Mixed Chlorometallate Ionic Liquids as C₄ Alkylation Catalysts: A Quantitative Study of Acceptor Properties

Xiaoying Pang, Ying Liu * and Juanfang Wang

College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, China; Pmmwhydedabai@163.com (X.P.); lavenderem@163.com (J.W.)

* Correspondence: celiuy@imu.edu.cn; Tel.: +86-471-499-2981

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Abstract: The acceptor properties of mixed chlorometallate ionic liquids for isobutane-butene alkylation (C₄ alkylation) reaction were studied. These ionic liquids were prepared by mixing metal chlorides with either triethylamine hydrochloride or 1-butyl-3-methylimidazolium chloride in various molar ratios. Using triethylphosphine oxide as a probe, Gutmann Acceptor Numbers (AN) of the catalysts were determined, and the Lewis acidity of mixed chlorometallate ionic liquids was quantitatively measured. Additionally, AN value was developed to determine the relationship between Lewis acidity and catalytic selectivity. The favorite AN value for the C₄ alkylation reaction should be around 93.0. The [(C₂H₅)₃NH]Cl–AlCl₃–CuCl appears to be more Lewis acidity than that of [(C₂H₅)₃NH]Cl–AlCl₃. The correlation of the acceptor numbers to speciation of the mixed chlorometallate ionic liquids has also been investigated. [AlCl₄]⁻, [Al₂Cl₇]⁻, and [MAICl₃]⁻ (M = Cu, Ag) are the main anionic species of the mixed chlorometallate ILs. While the presence of [(C₂H₅)₃N·M]⁺ cation always decreases the acidity of the [(C₂H₅)₃NH]Cl–AlCl₃–MCl ionic liquids.

Keywords: ionic liquid; isobutane; alkylation; Lewis acidity; acceptor properties

1. Introduction

In the last decade, the use of chloroaluminate ionic liquids (ILs) to replace conventional acid catalysts has received much attention [1,2]. Due to their versatile properties, ionic liquids have been used in many fields [3]. The applications of chloroaluminate ILs primarily focus on the industrial Friedel–Crafts alkylation, oligomerization, and isomerization reactions of olefins [4]. A well-known example of catalysis in chloroaluminate ILs may be the alkylation of isobutane and butenes (C₄ alkylation) [5]. In this reaction, [C₄mim]Cl–AlCl₃ [6], [(C₂H₅)₃NH]Cl–AlCl₃ [7], and amide-AlCl₃-based [8] ionic liquids were used instead of concentrated sulfuric acid and hyper-toxic hydrogen fluoride. In addition, the isomerization of dicyclopentadienes could be catalyzed by [Hpy]Cl–AlCl₃ chloroaluminate ILs [9,10]. Particularly, a pilot-scale oligomerization of the olefins process has been established by BP (British Petroleum Company plc), which uses the [(CH₃)₃NH]Cl–AlCl₃ ionic liquid as a catalyst. Akzo Nobel also developed an industrial application of the benzene alkylation employing a similar chloroaluminate ionic liquid [11].

Introducing metal salts to chloroaluminate ILs can either change the activity of chloroaluminate anions, or coordinate the added metal ions to chloroaluminate anions [12]. Compared with net chloroaluminate ILs, this feature of mixed chlorometallate ILs might be one of the key benefits for some reactions. For example, a significant catalytic activity could be observed in a Beckman rearrangement reaction of acetophenone oxime, when the mixed metal [(C₂H₅)₃NH]₂[(1–x)AlCl₃ + xZnCl₂] double salt ILs were adopted. The activity of the ionic liquid was found even higher than that of [(C₂H₅)₃NH][Al₂Cl₇] or AlCl₃ [13]. Zinurov et al. [14] have found that the route of the n-pentane
isomerization could be controlled by using [(CH$_3$)$_3$NH]Cl–AlCl$_3$/copper-salt mixtures. Additionally, high yields of branched olefin polymers can be obtained by adding TiCl$_4$ to the [C$_4$ mim]Cl–AlCl$_3$ ionic liquid [15]. Yang et al. also found that the mixed chlorometallate [(C$_2$H$_5$)$_3$NH]Cl–FeCl$_3$–CuCl might enhance the conversion and selectivity of the isobutene oligomerization [16]. Perhaps the most famous application of mixed chlorometallate ionic liquids is the Difasol process, which was developed by IFP (Institut Francais Du Petrole) and the [C$_4$ mim][AlCl$_4$]–EtAlCl$_2$–NiCl$_2$ ionic liquid was employed for olefin dimerization [17,18].

As mentioned above, the C$_4$ alkylation reaction is one of the most important IL applications. However, the requirement of acidity for the C$_4$ alkylation reaction is very strict. When the acidity of the catalyst is strong, the product would contain many C$_5$–C$_7$ fractions. In contrast, if the acidity is weak, the C$_9$+ byproducts would be dominant. In order to improve the catalytic performance of ILs, the super acidity of chloroaluminate ILs usually need to be tuned by other compounds. In the cases of [Bmim]Cl–AlCl$_3$ and [(C$_2$H$_5$)$_3$NH]Cl–AlCl$_3$, the introduction of CuCl to these chloroaluminate ILs is beneficial to increase the content of the desired trimethylpentanes (TMP, C$_8$ fractions). Similarly, the presence of AgAlCl$_4$ in MTBE–AlCl$_3$ solution often leads to a high TMP selectivity. Adding CuCl to the ether–AlCl$_3$ system or the amide-AlCl$_3$-based ionic liquid analogues also significantly increased the TMP content. Therefore, the transition metal chlorides can significantly improve the catalytic performance of chloroaluminate ILs. This improvement is often interpreted as the decrease of super-acidity of the chloroaluminate ILs [19].

The size, shape, and relative energy of the acid and the base will markedly affect the interaction of a Lewis acid-base pair. It means that the base of a Lewis acid interacting with can determine the acid strength [5]. Although a universal scale of Lewis acidity could not be established [20], several studies on the determination of the quantitative behavior of chloroaluminate ILs have been reported. For example, Thomazeau et al. have measured the acid strength of a series of imidazolium ILs by using UV-vis spectroscopy and Hammett indicators [21]. The acceptor properties of chlorometallate ILs have been studied by Osteryoung [22,23] and Swadźba-Kwaśny [24], respectively. In addition, the Lewis acidity of halometallate-based ILs and the basicity of hydrogen bond could be obtained by X-ray photoelectron spectroscopy [25]. Using infrared spectroscopy and pyridine probe, Kou et al. [26] developed a new method for determining the acid strength of chloroaluminate ILs, and Hu [27] made a more detailed measurement for these ILs. However, the Lewis acidity of the mixed chlorometallate ILs for C$_4$ alkylation reaction is still ambiguous.

Apart from the changes of acidity, adding metal salts to chloroaluminate ILs would lead to an interaction of the added metal ions and the chloroaluminate anions. In the previous works, we found that the catalytic performance of C$_4$ alkylation is probably determined by the compositions of the mixed chlorometallate ILs rather than by the Lewis acid strength. That is, the presence of heterometallic chlorometallate anion [CuAlCl$_5$]$^-$ might improve the catalytic selectivity. This anion has been detected in the $^{27}$Al NMR spectra of [Bmim]Cl–AlCl$_3$–CuCl and [(C$_2$H$_5$)$_3$NH]Cl–AlCl$_3$–CuCl ionic liquids [28–30]. However, other researchers argued that the peak of [CuAlCl$_5$]$^-$ should be identified as the signal of [Al$_2$Cl$_6$OH]$^-$ [31]. They proposed that Cu(I) could substitute the proton in the [(C$_2$H$_5$)$_3$NH]$^+$ cation and generate [(C$_2$H$_5$)$_3$N-Cu]$^+$ and HCl [19]. Generally, the speciation of chlorometallate ionic liquids are closely related to their Lewis acidity [1,5,32]. Thus, a quantitative study of the Lewis acidity may be helpful to clarify the speciation of the ionic liquids.

We want to make a quantitative investigation on the acidity of mixed chlorometallate ILs by using $^{31}$P NMR chemical shifts. Gutmann Acceptor Number (AN) is considered as an effective methodology for quantitatively determining the Lewis acidity [33]. When triethylphosphine oxide (tepo) was added to the acidic sample, the coordination of tepo with the Lewis acid always induces a change of the $^{31}$P NMR chemical shift, and then the AN can be calculated by the equation: $\text{AN} = 2.348 \times \delta_{\text{inf}}$. In order to obtain the $\delta_{\text{inf}}$ value ($^{31}$P chemical shift at infinite dilution of tepo), the chemical shifts of $^{31}$P NMR at several concentrations of tepo need to be measured at first, and then these data should be
extrapolated to infinite dilution. Using tepo probe, the AN values can precisely indicate the Lewis acidity of many compounds.

In this paper, the Lewis acidity of mixed chlorometallate ILs for isobutane alkylation was quantitatively studied by determining the AN values. The relationship between the Lewis acidity of ionic liquids and their catalytic performance of \( \text{C}_4 \) alkylation has been studied. In addition, the speciation of ions has been determined for the [Bmim]Cl—AlCl\(_3\)—CuCl and \([\text{C}_2\text{H}_5\text{NH}]\text{Cl—AlCl}_3—\text{CuCl}\) mixed chlorometallate systems. The correlation of the observed changes in the acidity to speciation has also been investigated.

2. Results and Discussion

2.1. Estimation of \( \delta_{\text{corr}} \) at Infinite Dilution

The Gutmann Acceptor Number is an experimental procedure to evaluate the Lewis acidity of molecules. Generally, triethylphosphine oxide (tepo) is very sensitive to the Lewis acidic environment. When tepo is used as a probe molecule, the interaction between tepo and the Lewis acid will cause deshielding of the 31P chemical shift of tepo. Therefore, the Lewis acidity of ionic liquids could be assessed by 31P NMR spectroscopy. The AN values of Lewis acidic compounds are usually between the two reference points of the weak Lewis acid hexane (\( \delta = 41.0 \) ppm, AN = 0) and the strong Lewis acid SbCl\(_5\) (\( \delta = 86.1 \) ppm, AN 100). Thus, an acceptor number scale for solvent Lewis acidity is established. The acceptor numbers can be calculated from the equation AN = 2.21 \times (\delta_{\text{sample}} − \delta_{\text{inf}}).

Higher AN value often indicates that the compound has a greater Lewis acidity. For example, the AN of AlCl\(_3\) is 87 and the AN value is 70 for transition-metal compound TiCl\(_4\), which all display Lewis acidic properties.

In all studied ILs, the 31P NMR (Nuclear Magnetic Resonance) signal of tepo was a single peak. Because of the volume susceptibility differences between the studied ILs and hexane, the acceptor numbers of ILs should be calculated by extrapolating the chemical shift to infinite dilution. It means that the 31P NMR chemical shifts of infinite dilution tepo in the ionic liquid (\( \delta_{\text{inf}} \)) must be obtained at first. Here, the values of \( \delta_{\text{inf}} \) were determined by extrapolation, and the acceptor numbers were calculated through AN = 2.348 \times \delta_{\text{corr}} instead of using AN = 2.21 \times (\delta_{\text{sample}} − \delta_{\text{inf}}). The number of \( \delta_{\text{corr}} \) is the susceptibility-corrected value, which is defined as the infinite-dilution chemical shift of the probe molecule in a solvent (i) relative to that of the probe molecule in hexane. For instance, the 31P NMR chemical shift of tepo with different concentrations in \([\text{C}_2\text{H}_5\text{NH}]\text{Cl—AlCl}_3\) and the fitted straight lines are depicted in Figure 1. These data (\( \delta_{\text{exp}} \)) were fitted by regression analysis to get a linear equation: \( \delta_{\text{exp}} = m\text{teto} + \delta_{\text{corr}} \). The values of \( m \) and \( R^2 \) were collected in Table 1, and the \( \delta_{\text{corr}} \) values were finally obtained by the linear regression approach.

\[ \delta_{\text{exp}} = m\text{teto} + \delta_{\text{corr}} \]

**Figure 1.** Experimental 31P NMR chemical shifts for tepo as a function of tepo concentration in chloroaluminate compositions: (a) \([\text{C}_2\text{H}_5\text{NH}]^+\)—based ILs, \([\text{C}_2\text{H}_5\text{NH}]\text{Cl—AlCl}_3\) (\( \Delta \)), \([\text{C}_2\text{H}_5\text{NH}]\text{Cl—AlCl}_3—\text{CuCl}\) (○), and \([\text{C}_2\text{H}_5\text{NH}]\text{Cl—AlCl}_3—\text{AgCl}\) (*); (b) [Bmim]+—based ionic liquids (ILs), [Bmim]Cl—AlCl\(_3\) (\( \Delta \)), [Bmim]Cl—AlCl\(_3—\text{CuCl}\) (○), and [Bmim]Cl—AlCl\(_3—\text{AgCl}\) (*).
Table 1. Parameters of linear regression for various ionic liquids.

| Entry | Ionic Liquids | m   | $\delta_{i,cor}$ | $R^2$ |
|-------|---------------|-----|-----------------|-------|
| 1     | [(C$_2$H$_5$)$_3$NH]Cl−AlCl$_3$ | −0.0016 | 39.9123 | 0.9591 |
| 2     | [(C$_2$H$_5$)$_3$NH]Cl−AlCl$_3$−CuCl | −0.0082 | 40.1273 | 0.9611 |
| 3     | [(C$_2$H$_5$)$_3$NH]Cl−AlCl$_3$−AgCl | −0.0057 | 40.2422 | 0.9631 |
| 4     | [Bmim]Cl−AlCl$_3$ | −0.0109 | 40.2572 | 0.9983 |
| 5     | [Bmim]Cl−AlCl$_3$−CuCl | −0.0502 | 39.7951 | 0.9203 |
| 6     | [Bmim]Cl−AlCl$_3$−AgCl | −0.0444 | 39.2126 | 0.9921 |
| 7     | [(C$_2$H$_5$)$_3$NH]Cl−CuCl | −0.0361 | 35.9313 | 0.9998 |
| 8     | [(C$_2$H$_5$)$_3$NH]Cl−ZnCl$_2$ | −0.0316 | 36.3523 | 0.9877 |

1 The molar ratio of AlCl$_3$, CuCl, or ZnCl$_2$ to organic salt is 1:6:1.

2.2. AN Values and C$_4$ Alkylation Performance

In this work, $^{31}$P NMR chemical shifts of the ILs for alkylation reaction were determined. The chemical shifts of those ILs with weaker Lewis acidity [34,35], such as [(C$_2$H$_5$)$_3$NH]Cl−CuCl and [(C$_2$H$_5$)$_3$NH]Cl−ZnCl$_2$, benzene−CuAlCl$_4$, and ether−CuClAl$_4$, were also measured for comparison. For convenience, the apparent molar ratio of organic salt to AlCl$_3$ was 1:1.6, while the apparent molar ratio of MCl$_x$ (M = Cu, Ag, or Zn; x = 1 or 2) to AlCl$_3$ was 0.5:1. Generally, the metal chlorides would react with the ions of net chloroaluminate ILs. Although some of the transition metal chlorides at this ratio might not be completely dissolved to the chloroaluminate ionic liquids, it did not significantly reduce the catalytic activities of the chloroaluminate ILs. To better understand these changes, we measured the AN values at first, and then the catalytic selectivities of various ILs were compared.

As Table 2 shown, most TMP selectivities of chloroaluminate ionic liquids could be improved by the modification of metal chlorides. Meanwhile, it is found that the transition metal chlorides would reduce the Lewis acid strength of the [Bmim]$^+$−based chloroaluminate IL. For example, the AN value of [Bmim]Cl−AlCl$_3$−AgCl is about 2.5 lower than that of [Bmim]Cl−AlCl$_3$. The other [Bmim]Cl−AlCl$_3$−MCl$_x$ (M = Cu, Zn) ionic liquids also have the same trend. If AN over 95, the catalysts can be defined as superacids. For an extreme case, the super-acidity of trifluoromethanesulfonic acid (CF$_3$SO$_2$H) is not good for the C$_4$ alkylation reaction (Entry 11: AN > 126, but RON < 85). Similarly, the trifluoroacetic acid (CF$_3$COOH) that with strong acidity also lead to a relatively poor product quality (Entry 14: AN > 110, but RON < 87). In contrast, those ionic liquids with weak Lewis acidity (AN < 86), such as CH$_3$COOH, [(C$_2$H$_5$)$_3$NH]Cl−CuCl, CH$_3$COOCH, and [(C$_2$H$_5$)$_3$NH]Cl−ZnCl$_2$, cannot catalyze the alkylation reaction. However, acceptor number determination for the [(C$_2$H$_5$)$_3$NH]$^+$−based chloroaluminate ILs indicates that the Lewis acidity of the IL [(C$_2$H$_5$)$_3$NH]Cl−AlCl$_3$ was not reduced by the introduction of CuCl or AgCl. [(C$_2$H$_5$)$_3$NH]Cl−AlCl$_3$−CuCl or [(C$_2$H$_5$)$_3$NH]Cl−AlCl$_3$−AgCl usually results in much better catalytic selectivity than that of [(C$_2$H$_5$)$_3$NH]Cl−AlCl$_3$ (Entries 2 and 3 vs. Entry 1). Thus, the effects of Lewis acidity on the selectivity of alkylation reaction may be much more complicated than the previous conclusions [19].

On the other hand, it is well known that the chloroaluminate ionic liquid appears to be Lewis acidity only when the molar ratio of AlCl$_3$ to the organic salt is greater than 1:1. Therefore, if we investigated the relationship between the acceptor number of ILs with various mole ratios of AlCl$_3$ and the alkylation results, it is possible to provide a quantitative scale of Lewis acidity for the C$_4$ alkylation reaction. Figure 2 depicts this evaluation, which again indicates that the C$_4$ alkylation reaction is strict to the acidity. Only the AN value of [(C$_2$H$_5$)$_3$NH]Cl−AlCl$_3$ is greater than 92.0 (e.g., mole ratio of AlCl$_3$ to [(C$_2$H$_5$)$_3$NH]Cl is 1.3), the isobutane can be completely reacted with butenes (olefin conversion > 97%). While the AN value is greater than 95.0, the product quality will be lowered (e.g., [(C$_2$H$_5$)$_3$NH]Cl−2AlCl$_3$). In general, the favorite AN value for the C$_4$ alkylation reaction should be around 93.0.
Table 2. The relationship between Acceptor Number (AN) value and the alkylate selectivity.

| Entry | Catalysts | AN  | TMP 1, wt.% | Calculated RON 2 |
|-------|-----------|-----|-------------|-----------------|
| 1     | [(C₂H₅)₃NH]Cl−AlCl₃ | 93.71 | 37.5 | 88.6 |
| 2     | [(C₂H₅)₃NH]Cl−AlCl₃−CuCl | 94.22 | 78.2 | 99.0 |
| 3     | [(C₂H₅)₃NH]Cl−AlCl₃−AgCl | 94.49 | 80.5 | 99.6 |
| 4     | [Bmim]Cl−AlCl₃ | 94.52 | 43.7 | 90.6 |
| 5     | [Bmim]Cl−AlCl₃−CuCl | 93.44 | 74.8 | 98.3 |
| 6     | [Bmim]Cl−AlCl₃−AgCl | 92.07 | 76.5 | 98.9 |
| 7     | [Bmim]Cl−AlCl₃−ZnCl₂ | 92.61 | 71.6 | 97.5 |
| 8     | benzene−CuAlCl₄ | 91.08 | 68.7 | 97.0 |
| 9     | ether−CuClAl₄ | 91.95 | 69.1 | 97.2 |
| 10    | CH₃COOH | 55.68 | none | - |
| 11    | CF₃SO₃H | 126.21 | 28.2 | 84.9 |
| 12    | [(C₂H₅)₃NH]Cl−CuCl | 84.37 | none | - |
| 13    | [(C₂H₅)₃NH]Cl−ZnCl₂ | 85.36 | none | - |
| 14    | CF₃COOH | 115.14 | 34.0 | 86.4 |
| 15    | CH₃COOOH | 70.25 | none | - |

1 TMP (trimethylpentanes) is the most desired product, which include 2,2,4−, 2,3,3−, and 2,3,4−TMP. The selectivity of TMP is equal to the total amount of trimethylpentanes in the alklylation product. Data of [(C₂H₅)₃NH]⁺− and [Bmim]−− based ILs are from Refs. [28,29], respectively. The other TMP data are obtained in this work. The research octane number (RON) was calculated according to the method of Ref. [5].

2.3. Effects of Metal Chloride (MCl) on the Acidity of the Chloroaluminate IL

In order to further study the acidity of mixed chlorometallate ionic liquids, the change in the 31P chemical shift of the tepo vs. the composition of metal chloride (MCl, M = Cu or Ag) was investigated. Here, the apparent mole ratio of organic salt to AlCl₃ is 1:1.6, while the ratio of MCl to AlCl₃ is 0.60:1, 0.55:1, 0.50:1, 0.40:1, 0.30:1, 0.20:1, 0.10:1, and 0.05:1, respectively. Tepo was added to each ILs, and then the acceptor numbers were obtained for each sample.

When CuCl was added to the IL [(C₂H₅)₃NH]Cl−AlCl₃, AN values exhibit a tendency of first decreasing and then increasing (Figure 3a). It might be explained by the reactions (1)−(8). [Al₂Cl₇]− is a strong acidic anion in contrast to the [AlCl₄]− anion. With the molar ratio of CuCl to AlCl₃ increasing, the concentration of [Al₂Cl₇]− would be proportionately decreased (reactions (1) and (2)). Subsequently, the tepo reacted with AlCl₃ or [AlCl₄]−. The presence of tepo-AlCl₃ indicated that the acid strength of
[(C2H5)3NH]Cl−AlCl3 was reduced (reactions (3)–(6)). In particular, as we increased the concentration of CuCl, a little solid would precipitate. This solid is presumably CuAlCl4 (reaction (6)).

$$\text{Al}_2\text{Cl}_7^- + \text{CuCl} \rightleftharpoons \text{CuAlCl}_5^- + \text{AlCl}_3 \quad (1)$$

$$[(\text{C}_2\text{H}_5\text{N})_3\text{H}]^+\text{AlCl}_4^- + \text{CuCl} \rightarrow [(\text{C}_2\text{H}_5\text{N})_3\text{H}]\text{CuAlCl}_5^- \quad (2)$$

$$\text{Al}_2\text{Cl}_7^- + \text{Cl}^- \rightleftharpoons 2\text{AlCl}_4^- \quad (3)$$

tepo + AlCl3 → tepo-AlCl3 \quad (4)

tepo + AlCl4− → tepo-AlCl3 + Cl− \quad (5)

$$\text{CuAlCl}_5^- \rightarrow \text{CuAlCl}_4 + \text{Cl}^- \quad (6)$$

However, when the mole ratio of CuCl to AlCl3 is greater than 0.5, it is found that the AN value of the IL was increased with respect to the 0.5 mole ratio. This result should be attributed to the following reactions (7) and (8).

$$[(\text{C}_2\text{H}_5\text{N})_3\text{H}]^+\text{AlCl}_4^- + \text{CuCl} \rightarrow [(\text{C}_2\text{H}_5\text{N})_3\text{NCu}]^+ + \text{AlCl}_4^- + \text{HCl} \quad (7)$$

$$\text{tepo} + \text{AlCl}_3 + \text{AlCl}_4^- + \text{Cu}^+ \rightleftharpoons \text{tepo-2AlCl}_3 + \text{CuCl} \quad (8)$$

where tepo·2AlCl3 is more acidic than the tepo·AlCl3, resulting in an increase of the acidity.

Quantum theory calculation maybe provides another support of the above explanation. $V_{s,max}$ is an effective parameter for interpreting and predicting the acidic region of ILs. The larger magnitude of $V_{s,max}$ usually implies stronger acidity or interaction [36]. It is found that the $V_{s,max}$ of $[(\text{C}_2\text{H}_5\text{N})_3\text{H}]^+[\text{CuAlCl}_5^-]$ is slightly larger than that of $[(\text{C}_2\text{H}_5\text{N})_3\text{H}]^+[\text{AlCl}_4^-]$, and the order of Lewis acidity is $[(\text{C}_2\text{H}_5\text{N})_3\text{H}]^+[\text{Al}_2\text{Cl}_7^-] > [(\text{C}_2\text{H}_5\text{N})_3\text{H}]^+[\text{CuAlCl}_5^-] > [(\text{C}_2\text{H}_5\text{N})_3\text{H}]^+[\text{AlCl}_4^-] > [(\text{C}_2\text{H}_5\text{N})_3\text{NCu}]^+[\text{AlCl}_4^-]$ [37,38]. When a small amount of CuCl was introduced into the IL, CuCl might first react with [Al2Cl7−] to form CuAlCl4 or [CuAlCl5−]. Decreasing the concentration of [Al2Cl7−] would lead to reducing the acidity of the whole [(C2H5)3NH]Cl−AlCl3. However, adding more CuCl to the IL, [(C2H5)3NH]+ would react with Cu+ to form [(C2H5)3NCu]+ in accordance with the reaction (7). Meanwhile, a large quantity of [AlCl4−] anion might have more opportunity to react with Cu+, and finally formed more acidic [(C2H5)3NH]+[CuAlCl5−]. Therefore, it may be deduced that [(C2H5)3NCu]+ and [CuAlCl5−] should all exist in the [(C2H5)3NH]+-based chloroaluminate IL. The change of 31P chemical shifts for [(C2H5)3NH]Cl−AlCl3−AgCl is very similar to that of [(C2H5)3NH]Cl−AlCl3−CuCl, indicating that [AgAlCl5]− and [(C2H5)3N·Ag]+ ions should also present in the IL.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Effects of MCl on the acidity of the chloroaluminate IL: (a) adding MCl (M = Cu, Ag) into [(C2H5)3NH]Cl−AlCl3; (b) adding CuCl into [Bmim]Cl−AlCl3.
However, the AN value of the [Bmim]Cl−AlCl$_3$−CuCl system is different from those of [(C$_2$H$_5$)$_3$NH]Cl−AlCl$_3$−CuCl. With the mole ratio of CuCl to AlCl$_3$ increasing, the $^{31}$P shifts shows a monotonic decreasing trend (Figure 3b). When CuCl continues to be added to [Bmim]Cl−AlCl$_3$, CuCl would react with chloroaluminate anions according to the reaction (1), and thus the acidity of ionic liquids decreased with increasing the content of [AlCl$_4$]$^-$. It is well known that [Bmim]$^+$$[Al_2Cl_7]^-$$,$ would give more stronger acidity than that of [Bmim]$^+$$[AlCl_4]^-$$ or [Bmim]$^+$$[CuAlCl_5]^-$$ $^{[39,40]}$. With more CuCl being added, the acidity of [Bmim]Cl−AlCl$_3$−CuCl would become weaker than that of [Bmim]Cl−AlCl$_3$ because of the consumption of [Al$_2$Cl$_7$]$^-$$.$

2.4. The Speciation of Mixed Chlorometallate Ions

To further clarify the mixed metal ions, effects of AlCl$_3$ on the acidity of net chlorometallate IL (e.g., [(C$_2$H$_5$)$_3$NH]Cl−CuCl, [Bmim]Cl−CuCl) were investigated. In this work, the ratio of organic salt to CuCl is kept constant 1:1. After [(C$_2$H$_5$)$_3$NH]Cl−CuCl or [Bmim]Cl−CuCl was prepared, AlCl$_3$ was then added to the IL. The ratios of AlCl$_3$ to organic salt were 0.5:1−1.5:1. All ionic liquids were homogeneous solutions, and no solid precipitate has been found. Because the CuCl was the main inorganic species of the IL, there were a large quantity of [CuCl$_2$]$^-$ and [Cu$_2$Cl$_2$]$^-$ anions.

With the mole ratio of AlCl$_3$ to CuCl increasing, the changes of the AN value for [(C$_2$H$_5$)$_3$NH]Cl−CuCl−AlCl$_3$ have shown three distinct stages (Figure 4). Therefore, the interaction model between AlCl$_3$ and the original cations/anions may be deduced through these phenomena. The addition of AlCl$_3$ increases the AN value of [(C$_2$H$_5$)$_3$NH]Cl−CuCl at the first stage, indicating that [(C$_2$H$_5$)$_3$NH]+$^+$$[AlCl_4]^-$$ were formed (reaction (7)). Because the Lewis acidity of [(C$_2$H$_5$)$_3$N-Cu]+$^+$$[AlCl_4]^-$$ is significantly less than that of [(C$_2$H$_5$)$_3$NH]+$^+$$[AlCl_4]^-$$, the presence of the [(C$_2$H$_5$)$_3$N-Cu]+$^+$$ would neutralize the acidity resulted from the addition of AlCl$_3$. When the ratio of AlCl$_3$:CuCl exceeded 1:1, the AN value was increased again. A large amount of [CuAlCl$_5$]$^-$ anion should be formed at this stage (reaction (2)), which enhanced the Lewis acidity of the ionic liquid.

The change of AN values caused by the interaction of AlCl$_3$ and [Bmim]Cl−CuCl is illustrated in Figure 5. Unlike the system of [(C$_2$H$_5$)$_3$NH]Cl−CuCl, the AN value of [Bmim]Cl−CuCl is almost kept a monotone increasing trend when the ratio of AlCl$_3$:BmimCl is from 0.50:1 to 1.3:1. It means that [AlCl$_4$]$^-$ and [Al$_2$Cl$_7$]$^-$ anions were formed in the [(C$_2$H$_5$)$_3$NH]Cl−CuCl ionic liquid.

\[
[(C_2H_5)_3NH]^+ + Cl^- + AlCl_3 \rightarrow [(C_2H_5)_3NH][AlCl_4]^- \tag{9}
\]

However, the change of AN values exhibits a platform when more AlCl$_3$ was added, suggesting that the ions of [(C$_2$H$_5$)$_3$N-Cu]$^+$$[AlCl_4]^-$$ were formed (reaction (7)). Because the Lewis acidity of [(C$_2$H$_5$)$_3$N-Cu]$^+$$[AlCl_4]^-$$ is significantly less than that of [(C$_2$H$_5$)$_3$NH]+$^+$$[AlCl_4]^-$$, the presence of the [(C$_2$H$_5$)$_3$N-Cu]$^+$$ would neutralize the acidity resulted from the addition of AlCl$_3$. When the ratio of AlCl$_3$:CuCl exceeded 1:1, the AN value was increased again. A large amount of [CuAlCl$_5$]$^-$ anion should be formed at this stage (reaction (2)), which enhanced the Lewis acidity of the ionic liquid.

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\[
AlCl_3+Cl^-\rightarrow AlCl_4^- \tag{10}
\]
\[
2AlCl_3+Cl^-\rightarrow Al_2Cl_7^- \tag{11}
\]

However, the acidity of [Bmim]Cl−CuCl−AlCl$_3$ would be reduced slightly as AlCl$_3$: [Bmim]Cl $>$ 1.3:1, indicating that the [CuAlCl$_5$]$^-$ anions were present in the IL (reaction (1)). Because the acidity of [Bmim]$^+$$[CuAlCl_5]^-$$ is lower than that of [Bmim]$^+$$[AlCl_4]^-$$, a large amount of [CuAlCl$_5$]$^-$$ would lower the acidity of the ionic liquid. On the other hand, benzene−CuAlCl$_4$ and ether−CuAlCl$_4$ are two common solvents for the absorption of C$_2$−C$_4$ olefins. The structure of benzene−CuAlCl$_4$ has been investigated by many works $^{[34,41−43]}$. That is, CuAlCl$_4$ is the main species of the metal ion-aromatic complexes. When AlCl$_3$ was added to these solvents, the changed trend of AN values (Figure 5b) is very similar to that of [Bmim]Cl−CuCl−AlCl$_3$ system. The results suggest that [Al$_2$Cl$_7$]$^-$$, [AlCl$_4$]$^-$$, and [CuAlCl$_5$]$^-$$ should be the dominated anions in these solvents.

In summary, the mixed metal ions [CuAlCl$_5$]$^-$ and [(C$_2$H$_5$)$_3$N-Cu]$^+$ would be formed in the [(C$_2$H$_5$)$_3$NH]Cl−CuCl−AlCl$_3$ system. Whereas, only one type of mixed chlorometallate ions [CuAlCl$_5$]$^-$ should be present in the [Bmim]Cl−CuCl−AlCl$_3$ ionic liquid.
was first added to a round-bottomed flask that contains 0.1 mol 1-butyl-3-methyl-imidazolium chloride. The reaction was then protected by nitrogen atmosphere at 110 °C. When the ionic liquid was formed, 0.05 mol metal chloride (e.g., CuCl) was mixed with the above IL. Finally, the mixture was stirred at 110 °C overnight until a homogeneous ionic liquid was obtained.

3. Materials and Methods

3.1. Preparation of Ionic Liquids

All metal chlorides were anhydrous and high purity materials (>99%), which purchased from Sigma–Aldrich Co. (Saint Louis, MO, USA). Triethylamine hydrochloride chloroaluminate ([C₂H₅)₃NH]Cl−AlCl₃) and 1-butyl-3-methyl-imidazolium chloroaluminate ([Bmim]Cl−AlCl₃) were prepared and characterized using methods as reported previously [29,44]. In this work, the mole ratio of AlCl₃ to [Bmim]Cl is kept at 1.6:1. The mixed chlorometallate IL were prepared by directly adding metal chlorides to the chloroaluminate IL. According to the literature methods, benzene–CuAlCl₄ [41,42] and ether–CuAlCl₄ [35] can be easily synthesized from the melt of CuCl and AlCl₃ (<250 °C), and then dissolved in the benzene or diethyl ether.

In a typical preparation for mixed chlorometallate IL, anhydrous aluminum chloride (~0.16 mol) was first added to a round-bottomed flask that contains 0.1 mol 1-butyl-3-methyl-imidazolium chloride. The reaction was then protected by nitrogen atmosphere at 110 °C. When the chloroaluminate ionic liquid was formed, 0.05 mol metal chloride (e.g., CuCl) was mixed with the above IL. Finally, the mixture was stirred at 110 °C overnight until a homogenous ionic liquid was obtained.

3.2. 3¹P NMR Spectroscopy

Triethylphosphine oxide (tepo) was obtained from Sigma–Aldrich Co. (Saint Louis, MO, USA). It was stored in a nitrogen-filled glove box until used. Sample preparation for 3¹P NMR spectroscopy
experiment was carried out in the glove box. The samples of chlorometallate ionic liquids were weighed, and then tepo (5, 10, or 15 mol%) was mixed with the IL. The sample vial was put in an ultrasonic mixer at room temperature overnight to ensure full dissolution. Before measuring the acceptor number, the ionic liquid/tepo mixture was loaded into a NMR tube. Each NMR tube contained a sealed capillary with deuterated dimethyl sulfoxide for external lock. In addition, 85% phosphoric acid solution was also sealed in a capillary and loaded into the NMR tube, which was used as an external reference (Scheme 1).

$^{31}$P NMR measurements were performed on a Bruker WB-400 AMX Spectrometer (Zurich, Switzerland). The spectra were obtained at 130.32 MHz with a pre-acquisition delay time of 0.5 s. All samples were measured at 25 °C. Additionally, 5, 10, and 15 mol% solutions of tepo in hexane were prepared and measured as described above. From the $^{31}$P NMR chemical shifts measured for tepo in hexane, the $\delta_{\text{inf}}$ for the infinite dilution of the IL could be obtained by extrapolation. Moreover, the acceptor number that related to this chemical shift can be defined as AN = 0.

![Scheme 1. NMR tube for the measurement of $^{31}$P chemical shifts.](image)

### 3.3. C$_4$ Alkylation Reaction

In this work, C$_4$ alkylation refers specifically to the reaction between isobutane and 2-butene. Hydrocarbon materials (>99 wt.%) were all purchased from China National Petroleum Corporation (Lanzhou, China) without further purification. As Scheme 2 shown, C$_4$ alkylation reactions were carried out in a batch reactor (50 mL). The reactor includes a mechanical stirrer, which can provide 1200 r/min agitation. In a typical alkylation procedure, the ionic liquid (~10 mL) was charged to the column box to 60 °C at a rate of 1 °C/min; (3) increasing the temperature to 120 °C at a rate of 2 °C/min; (4) increasing the temperature to 180 °C at a rate of 1 °C/min; (5) holding 180 °C for 2 min.

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The qualitative identification of the product was analyzed by means of a mass spectrometer (MS), Hewlett-Packard, 5972 Series II column, Santa Clara, CA, USA.

**Scheme 2.** The reaction scheme of C₄ alkylation.

4. Conclusions

Gutmann acceptor numbers of the mixed chlorometallate ILs for C₄ alkylation reaction have been determined by using ³¹P chemical shifts of tepo. The requirement of the acidity for the C₄ alkylation reaction is very strict, and the appropriate AN value should be around 93. If AN is less than 88, the reaction would be difficult to carry out. However, too high AN values (e.g., >95) would reduce the quality of the alkylates. When metal chlorides are added to different chloroaluminate ILs, their AN values would change to different directions. The introduction of metal chlorides would decrease the acidity of [Bmim]Cl−AlCl₃, while slightly increase the AN value of [(C₂H₅)₃NH]Cl−AlCl₃ system. AN values show that [AlCl₄]−, [Al₂Cl₅]−, and [MAlCl₅]− (M = Cu, Ag) are the dominant anions of the mixed chlorometallate ILs. Although [(C₂H₅)₃N·M]+ cations maybe exist in the [(C₂H₅)₃NH]Cl−AlCl₃−MCl system, these ions often reduce the Lewis acidity of the ionic liquids.

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