Activity Investigation of Imidazolium-Based Ionic Liquid as Catalyst for Friedel-Crafts Alkylation of Aromatic Compounds

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N-Methylimidazolium ionic liquids were synthesised from N-methylimidazole and 1-bromobutane by two-step method. The alkylation of benzene and other aromatic compounds through improved Friedel-Crafts reaction was investigated in these ionic liquids. The imidazolium-based ionic liquids showed both high activity and high selectivity for this reaction. In particular, remarkable enhancement of the catalytic effect of the imidazolium-based ionic liquids was observed for the ionic liquids containing the PF_6^- anion. The effects of various types of anions, ionic liquid dosage, reaction temperature and molar ratio of aromatic compound to 1-bromobutane/tertbutyl alcohol were explored using $[Bmim]PF_6$ or its mixture with $AlCl_3$ as catalyst. The synthesis yielded improved results over those obtained using either neat $AlCl_3$ or other imidazolium-based ionic liquids as catalyst. The ionic liquids can also be recycled and reused in contrast to traditional solvent-catalyst systems.

Keywords: Imidazolium-based ionic liquids, Alkylation, Friedel-Crafts, Aluminium chloride.

INTRODUCTION

Friedel and Crafts discovered the reaction of benzene with alkyl halides in the presence of aluminium chloride in 1877. Since then, Friedel-Crafts alkylation of aromatic compounds catalyzed by Lewis acids, such as BF_3, $ZnCl_2$, $TiCl_4$ and SbF_5, using various alkylating reagents, such as alkyl halides and alkenes, have been used both in the laboratory and in the petroleum industry[1,2].

Current commercial alkylation processes are catalyzed primarily by concentrated sulfuric acid or hydrofluoric acid. The sulfuric acid process produces large amounts of spent acid and acid-soluble oils, which are costly to regenerate. Anhydrous HF is highly toxic and its leakage produces dangerously stable aerosols at the ground level. In addition, equipment corrosion, transport, hazard management and environmental liability associated with the disposal of spent acids are disadvantageous for both processes. Hence, alternative processes that are relatively safe are continuously developed[3]. Great effort has been focused on improving this process using environmentally safer catalysts, such as H-ZSM-5, H-ZSM-12, HY, lays[4,5], cation-exchange resin[6], mesoporous materials[7], zeolites[8,9] and molecular sieves[10]. However, these catalysts often have certain disadvantages, such as rapid deactivation due to the fouling of pores, which results in low product yield, loss of reaction selectivity[11] and lack of recyclability.

Recently, ionic liquids (ILs) have been extensively applied as catalyst or reagent in organic and refinery chemistry because of their unique properties, such as negligible vapour pressure, good solvating ability, potential recoverability and recyclability and tuneable acid types (Lewis or Brønsted) and strength[12-14]. However, before these liquids can be used commercially on an industrial scale, the process variables need to be optimized in the laboratory, not only in batch and continuous reactor systems for maximum reactant conversion, but also the product yield and catalyst selective ability.

In the viewpoint of its application, this study reports the alkylation of several aromatic compounds including benzene, phenol, toluene, thiophene, anisole and acetanilide with alkyl halide and alcohol in the presence of dialkylimidazolium-based ionic liquids, such as 1-butyl-3-methylimidazolium bromide ([Bmim]Br), 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF_6), 1-butyl-3-methylimidazolium tetrafluorobarate ([Bmim]BF_4) and 1-butyl-3-methylimidazolium hydrogensulfate ([Bmim]HSO_4) (Fig. 1). For comparison, $AlCl_3$ was also used to catalyze the reaction.

EXPERIMENTAL

The experiments were conducted using analytical grade solvent and chemicals without further purification. The component and distribution of the products were verified by gas
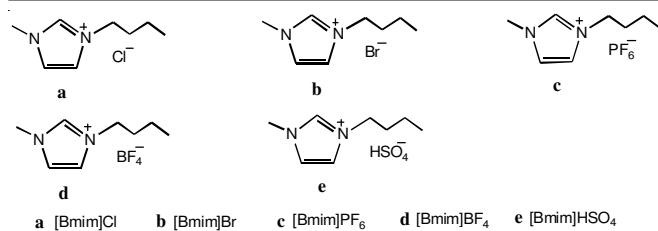
Fig. 1.   Structures of the alkylimidazolium-based ionic liquids used in this investigation

chromatography/mass spectrometry [GC (Agilent 6890)/MS (Hewlett-Packard 5973)]. The infrared (IR) spectrometer used to analyse the catalyst was supplied by Brucher Co., Germany.

Synthesis of ionic liquid: [Bmim]Cl and [Bmim]Br were prepared using the following procedure. Toluene, N-methylimidazolium and 1-chlorobutane or 1-bromobutane were placed into a dry round-bottomed flask equipped with a reflux cooler, a magnetic agitator and a glass thermometer. The mixture was heated under agitation and the temperature was maintained between 80 and 85 °C. After 24 h of reaction, the mixture was cooled to room temperature. After freezing in a refrigerator, toluene and the unreacted reactants were decanted. The product was then washed using acetonitrile as solvent. The washed product was dried in a vacuum drying box to remove residual solvent and water.

[Bmim]PF$_6$, [Bmim]BF$_4$ and [Bmim]HSO$_4$ were prepared from the anion exchange of [Bmim]Cl with sodium hexafluoro phosphate, ammonium tetrafluoroborate, sodium sulfate and sulfuric acid, respectively, according to the modified procedure described in the literature[15-17].

General alkylation procedure: The utility of dialkylimidazolium-based ionic liquids were investigated in the alkylation of aromatic compounds with bromoethane(*t*-butyl alcohol) (**Scheme-I**). The specified amount of catalyst and other reactants were added together, *i.e.*, the catalyst and alkylating reagent were allowed to react prior to the addition of the substrate. A solution of aromatic compounds in the chosen solvent was added dropwise for over 5 min to a stirred mixture of alkylating reagent and ionic liquid (or AlCl$_3$) in the same solvent at 25 °C. Stirring was continued at the specified temperature and time described in the tables. The molar ratio

Scheme-I: Alkylation of the aromatic compounds with bromoethane (*t*-butyl alcohol)

of the aromatic compound:bromoethane (or *t*-butyl alcohol): ionic liquid is shown in every table. At the end of the reaction, the organic layer was easily decanted from the catalyst-ionic liquid system and any organic residues were removed by extraction with diethylether. When the catalyst containing AlCl$_3$ was used, the reactive mixtures were handled as follows. The mixture was added to an excess of crushed ice and 3 M HCl. The organic phase was separated, the extract was added to wash (solvent) the acid layer, the combined extracts were washed three times with water and the solvent was removed by rotary evaporator. For nitromethane, the organic layer was washed with 3M NaOH. The viscous residue was dissolved in benzene and passed through a short column of silica gel to remove any polymeric materials.

The reactive product was then analysed quantitatively by GC. The contents of the major product were determined using the normalization method. The product yields are presented in the tables. The synthesized mono and dialkylation products were directly isolated from the reaction mixture and positively identified through their IR and mass spectra and elemental analysis.

Inlet and detector temperatures were set constant to 300 °C. The aromatic compounds were used as internal standard to calculate the reaction conversions or yield. GC-MS analyses were performed using a Hewlett Packard GC-MS 5973 with RTX-5MS column (length = 30 m, inner diameter = 0.25 mm and film thickness = 0.5 μm). The temperature for the GC-MS analysis heated samples was programmed from 60 to 280 °C at 10 °C/min and then held at 280 °C for 2 min. The inlet tempe-rature was set constant to 280 °C. MS spectra were compared with the spectra obtained in the NIST library.

RESULTS AND DISCUSSION

Reactive sites in electrophilic substitution are generally affected by the original substituent. In our work, investigations on the Friedel-Crafts alkylation of the non-substituted and mono-substituted aromatic compounds with *ortho-* and *para-* directing groups as reactive substrate was conducted as initial efforts for preparing the mono and disubstituted compounds in good conversion by direct electrophilic substitution reaction.

Influences of various of catalysts on the reaction results: Reactions were studied using aromatic compounds and bromoehane (*t*-butyl alcohol) in ionic liquid under specific conditions (**Scheme-I**). Table-1 shows the effect of the ionic liquid catalysts on the alkylation reaction. ionic liquids, such as [Bmim]PF$_6$, [Bmim]BF$_4$ and [Bmim]HSO$_4$ exhibited greater activity than the other two ionic liquids studied in this work (Table-1, Entries 8-10, 13-15 and 18-20). In particular, [Bmim]PF$_6$ (Table-1, Entries 8, 13, 18) exhibited excellent performance in the alkylation of aromatic compounds. Moreover, the same cation and different anions of the ionic liquids have significant effects on the alkylation of aromatic compounds. Generally, Lewis acid strength has a vital role in the catalysis of electrophilic aromatic substitution. Anions with high basicity (*e.g.*, acetate) enable proton transfer in imidazolium-based ionic liquids, providing an imidazole-2-ylidene derivative (N-heterocyclic carbene) and an acid (*e.g.*,
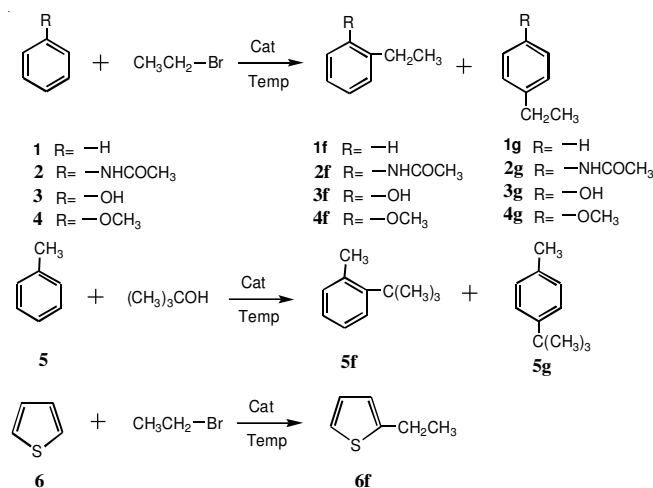
TABLE-1
ALKYLATION OF AROMATIC COMPOUNDS WITH BROMOETHANE (*t*-BUTYL ALCOHOL) USING DIFFERENT TYPES OF CATALYST

Entry	Aromatic compound	Bromoethane/ *t*-butyl alcohol	Catalyst	Conversion of aromatic compound (%)
1	1	CH_3CH_2Br	a	22.5
2	1	CH_3CH_2Br	b	24.5
3	1	CH_3CH_2Br	c	30.2
4	1	CH_3CH_2Br	d	31.3
5	1	CH_3CH_2Br	e	29.7
6	2	CH_3CH_2Br	a	75.6
7	2	CH_3CH_2Br	b	79.2
8	2	CH_3CH_2Br	c	97.5
9	2	CH_3CH_2Br	d	83.3
10	2	CH_3CH_2Br	e	80.4
11	3	CH_3CH_2Br	a	73.2
12	3	CH_3CH_2Br	b	74.5
13	3	CH_3CH_2Br	c	98.8
14	3	CH_3CH_2Br	d	83.1
15	3	CH_3CH_2Br	e	81.2
16	4	CH_3CH_2Br	a	25.4
17	4	CH_3CH_2Br	b	31.3
18	4	CH_3CH_2Br	c	94.8
19	4	CH_3CH_2Br	d	80.0
20	4	CH_3CH_2Br	e	65.8
21	5	$(CH_3)_3COH$	a	22.9
22	5	$(CH_3)_3COH$	b	34.7
23	5	$(CH_3)_3COH$	c	35.8
24	5	$(CH_3)_3COH$	d	37.2
25	5	$(CH_3)_3COH$	e	40.4
26	6	CH_3CH_2Br	a	24.7
27	6	CH_3CH_2Br	b	29.7
28	6	CH_3CH_2Br	c	35.3
29	6	CH_3CH_2Br	d	32.6
30	6	CH_3CH_2Br	e	36.8

Reaction conditions: molar ratio aromatic compound/bromoethane (*t*-butyl alcohol)= 1:1.1; W_{cat} = 15 %; T = Reflux temp; t = 2 h

acetic acid), as shown in **Scheme-II**[18]. This finding probably indicates that the anion strongly interacts with the proton on the 2-position of the imidazolium ring. [Bmim]PF_6 also exhibits greater acidity than the other ionic liquids, such as [Bmim]BF_4, [Bmim]Br and even [Bmim]HSO_4. The possible reason for the high reactivity of [Bmim]PF_6 for this reaction is that [Bmim]PF_6 is equal to the Lewis acidic ionic liquid and may reduce the formation of a nucleophilic carbene catalyst in the alkylation, as displayed in **Scheme-II**. Nucleophilic carbene may hinder the production of alkanium ion, which is the reactive intermediate according to the mechanism of Friedel-Crafts alkylation reaction. The results showed that [Bmim]PF_6 is an excellent catalyst and solvent for the alkylation of aromatic compounds.

To obtain more information on the reaction performances of ionic liquids as catalyst and reagent, a mixed catalyst of ionic liquid and aluminium chloride was investigated.

The molar ratio of aromatic compounds to bromoethane (*t*-butyl alcohol) with 1:1.1 constant was maintained and the catalyst with 15 % mass of reactants was added. The results are summarised in Table-2, which shows that better results were obtained with the mixed catalyst of ionic liquid and aluminium chloride. Notably, good result was achieved with the ionic liquid containing aluminium chloride (Table-2, Entries
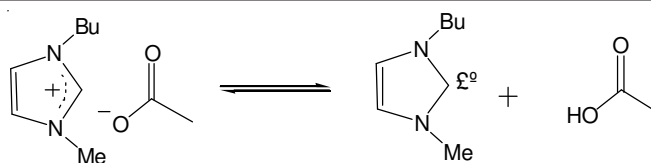
Scheme-II: Possible acid-base equilibrium between the constitutive ions of a 1,3-dialkylimidazolium ionic liquid

4-5, 10 and 15-16), whereas weak catalytic activity was observed for the alkylation of the ionic liquid alone (Table-1, Entries 1-5, 21-30). Moreover, the performance of the mixed catalyst was better than that of neat aluminium chloride. However, exceptions were also noted (Table-2, Entries 8, 11-12 and 17). The catalytic activity of the mixed catalyst containing [Bmim]PF_6 was superior to that of any other combined catalysts. However, some factors causing the deactivation of ionic liquid and aluminium chloride were found. For instance, the moisture-sensitivity of [Bmim]$AlCl_4$ ionic liquid and the dissolving elution of [Bmim]$AlCl_4$ owing to both benzene and trace water in materials may be the main causes for the catalyst deactivation[19]. In addition, the deactivation of ionic liquids could also attributed to the decrease of the Lewis acidic strength and density resulting from the loss of the highly Lewis acidic species $Al_2Cl_6Br^-$[20].

TABLE-2
ALKYLATION OF AROMATIC COMPOUNDS WITH BROMOETHANE (*t*-BUTYL ALCOHOL) USING MIXED CATALYSTS

Entry	Aromatic compound	Bromoethane (*tert*-butyl alcohol)	Catalyst	Conversion of aromatic compound (%)
1	1	CH_3CH_2Br	$AlCl_3$	60.8
2	1	CH_3CH_2Br	a-$AlCl_3$	64.2
3	1	CH_3CH_2Br	b-$AlCl_3$	72.8
4	1	CH_3CH_2Br	c-$AlCl_3$	92.3
5	1	CH_3CH_2Br	d-$AlCl_3$	86.2
6	1	CH_3CH_2Br	e-$AlCl_3$	72.2
7	5	$(CH_3)_3COH$	$AlCl_3$	75.1
8	5	$(CH_3)_3COH$	a-$AlCl_3$	74.2
9	5	$(CH_3)_3COH$	b-$AlCl_3$	75.2
10	5	$(CH_3)_3COH$	c-$AlCl_3$	90.3
11	5	$(CH_3)_3COH$	d-$AlCl_3$	55.6
12	5	$(CH_3)_3COH$	e-$AlCl_3$	71.8
13	6	CH_3CH_2Br	$AlCl_3$	63.9
14	6	CH_3CH_2Br	a-$AlCl_3$	65.1
15	6	CH_3CH_2Br	b-$AlCl_3$	77.4
16	6	CH_3CH_2Br	c-$AlCl_3$	80.3
17	6	CH_3CH_2Br	d-$AlCl_3$	56.6
18	6	CH_3CH_2Br	e-$AlCl_3$	73.9

Reaction conditions: molar ratio aromatic compound/bromoethane (*t*-butyl alcohol) = 1:1.1; W_{cat} = 15 %; T = Reflux temp; *t* = 2 h

Influences of the dosage of catalysts on the reaction results: [Bmim]PF_6, which was effective for alkylation when used alone (Fig. 2, benzene, toluene, thiophene) but not when mixed with $AlCl_3$, was selected as specified catalyst to investigate the effect of its dosage on the results. Obviously, the yield increased with increasing ionic liquid. Fig. 3 shows the result of experimental investigations of [Bmim]PF_6 with $AlCl_3$ were used to catalyse the aromatic compound alkylation with alkylhalide(alcohol) under specified conditions. The high activation began almost from the start of the addition of the
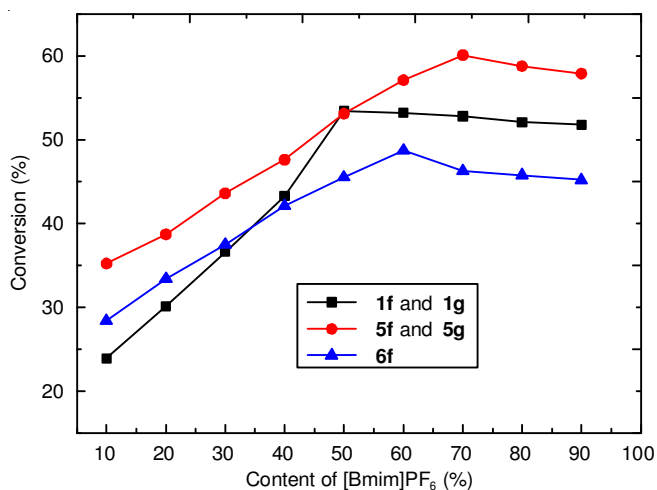
Fig. 2. Overall effect of catalyst loading; Reaction conditions: molar ratio aromatic compound/bromoethane (*t*-butyl alcohol) = 1:1.1; T = Reflux temp; *t* = 2 h
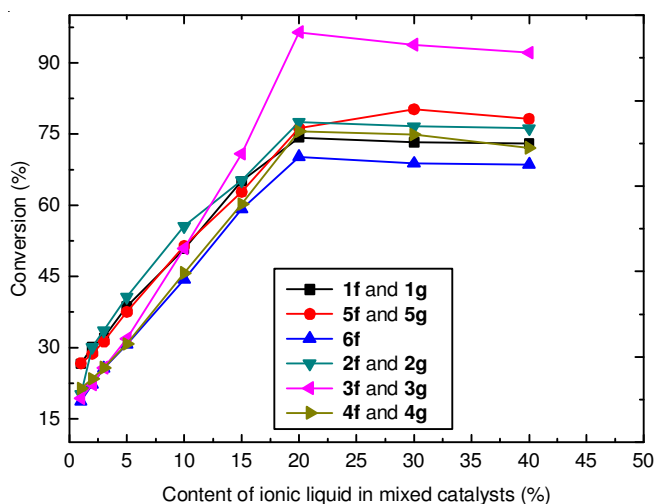

Fig. 3. Results of the alkylation of aromatic compounds with bromoethane (*t*-butyl alcohol) under different kinds and dosages of catalysts; Reaction conditions: molar ratio aromatic compound/ bromoethane (*t*-butyl alcohol) = 1:1.1; T = Reflux temp; t = 2 h; W$_{mixed}$ catalyst = 10 %

catalyst. The conversion increased with increasing catalyst amount. When the ionic liquid (AlCl$_3$) content reached 20 to 30 %, the conversion reached its maximum [96 % (phenol, wt. %) and 68.8 % (thiophene, wt. %)]. Afterward, the conversion remained unchanged or decreased with increasing catalyst content. This phenomenon may be due to the fact that the concentration of carbonium ion increases with increase in catalyst, which can accelerate the reaction and increase the conversion of the aromatic compound. However, a series of side reactions also occurred simultaneously and the yield of

appointed product decreased when [Bmim]PF$_6$ exceeded 30 % of the total mass of the catalyst. Considering all these factors, 20 to 30 % W([Bmim]PF$_6$) is appropriate.

Influence of catalyst on product selectivity: The results of the alkylation of aromatic compounds with bromoethane-(*t*-butyl alcohol) in different catalyst-ionic liquid systems are shown in Table-3. **Scheme-I** shows that '*o*-' and '*p*-' position isomer products (**Scheme-I**, 2-5 f, 2-5 g) were obtained in the alkylation. We would expect '*p*-' substituted aromatic compounds because of steric hindrance to be the major product. As a matter of fact, it fell out as we expected, '*p*-' isomer is the major product when we adopted [Bmim]PF$_6$ or its mixture with AlCl$_3$ as catalyst. In addition to steric hindrance, other reasons that lead to the phenomenon may exist, which is the subject of our next investigation.

Influence of reaction temperature on alkylation: Reaction temperature has an important effect on reaction dynamics and thermodynamics. Therefore, the effect of reaction temperature on the results of the alkylation catalysed by [Bmim]PF$_6$-AlCl$_3$ (W([Bmim]PF$_6$ = 50 %) or [Bmim]PF$_6$ was investigated in detail (Fig. 4). The influence of reaction temperature on the conversion is shown in Fig. 4. A remarkable effect on alkylated conversion was observed. Increasing the reaction temperature accelerated the molecular thermal agitation and the molecular collision probability between the carbonium ion and aromatic ring. Therefore, the alkylation was accelerated, 82.5 % (toluene) and 93.3 % (phenol) with high conversion for aromatic compound at 40 to 60 °C was achieved. If the reaction
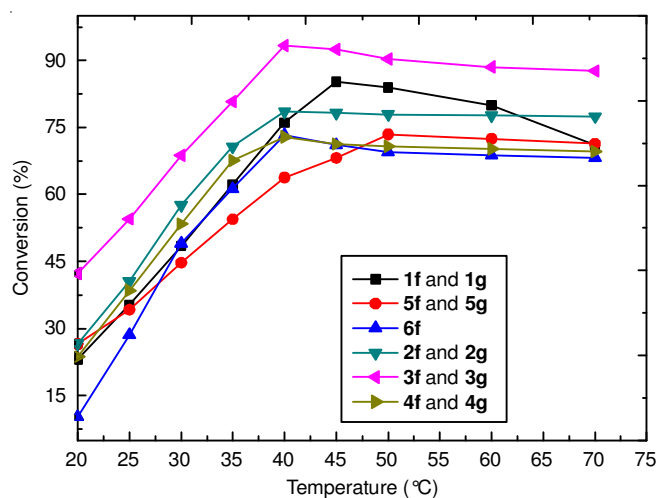

Fig. 4. Effect of reaction temperature on the results of the alkylation of aromatic compounds with bromoethane (*t*-butyl alcohol); Reaction conditions: molar ratio aromatic compound/bromoethane (*t*-butyl alcohol) = 1:1.1; W$_{cat}$ = 25 %; W ([Bmim]PF$_6$) =50 %; *t* = 2 h. Note that the temperature is the temperature of the heater

TABLE 3
FRIEDEL-CRAFTS ALKYLATION OF AROMATIC COMPOUNDS WITH BROMOETHANE (*t*-BUTYL ALCOHOL)

Entry	Reactant	Catalyst	Major product[b] yield (%)	Selectivity to major product (%)[c]
1	Toluene + *t*-butyl alcohol	[Bmim]PF$_6$ + AlCl$_3$	55.3	90.5
2	Acetanilide + chloroethane	[Bmim]PF$_6$	56.5	92.3
3	Phenol + chloroethane	[Bmim]PF$_6$	67.8	91.2
4	Anisole + chloroethane	[Bmim]PF$_6$	54.8	88.1

Reaction conditions: molar ratio aromatic compound/bromoethane(*t*-butyl alcohol)= 1:1.1; W$_{cat}$ = 15 %; T = Reflux temp; t = 2 h. b. Major product is '*p*-' isomer; c. Molar ratio of '*p*-' to '*o*-'isomer

temperature is further raised, the conversion of aromatic compound would inevitably decrease. From the viewpoint of conversion and energy consumption, 40 to 60 °C is the optimal reaction temperature for the alkylation of aromatic compounds.

Influences of molar ratio of aromatic compound and bromoethane (*t*-butyl alcohol) on the alkylation: The influence of the molar ratio of aromatic compound and bromoethane (*t*-butyl alcohol) on the conversion of the alkylation using [Bmim]PF$_6$ ionic liquid is shown in Fig. 5. The alkylation results show that as n(bromoethane/*t*-butyl alcohol) increased, the conversion of the aromatic compound increased until the maximum was reached and then declined. The maximum of 88.1 % (benzene), 65.6 % (toluene), 73.5 % (thiophene), 69.6 % (acetanilide), 93.2 % (phenol) and 73.4 % (anisole) in conversion were observed when n(bromoethane/*tert*-butanol) were 3, 3, 3.5, 2, 2 and 2, respectively. At higher n(bromoethane/*tert*-butanol) value, the concentration of active carbonium ion would be diluted and the alkylation would be weakened, resulting in a lower conversion. However, with an increase in n(bromoethane/*tert*-butanol), the cubic capacity effect decreases; thus, the circulation amounts increased to a great extent, consequently resulting in higher production cost[21].
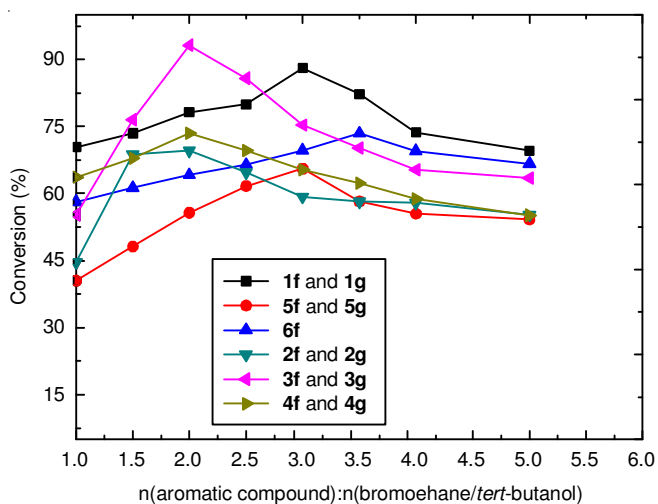

Fig. 5.   Reaction results of the alkylation of aromatic compounds at different molar ratio values; Reaction conditions: T = Reflux temp; t = 2 h; W$_{cat}$ = 10 %

Reusability of the ionic liquid: The potential reusability of [Bmim]PF$_6$ in the alkylation was studied. A gradual decrease in overall product yield was observed with the increase in frequency of use. The quality and yield of alkylate varied gradually in the four runs and then dropped significantly after the fifth run. On one hand, the colour of the catalyst changed from light yellow to brown because of the accumulation of colour materials. On the other hand, the volume of the catalyst was reduced as the number of use increased, which may be due to the lose of recovery operation of catalyst, or its dissolution/entrainment in the alkylate during the post-treatment operation. This result indicates that the activity of the ionic liquid declined, resulting in the decrease of the Lewis acid strength and quantity.

Conclusion

The alkylation of aromatic compounds with bromoehane/*tert*-butyl alcohol was carried out in a series of imidazolium ionic liquids or its mixtures with AlCl$_3$. The results showed that [Bmim]PF$_6$ ionic liquids are the most suitable media for the Friedel-Crafts alkylation of aromatic compounds. The reactions proceeded at an improved rate at relatively lower temperature, yielding high product conversion. [Bmim]PF$_6$ was found to be the better solvent-catalyst system than the AlCl$_3$ system, which can efficiently substitute the AlCl$_3$ catalysis system. High conversion of the limiting reactant could be obtained using this catalyst. Moreover, the selectivity of the target product exhibited a large increase. The effects of various parameters, such as temperature, catalyst type and catalyst loading, on the aromatic compound conversion and product selectivity were studied. The applications of imidazolium-based ionic liquids as solvents or catalyst for other reactions are under investigation in our laboratory.

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