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Mixed Chlorometallate Ionic Liquids as C_4 Alkylation Catalysts: A Quantitative Study of Acceptor Properties

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Abstract: The acceptor properties of mixed chlorometallate ionic liquids for isobutane-butene alkylation (C_4 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 C_4 alkylation reaction should be around 93.0. The $[(C_2H_5)_3NH]Cl–AlCl_3–CuCl$ appears to be more Lewis acidity than that of $[(C_2H_5)_3NH]Cl–AlCl_3$. The correlation of the acceptor numbers to speciation of the mixed chlorometallate ionic liquids has also been investigated. $[AlCl_4]^-$, $[Al_2Cl_7]^-$, and $[MAlCl_5]^-$ (M = Cu, Ag) are the main anionic species of the mixed chlorometallate ILs. While the presence of $[(C_2H_5)_3N{\cdot}M]^+$ cation always decreases the acidity of the $[(C_2H_5)_3NH]Cl–AlCl_3–MCl$ 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 (C_4 alkylation) [5]. In this reaction, $[C_4mim]Cl–AlCl_3$ [6], $[(C_2H_5)_3NH]Cl–AlCl_3$ [7], and amide-$AlCl_3$-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 $[Hpy]Cl–AlCl_3$ 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 $[(CH_3)_3NH]Cl–AlCl_3$ 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 $[(C_2H_5)_3NH]_{2x}[(1-x)AlCl_3 + xZnCl_4]$ double salt ILs were adopted. The activity of the ionic liquid was found even higher than that of $[(C_2H_5)_3NH][Al_2Cl_7]$ or $AlCl_3$ [13]. Zinurov et al. [14] have found that the route of the *n*-pentane

isomerization could be controlled by using $[(CH_3)_3NH]Cl–AlCl_3$/copper-salt mixtures. Additionally, high yields of branched olefin polymers can be obtained by adding $TiCl_4$ to the $[C_4mim]Cl–AlCl_3$ ionic liquid [15]. Yang et al. also found that the mixed chlorometallate $[(C_2H_5)_3NH]Cl–FeCl_3–CuCl$ 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 $[C_4mim][AlCl_4]$ $–EtAlCl_2–NiCl_2$ 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 $[(C_2H_5)_3NH]Cl-AlCl_3$, 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 $[(C_2H_5)_3NH]Cl-AlCl_3-CuCl$ ionic liquids [28–30]. However, other researchers argued that the peak of $[CuAlCl_5]^-$ should be identified as the signal of $[Al_2Cl_6OH]^-$ [31]. They proposed that Cu(I) could substitute the proton in the $[(C_2H_5)_3NH]^+$ cation and generate $[(C_2H_5)_3N{\cdot}Cu]^+$ 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: $AN = 2.348 \times \delta_{inf}$. In order to obtain the δ_{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.

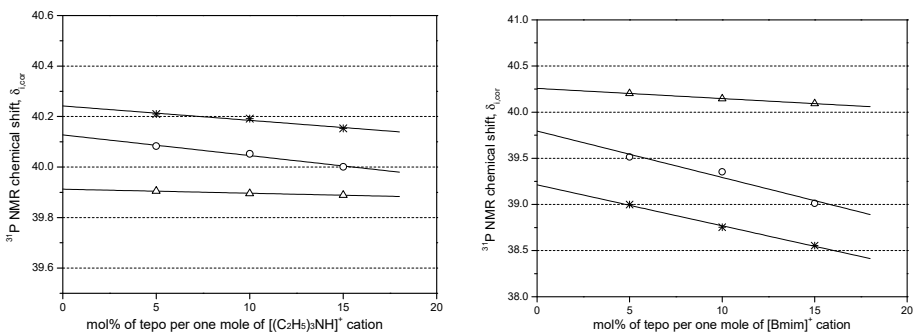
In this paper, the Lewis acidity of mixed chlorometallate ILs for isobutane alkylation was quantitatively studied by determining the AN values. The relationship between the Lewis acidity of ionic liquids and their catalytic performance of C_4 alkylation has been studied. In addition, the speciation of ions has been determined for the [Bmim]Cl−$AlCl_3$−CuCl and $[(C_2H_5)_3NH]$Cl−$AlCl_3$−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 $\delta_{i,cor}$ 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 ^{31}P chemical shift of tepo. Therefore, the Lewis acidity of ionic liquids could be assessed by ^{31}P NMR spectroscopy. The AN values of Lewis acidic compounds are usually between the two reference points of the weak Lewis acid hexane (δ = 41.0 ppm, AN = 0) and the strong Lewis acid $SbCl_5$ (δ = 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 × (δ_{sample} –41.0). 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 ^{31}P 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 ^{31}P NMR chemical shifts of infinite dilution tepo in the ionic liquid (δ_{inf}) must be obtained at first. Here, the values of δ_{inf} were determined by extrapolation, and the acceptor numbers were calculated through AN = 2.348 × $\delta_{i,cor}$ instead of using AN = 2.21 × (δ_{sample} –41.0). The number of $\delta_{i,cor}$ 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 ^{31}P NMR chemical shift of tepo with different concentrations in $[(C_2H_5)_3NH]$Cl−$AlCl_3$ and the fitted straight lines are depicted in Figure 1. These data (δ_{exp}) were fitted by regression analysis to get a linear equation: $\delta_{exp} = mc_{tepo} + \delta_{i,cor}$. The values of m and R^2 were collected in Table 1, and the $\delta_{i,cor}$ values were finally obtained by the linear regression approach.



(**a**) (**b**)

Figure 1. Experimental ^{31}P NMR chemical shifts for tepo as a function of tepo concentration in chloroaluminate compositions: (**a**) $[(C_2H_5)_3NH]^+$−based ILs, $[(C_2H_5)_3NH]$Cl−$AlCl_3$ (△), $[(C_2H_5)_3NH]$Cl−$AlCl_3$−CuCl (○), and $[(C_2H_5)_3NH]$Cl−$AlCl_3$−AgCl (*); (**b**) $[Bmim]^+$−based ionic liquids (ILs), [Bmim]Cl−$AlCl_3$ (△), [Bmim]Cl−$AlCl_3$−CuCl (○), and [Bmim]Cl−$AlCl_3$−AgCl (*).

Table 1. Parameters of linear regression for various ionic liquids.

Entry	Ionic Liquids [1]	m	$\delta_{i,cor}$	R^2
1	$[(C_2H_5)_3NH]Cl-AlCl_3$	−0.0016	39.9123	0.9591
2	$[(C_2H_5)_3NH]Cl-AlCl_3-CuCl$	−0.0082	40.1273	0.9611
3	$[(C_2H_5)_3NH]Cl-AlCl_3-AgCl$	−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	$[(C_2H_5)_3NH]Cl-CuCl$	−0.0361	35.9313	0.9998
8	$[(C_2H_5)_3NH]Cl-ZnCl_2$	−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 $[(C_2H_5)_3NH]Cl-CuCl$ and $[(C_2H_5)_3NH]Cl-ZnCl_2$, 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.

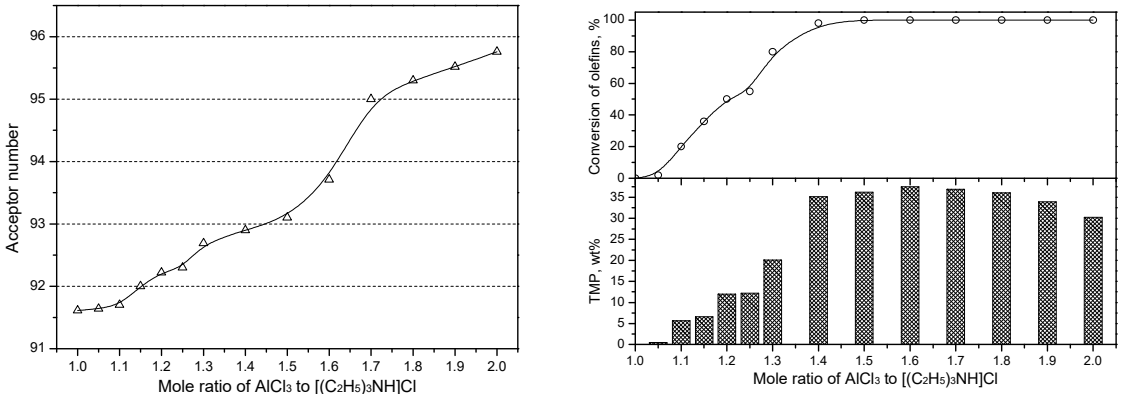
As Table 2 shown, most TMP selectivities of chloroaluminate ionic liquids could be improved by the modification of metal chlorides. Meanwhile, it is found that the transition metal chlorides would reduce the Lewis acid strength of the $[Bmim]^+$−based chloroaluminate IL. For example, the AN value of $[Bmim]Cl-AlCl_3-AgCl$ 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_3SO_3H) is not good for the C_4 alkylation reaction (Entry 11: AN > 126, but RON < 85). Similarly, the trifluoroacetic acid (CF_3COOH) 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_3COOH, $[(C_2H_5)_3NH]Cl-CuCl$, CH_3COOOH, and $[(C_2H_5)_3NH]Cl-ZnCl_2$, cannot catalyze the alkylation reaction. However, acceptor number determination for the $[(C_2H_5)_3NH]^+$−based chloroaluminate ILs indicates that the Lewis acidity of the IL $[(C_2H_5)_3NH]Cl-AlCl_3$ was not reduced by the introduction of CuCl or AgCl. $[(C_2H_5)_3NH]Cl-AlCl_3-CuCl$ or $[(C_2H_5)_3NH]Cl-AlCl_3-AgCl$ usually results in much better catalytic selectivity than that of $[(C_2H_5)_3NH]Cl-AlCl_3$ (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 $[(C_2H_5)_3NH]Cl-AlCl_3$ is greater than 92.0 (e.g., mole ratio of $AlCl_3$ to $[(C_2H_5)_3NH]Cl$ 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., $[(C_2H_5)_3NH]Cl-2AlCl_3$). 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	$[(C_2H_5)_3NH]Cl-AlCl_3$	93.71	37.5	88.6
2	$[(C_2H_5)_3NH]Cl-AlCl_3-CuCl$	94.22	78.2	99.0
3	$[(C_2H_5)_3NH]Cl-AlCl_3-AgCl$	94.49	80.5	99.6
4	$[Bmim]Cl-AlCl_3$	94.52	43.7	90.6
5	$[Bmim]Cl-AlCl_3-CuCl$	93.44	74.8	98.3
6	$[Bmim]Cl-AlCl_3-AgCl$	92.07	76.5	98.9
7	$[Bmim]Cl-AlCl_3-ZnCl_2$	92.61	71.6	97.5
8	$benzene-CuAlCl_4$	91.08	68.7	97.0
9	$ether-CuClAl_4$	91.95	69.1	97.2
10	CH_3COOH	55.68	none	-
11	CF_3SO_3H	126.21	28.2	84.9
12	$[(C_2H_5)_3NH]Cl-CuCl$	84.37	none	-
13	$[(C_2H_5)_3NH]Cl-ZnCl_2$	85.36	none	-
14	CF_3COOH	115.14	34.0	86.4
15	CH_3COOOH	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 alkylation product. Data of $[(C_2H_5)_3NH]^+-$ and $[Bmim]^+-$based ILs are from Refs. [28,29], respectively. The other TMP data are obtained in this work. [2] The research octane number (RON) was calculated according to the method of Ref. [6].



(**a**) (**b**)

Figure 2. The effects of Lewis acidity on acceptor number, TMP selectivity, and conversion of olefins: (**a**) Mole ratio of $AlCl_3$ to $[(C_2H_5)_3NH]Cl$ vs. acceptor number; (**b**) Mole ratio of $AlCl_3$ to $[(C_2H_5)_3NH]Cl$ vs. TMP selectivity and conversion of olefins.

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 ^{31}P 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 $AlCl_3$ is 1:1.6, while the ratio of MCl to $AlCl_3$ 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 $[(C_2H_5)_3NH]Cl-AlCl_3$, AN values exhibit a tendency of first decreasing and then increasing (Figure 3a). It might be explained by the reactions (1)−(8). $[Al_2Cl_7]^-$ is a strong acidic anion in contrast to the $[AlCl_4]^-$ anion. With the molar ratio of CuCl to $AlCl_3$ increasing, the concentration of $[Al_2Cl_7]^-$ would be proportionately decreased (reactions (1) and (2)). Subsequently, the tepo reacted with $AlCl_3$ or $[AlCl_4]^-$. The presence of tepo·$AlCl_3$ indicated that the acid strength of

$[(C_2H_5)_3NH]Cl-AlCl_3$ was reduced (reactions (3)–(6)). In particular, as we increased the concentration of CuCl, a little solid would precipitate. This solid is presumably $CuAlCl_4$ (reaction (6)).

$$Al_2Cl_7^- + CuCl \rightleftharpoons CuAlCl_5^- + AlCl_3 \quad (1)$$

$$[(C_2H_5)_3NH]^+\cdot AlCl_4^- + CuCl \rightarrow [(C_2H_5)_3NH]\cdot CuAlCl_5^- \quad (2)$$

$$Al_2Cl_7^- + Cl^- \rightleftharpoons 2AlCl_4^- \quad (3)$$

$$tepo + AlCl_3 \rightarrow tepo\cdot AlCl_3 \quad (4)$$

$$tepo + AlCl_4^- \rightarrow tepo\cdot AlCl_3 + Cl^- \quad (5)$$

$$CuAlCl_5^- \rightarrow CuAlCl_4 + Cl^- \quad (6)$$

However, when the mole ratio of CuCl to $AlCl_3$ is great 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).

$$[(C_2H_5)_3NH]^+\cdot AlCl_4^- + CuCl \rightarrow [(C_2H_5)_3NCu]^+ + AlCl_4^- + HCl \quad (7)$$

$$tepo\cdot AlCl_3 + AlCl_4^- + Cu^+ \rightleftharpoons tepo\cdot 2AlCl_3 + CuCl \quad (8)$$

where $tepo\cdot 2AlCl_3$ is more acidic than the $tepo\cdot AlCl_3$, 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 $[(C_2H_5)_3NH]^+[CuAlCl_5]^-$ is slightly larger than that of $[(C_2H_5)_3NH]^+[AlCl_4]^-$, and the order of Lewis acidity is $[(C_2H_5)_3NH]^+[Al_2Cl_7]^- > [(C_2H_5)_3NH]^+[CuAlCl_5]^- > [(C_2H_5)_3NH]^+[AlCl_4]^- > [(C_2H_5)_3NCu]^+[AlCl_4]^-$ [37,38]. When a small amount of CuCl was introduced into the IL, CuCl might first react with $[Al_2Cl_7]^-$ to form $CuAlCl_4$ or $[CuAlCl_5]^-$. Decreasing the concentration of $[Al_2Cl_7]^-$ would lead to reducing the acidity of the whole $[(C_2H_5)_3NH]Cl-AlCl_3$. However, adding more CuCl to the IL, $[(C_2H_5)_3NH]^+$ would react with Cu^+ to form $[(C_2H_5)_3NCu]^+$ in accordance with the reaction (7). Meanwhile, a large quantity of $[AlCl_4]^-$ anion might have more opportunity to react with Cu^+, and finally formed more acidic $[(C_2H_5)_3NH]^+[CuAlCl_5]^-$. Therefore, it may be deduced that $[(C_2H_5)_3NCu]^+$ and $[CuAlCl_5]^-$ should all exist in the $[(C_2H_5)_3NH]^+$−based chloroaluminate IL. The change of ^{31}P chemical shifts for $[(C_2H_5)_3NH]Cl-AlCl_3-AgCl$ is very similar to that of $[(C_2H_5)_3NH]Cl-AlCl_3-CuCl$, indicating that $[AgAlCl_5]^-$ and $[(C_2H_5)_3N\cdot Ag]^+$ ions should also present in the IL.

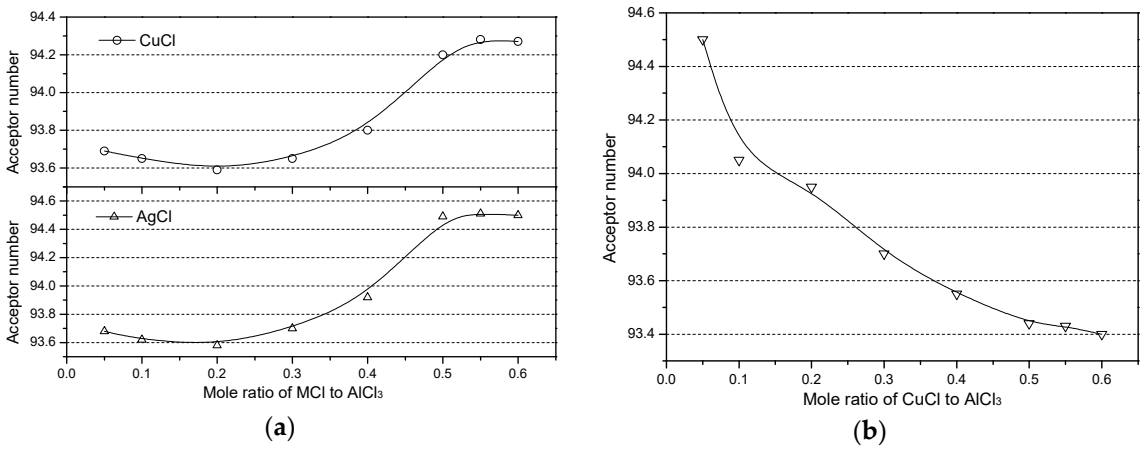


Figure 3. Effects of MCl on the acidity of the chloroaluminate IL: (**a**) adding MCl (M = Cu, Ag) into $[(C_2H_5)_3NH]Cl-AlCl_3$; (**b**) adding CuCl into $[Bmim]Cl-AlCl_3$.

However, the AN value of the [Bmim]Cl−$AlCl_3$−CuCl system is different from those of $[(C_2H_5)_3NH]Cl-AlCl_3-CuCl$. 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 $[Al_2Cl_7]^-$.

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., $[(C_2H_5)_3NH]Cl-CuCl$, [BMIM]Cl−CuCl) were investigated. In this work, the ratio of organic salt to CuCl is kept constant 1:1. After $[(C_2H_5)_3NH]Cl-CuCl$ 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 $[Cu_2Cl_3]^-$ anions.

With the mole ratio of $AlCl_3$ to CuCl increasing, the changes of the AN value for $[(C_2H_5)_3NH]Cl-CuCl-AlCl_3$ 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 $[(C_2H_5)_3NH]Cl-CuCl$ at the first stage, indicating that $[(C_2H_5)_3NH]^+$ and Cl^- ions would directly react with $AlCl_3$ to form $[(C_2H_5)_3NH]^+[AlCl_4]^-$ (reaction (9)).

$$[(C_2H_5)_3NH]^+ + Cl^- + AlCl_3 \rightarrow [(C_2H_5)_3NH]^+[AlCl_4]^- \quad (9)$$

However, the change of AN values exhibits a platform when more $AlCl_3$ was added, suggesting that the ions of $[(C_2H_5)_3N{\cdot}Cu]^+[AlCl_4]^-$ were formed (reaction (7)). Because the Lewis acidity of $[(C_2H_5)_3N{\cdot}Cu]^+[AlCl_4]^-$ is significantly less than that of $[(C_2H_5)_3NH]^+[AlCl_4]^-$, the presence of the $[(C_2H_5)_3N{\cdot}Cu]^+$ 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 $[(C_2H_5)_3NH]Cl-CuCl$, the AN value of [Bmim]Cl−CuCl is almost kept a monotone increasing trend when the ratio of $AlCl_3$:[Bmim]Cl is from 0.50:1 to 1.3:1. It means that $[AlCl_4]^-$ and $[Al_2Cl_7]^-$ anions were formed in the $[(C_2H_5)_3NH]Cl-CuCl$ ionic liquid.

$$AlCl_3 + Cl^- \rightarrow AlCl_4^- \quad (10)$$

$$2AlCl_3 + Cl^- \rightarrow Al_2Cl_7^- \quad (11)$$

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−$CuAlCl_4$ have 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 $[Al_2Cl_7]^-$, $[AlCl_4]^-$, and $[CuAlCl_5]^-$ should be the dominated anions in these solvents.

In summary, the mixed metal ions $[CuAlCl_5]^-$ and $[(C_2H_5)_3N{\cdot}Cu]^+$ would be formed in the $[(C_2H_5)_3NH]Cl-CuCl-AlCl_3$ system. Whereas, only one type of mixed chlorometallate ions $[CuAlCl_5]^-$ should be present in the [Bmim]Cl−CuCl−$AlCl_3$ ionic liquid.

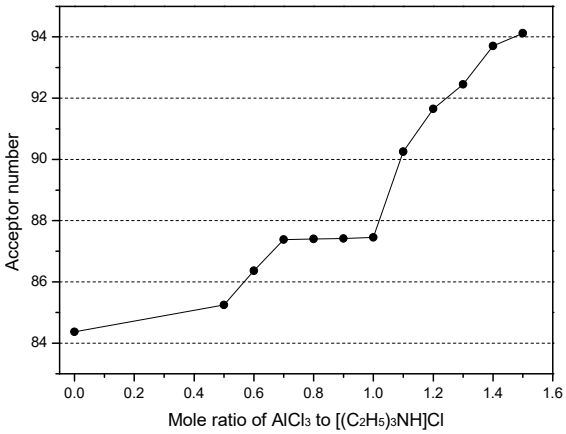
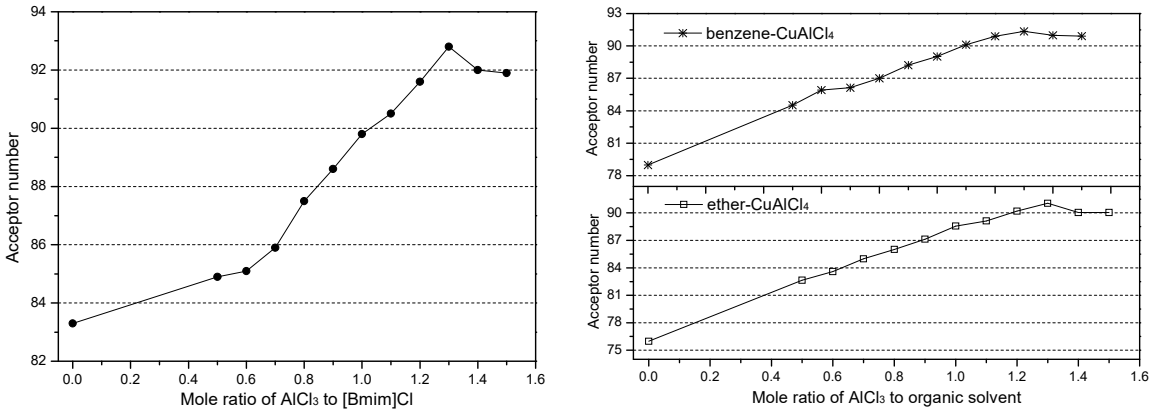


Figure 4. Effects of $AlCl_3$ on the AN value of $[(C_2H_5)_3NH]Cl-CuCl$.



(**a**) (**b**)

Figure 5. Effects of $AlCl_3$ on the acceptor number of chlorometallate ILs: (**a**) The relationship of AN and the mole ratio of $AlCl_3$ to [Bmim]Cl; (**b**) The relationship of AN and the mole ratio of $AlCl_3$ to [Bmim]Cl.

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 ($[(C_2H_5)_3NH]Cl-AlCl_3$) and 1-butyl-3-methyl-imidazolium chloroaluminate ($[BMIm]Cl-AlCl_3$) were prepared and characterized using methods as reported previously [29,44]. In this work, the mole ratio of $AlCl_3$ to organic salt 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$-CuAlCl_4$ [41,42] and ether$-CuAlCl_4$ [35] can be easily synthesized from the melt of CuCl and $AlCl_3$ (<250 °C), and then dissolved in the benzene or diethyl ether.

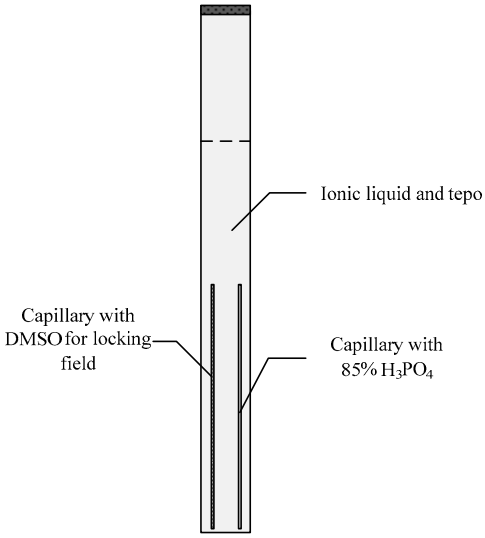
In a typical preparation for mixed chlorometallate IL, anhydrous aluminum chloride (~0.16 mol) was first added to a round-bottomed flask that contains 0.1 mol 1-butyl-3-methyl-imidazolium chloride. The reaction was then protected by nitrogen atmosphere at 110 °C. When the chloroaluminate ionic liquid 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. ^{31}P 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 ^{31}P 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 δ_{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.

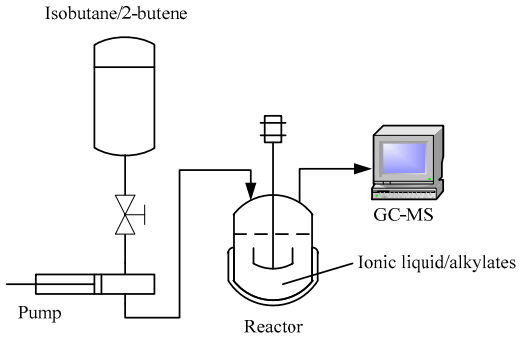


Scheme 1. NMR tube for the measurement of ^{31}P chemical shifts.

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 reactor at first. The mixture of isobutane/2-butene with a 7.5:1 molar ratio was then pumped into the reactor at the rate of 500 mL/h. Meanwhile, the impeller of the reactor began to stir. The reaction temperature was 25 °C, which was controlled by a water bath. The pump was stopped after the pressure of the reactor was higher than 0.4 MPa. However, the impeller kept stirring until the total reaction time was about 30 min. The alkylate and the ionic liquid were unloaded from the reactor and settled for 30 min. In a Claisen flask, the alkylation product was distilled to remove isobutane, and the remainder of the hydrocarbon phase was withdrawn for analysis. The alkylate samples were sent to a gas chromatograph (GC), Hewlett-Packard, 6890, Santa Clara, CA, USA). The GC column was used to quantitatively analyze the product, which was a Supelco Petrocol DH capillary column (Supelco Inc., Bellefonte, PA, USA) (50 m × 0.1 mm × 0.1 mm). The temperatures of the injector and the detector were 180 °C and 200 °C, respectively. The temperature program of GC was listed as follows: (1) holding the column temperature at 40 °C for 2 min; (2) increasing the temperature of 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.

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 C_4 alkylation.

4. Conclusions

Gutmann acceptor numbers of the mixed chlorometallate ILs for C_4 alkylation reaction have been determined by using ^{31}P chemical shifts of tepo. The requirement of the acidity for the C_4 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−$AlCl_3$, while slightly increase the AN value of $[(C_2H_5)_3NH]Cl-AlCl_3$ system. AN values show that $[AlCl_4]^-$, $[Al_2Cl_7]^-$, and $[MAlCl_5]^-$ (M = Cu, Ag) are the dominant anions of the mixed chlorometallate ILs. Although $[(C_2H_5)_3N{\cdot}M]^+$ cations maybe exist in the $[(C_2H_5)_3NH]Cl-AlCl_3-MCl$ system, these ions often reduce the Lewis acidity of the ionic liquids.

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