>
<td>100</td>
</tr>
<tr>
<td>Mol ratio</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Yield (%)</td>
<td>90.8</td>
<td>91.4</td>
<td>91.1</td>
</tr>
</tbody>
</table>

Conclusion

Three ionic liquids [C4MIM]Cl, [C4BIM]Cl and [C4BIM]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. [C4BIM]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 [C4MIM]Cl, [C4BIM]Cl, [C4BIM]Cl. Under the temperature (95°C-100°C) and fixed molar ratio of alkyl chloride/imidazole (1.0/1.2), the synthesis yields of [C4MIM]Cl, [C4BIM]Cl, [C4BIM]Cl reach 91.4%, 90.8%, and 91.1% after 120, 72 and 120 hours, respectively.

Reference

15. Kenneth R. Seddon, Christopher M. Kear, Phillip D. Amitage, Towner B. Schemer Charles L. Hussey,