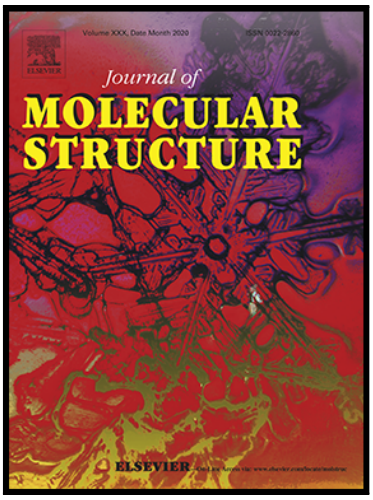
Journal Pre-proof



Deep Compositional Understanding of TBA:AlCl$_3$ Ionic Liquid for its Applications

Mangesh Sakhalkar , Rudra Prosad Choudhury ,
Vishnupriya Bhakthavatsalam , Sharad V. Lande ,
Jeevan Pradhan , Sudeshna Chandra

PII: S0022-2860(20)31261-8
DOI: https://doi.org/10.1016/j.molstruc.2020.128936
Reference: MOLSTR 128936

To appear in: *Journal of Molecular Structure*

Received date: 9 May 2020
Revised date: 28 June 2020
Accepted date: 18 July 2020

Please cite this article as: Mangesh Sakhalkar , Rudra Prosad Choudhury , Vishnupriya Bhakthavatsalam , Sharad V. Lande , Jeevan Pradhan , Sudeshna Chandra , Deep Compositional Understanding of TBA:AlCl$_3$ Ionic Liquid for its Applications, *Journal of Molecular Structure* (2020), doi: https://doi.org/10.1016/j.molstruc.2020.128936

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Elsevier B.V. All rights reserved.

Highlights

1. Characterisation study to elucidate the formation of novel TBA:$AlCl_3$ catalyst.
2. Confirmation of cation and anion composition at various mole ratio by NMR and FTIR.
3. Lewis acidity with compositional change for Structure-property relationship.
4. Green alternate catalyst for Friedel Crafts reactions with high conversion/yields.
5. New electrolyte system containing hydrophobic ligand for plausible Al deposition.

Journal Pre-proof

Deep Compositional Understanding of TBA:AlCl$_3$ Ionic Liquid for its Applications

Mangesh Sakhalkar[1,2], Rudra Prosad Choudhury[2],Vishnupriya Bhakthavatsalam[2], Sharad V. Lande[2],

Jeevan Pradhan[1], Sudeshna Chandra[1*]

[1]Department of Chemistry, Sunandan Divatia School of Science, SVKM's NMIMS (Deemed to-be University),
V. L. Mehta Road, Vile Parle (West), Mumbai -400056, India
[2]M/s Reliance Industries Ltd, TC30C, First floor, Reliance Corporate park, Thane - Belapur road, Ghansoli,
Navi Mumbai-400701, India

Graphical abstract for characterisation paper

Abstract

Chloroaluminate ionic liquids (ILs) have been immensely used as homogeneous catalyst in Friedel-Crafts reaction. We have recently synthesized chloroaluminate ILs by reacting aluminium chloride with a hydrophobic neutral ligand i.e. tributylamine (TBA:AlCl$_3$). The current study elaborates on the investigations of the composition of the ionic liquids at various stages of their formation. The ionic liquids were synthesized using various mole ratios of tributyl amine and aluminium chloride in range of 1:1 to 1:2.3, in presence of an aromatic solvent in a one pot reaction. Various characterization techniques like Mass spectrometry, ^{27}Al Nuclear Magnetic Resonance, ^{31}P Nuclear Magnetic Resonance and Fourier Transform Infrared spectroscopy were used to elucidate the formation of various moieties of the TBA:AlCl$_3$ Ionic Liquid. This study also elaborates on the investigations of the cationic and anionic moieties and their structure-property relationship for various applications. Various Friedel-Crafts reaction of industrial importance were performed using the ionic liquid having $(Al_2Cl_7)^-$ moiety to assess its performance and compare with conventional processes. The synthesized products were characterised by sophisticated analytical techniques like ^{1}H NMR, ^{13}C NMR, FTIR, GC-MS, GC-FID, to name a few. This

Journal Pre-proof

class of ionic liquids also have importance in various electrochemical applications like aluminium deposition and aluminium batteries.

Keywords: TBA:$AlCl_3$ Ionic Liquid; Characterization; ^{27}Al NMR; Aluminium deposition; Electrodeposition

Introduction

Use of room- temperature ionic liquids have been rapidly growing in various areas in chemistry [1]. Chloroaluminate ionic liquids are one of the first-generation ionic liquids having the wide range of application in catalysis [2], electrodeposition [3] and aluminium batteries [4]. These chloroaluminates are conventionally derived from quaternary nitrogen like alkyl amine, alkyl pyridinium, dialkyl imidazolium etc. Anions like $(AlCl_4)^-$ or $(Al_2Cl_7)^-$ are believed to have an active moiety of chloroaluminates where $(Al_2Cl_7)^-$ is considered electroactive. However, anionic aluminium species have to move against the electrostatic field during reduction in electrodeposition process. Ionic liquids having cationic aluminium is envisaged to promote easier aluminium deposition and therefore, now-a-days, chloroaluminates are synthesized with neutral ligands like acetamide [5], butylpyrolidine [6], dipropyl sulphide [7] etc.

Chloroaluminate ionic liquids are reported as catalyst for several organic and Friedel–Crafts reactions due to low catalyst requirement, higher activity, and biphasic reaction systems. The Friedel–Crafts reactions are used to produce pharmaceuticals, fine chemicals and their intermediates for many years. For acylation, various acylating agent like acyl chloride and anhydrides are used while for alkylation, alkylating agents like alkyl halides, alcohols, olefins are commonly used. These alkylated aromatics are produced conventionally by catalysing with various Lewis acids [8]. However, use of Lewis acid catalyst results in huge waste generation. Conventional chloroaluminate ionic liquids have demonstrated high catalytic

Journal Pre-proof

activity in various Friedel -Crafts reactions [9]. Even though, pertaining to their performance in many Friedel–Crafts reactions, most of the studies have focused on those derived from imidazolium based ionic liquid, which are very expensive.

Recently, we have reported a novel chloroaluminate ionic liquid synthesis in single step from tributyl amine, a hydrophobic neutral ligand in presence of solvent [10]. Tributyl amine was expected to give better stability towards air and water sensitivity due to hydrophobicity.

In this paper, chloroaluminates were designed and synthesized by reacting tributyl amine with aluminium chloride in various mole ratios in presence of solvent. Various characterization techniques were used to understand the step-wise formation of the ionic liquid and study their structure-property relationships for specific application. Spectroscopic techniques like FTIR, ^{27}Al NMR, ^{31}P NMR and ESI-MS were used to understand the compositional changes of cation and anions.

The synthesized ionic liquid has an edge over conventional chloroaluminates in terms of single step synthesis, better atom economy, effluent reduction, etc. Moreover, tributyl amine can be recovered by neutralisation and easily reused for catalyst synthesis, resulting in effluent reduction which is difficult in conventional catalyst. We have used this ionic liquid as catalyst for various Friedel-Crafts reaction of aliphatic and aromatic compounds to explore its catalytic activity as new greener alternative in industrially important processes. Further, this ionic liquid can be plausibly used in electrodeposition of aluminium.

Experimental

Materials and Apparatus

All the reagents were procured from M/s SD Fine Chem. and used without any further purification. All solvents (tributyl amine, benzene, cyclohexene, aniline, benzene etc) were

Journal Pre-proof

purchased from commercial sources M/s S D Finechem and Merck. All the chemicals used are of analytical or laboratory reagent grade.

Synthesis of TBA Chloroaluminate ionic liquid

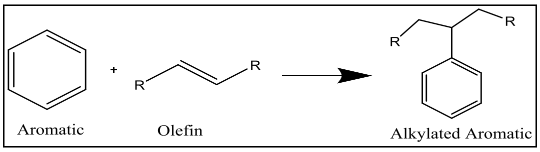
Tributyl amine i.e. TBA and benzene were added to reactor and stirred to ensure the complete mixing at ambient temperature. The temperature of the reactor was controlled by external heating device assembled with the reactor. The reactor was purged with nitrogen and kept in cabinet under dry nitrogen purging. Aluminium chloride was added as per pre-calculated mole ratio to the reactor and the reactor was heated at 80 °C. Reactants were thoroughly mixed by overhead stirrer followed by heating to ensure complete formation of the ionic liquid which was obtained as a homogeneous dark brown liquid. The reactor was cooled to ambient temperature and ionic liquid was isolated and stored in air tight glass bottle under nitrogen atmosphere. The ionic liquid was characterised by Mass spectroscopy, ^{27}Al NMR spectroscopy, Fourier transform spectroscopy and ^{31}P NMR to understand the structural composition and spatial arrangements of cation and anions for possible applications in electrochemistry and synthetic (catalytic) processes. The synthesized ionic liquid was used without any further purification for catalytic applications i. e. Friedel-Crafts reactions.

Various Friedel-Crafts reactions were carried out using the ILs and are mentioned below.

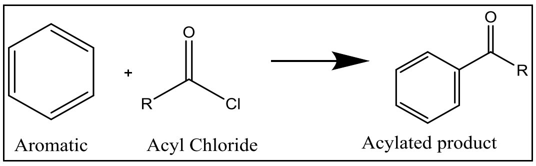
Journal Pre-proof

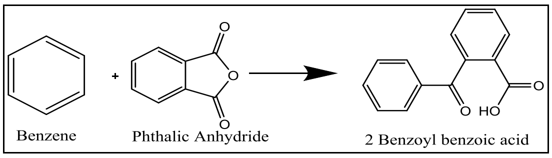
Reaction Schemes

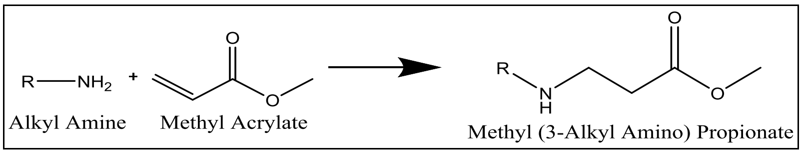
1.

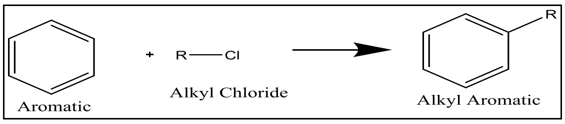


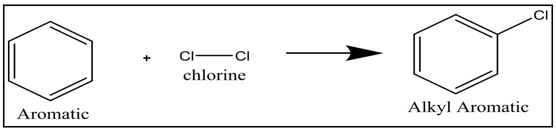
2.

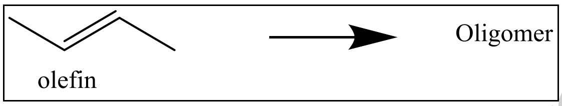


3. 

4. 

5. 

6. 

7. 

Typical procedure Friedel-Crafts reactions usingTBA:$AlCl_3$ Chloroaluminate Ionic liquid

In 100 ml reactor, reactants A and B were mixed by mechanical stirrer and assembled with condenser with chilled water circulation. Reactant A was taken in excess mole ratio to reactant B and which varied from 2-10 mole depending on type of reaction. Reaction was maintained at 25-70 °C and 1-10 w/v% of freshly prepared ionic liquid was added to the reaction mixture. The reaction was continued for 30 min and then cooled. The organic layer was separated and de-acidified. Reaction feeds and products were analysed with gas chromatography to estimate conversion and yield.

Alkylation of benzene with olefins were conducted by using inert solvent like paraffins. In chlorination reaction, chlorine was produced by adding hydrogen peroxide to conc. HCl and the chlorine gas was bubbled through reactant with catalyst. In acylation of benzene with phthalic anhydride, ionic liquid equivalent to 3 moles of $AlCl_3$ per mole of anhydride was added. The upper layer containing hydrocarbon was washed with water and treated with 2N

Journal Pre-proof

sodium hydroxide solution. Sodium salt of benzoyl benzoic acid in aqueous layer was washed with dichloromethane. The product in the aqueous layer was reconstituted by treating with dilute HCl and recrystallized by dichloromethane – hexane solvent and confirmed by melting point, LC- MS and NMR.

Results and discussion

The ionic liquid was examined with various characterisation techniques to identify its composition at different mole ratios. The properties of the ionic liquids are essentially governed by the nature of their cationic as well as anionic species. Based on the nature, cation and anion composition, the ionic liquids can be used for specific applications. Chloroaluminates are primarily used as a catalyst in Friedel-Crafts reaction due to its unique properties like low catalyst requirement and easy separation. Various spectral analysis methods, mainly UV-vis, NMR, and IR spectroscopies are traditionally used for measurement of the acidity of the ionic liquids. The UV-vis spectroscopy method for Hammett function are used for semi-quantitative determination of Bronsted acidity in ionic liquids, however, it is not applicable for determining Lewis acidity of the chloroaluminate ionic liquids containing (Al_2Cl_7) moiety. Similarly, cationic Al species is preferred for electrodeposition than anionic Al species as it can move against the applied electrostatic field. Therefore, in order to get the deep structural and compositional understanding of the ionic liquids prepared with different mole ratios, they were characterised by using FTIR, Mass spectroscopy, ^{27}Al NMR. ^{31}P NMR was used t ascertain the Lewis acidity of the ionic liquids.

Characterisation of Ionic Liquids

FTIR was used to understand the speciation of cationic and anionic moieties formed by reaction of various mole ratios of Tributylamine with Aluminium chloride.

Journal Pre-proof

Thermo iS50 Fourier Transform Infrared Spectrometer equipped with attenuated total reflection (ATR) with Diamond crystal with 45° single bounce mounted directly onto the spectrometer bench compartment was used to record the IR spectra. A drop of sample, under nitrogen blanket, was placed on the diamond crystal for measurement.

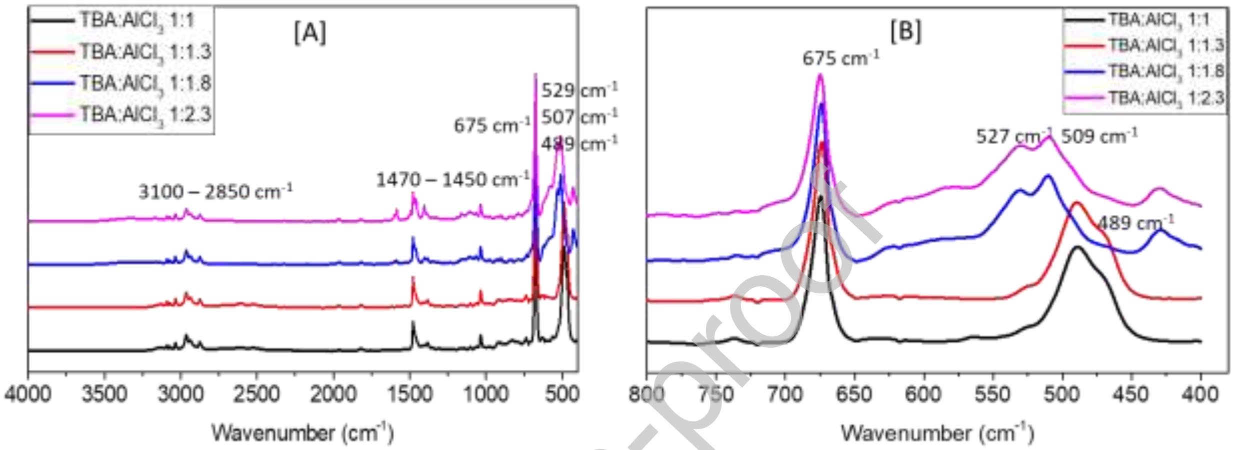


Fig 1: (A) Overlay of FTIR of various mole ratios of TBA and Aluminium chloride and (B) enlarged overlay spectrum in wave number region of 800 - 400 cm^{-1}

FTIR studies of the ionic liquids as indicated in Fig 1, shows the characteristic bands which can be related to composition as tabulated below.

Reactant	Characteristic band	Characteristic Frequency (cm^{-1})
TBA	Aliphatic C-H stretch	3000-2850
	C-H bend scissoring	1470-1450
Benzene	Aromatic C-H	3000-3100

Table 1: Characteristic frequency and band in FTIR

Additionally, samples with 1:1 and 1:1.3 mole ratio of TBA and aluminium chloride shows peak with shoulder at 489 cm^{-1} which is associated to the mononuclear aluminium $(AlCl_4)^-$ moiety [11]. The FTIR spectra for 1:1.8 and 1:2.3 mole ratio of TBA and $AlCl_3$ shows peaks at 529 and 507 cm^{-1} which indicates the formation of binuclear aluminium $(Al_2Cl_7)^-$ moiety [6,11]. The peak at 489 cm^{-1} disappears with higher mole ratios i.e.1:1.8 and 1:2.3. The FTIR

Journal Pre-proof

spectra of these two samples also shows additional broad shoulder at 625 – 575 cm^{-1}. This broad shoulder may be due to the presence of multiple anionic components present in the samples. Distorted C-N linkage at wavenumber 1080-1360 cm^{-1} with prominent and sharp peak at 675 cm^{-1} are indicative of Al-N linkage which is expected in cationic moiety [12]. This has been supported by ESI-MS of ionic liquid with 2.3 mole ratio of the aluminium chloride to tributyl amine. There are many visible peaks with various m/z values, mainly showing TBA$^+$ cation signal at m/z 186 as base peak, and the cluster $[(TBA)(Al_3Cl_4)]^+$ at m/z 407 in positive ionisation mode while $(AlCl_4)^-$ moiety as base peak with m/z of 168 in negative ionisation mode. In ESI - MS spectra for the neutral ligand based chloroaluminate ionic liquids, $(Al_2Cl_7)^-$ moieties were not observed [13,14,15]. Though the phenomenon is not clear, it may be envisaged that there might be problems with using mass spectrometry for speciation of chlorometallate ILs. However, the phenomenon is validated for a similar system of ILS consisting of 1-butylpyrolidine and $AlCl_3$ using vibrational spectroscopy which is considered more relevant in this context, showing the absence of acidic, $(Al_2Cl_7)^-$ anion [16].

NMR spectra were recorded using a Bruker Avance III HD spectrometer equipped with 9.1 T and 400 MHz proton frequency. The ^{27}Al NMR spectra were externally referenced to aluminium chloride ($AlCl_3$) solution at 0.0 ppm chemical shift. All the chemical shifts are observed in 90 ppm – 110 ppm region confirming the tetrahedral symmetric arrangements in strong ionic environment for all the moieties formed with various mole ratios of tributyl amine and aluminium chloride.

Journal Pre-proof

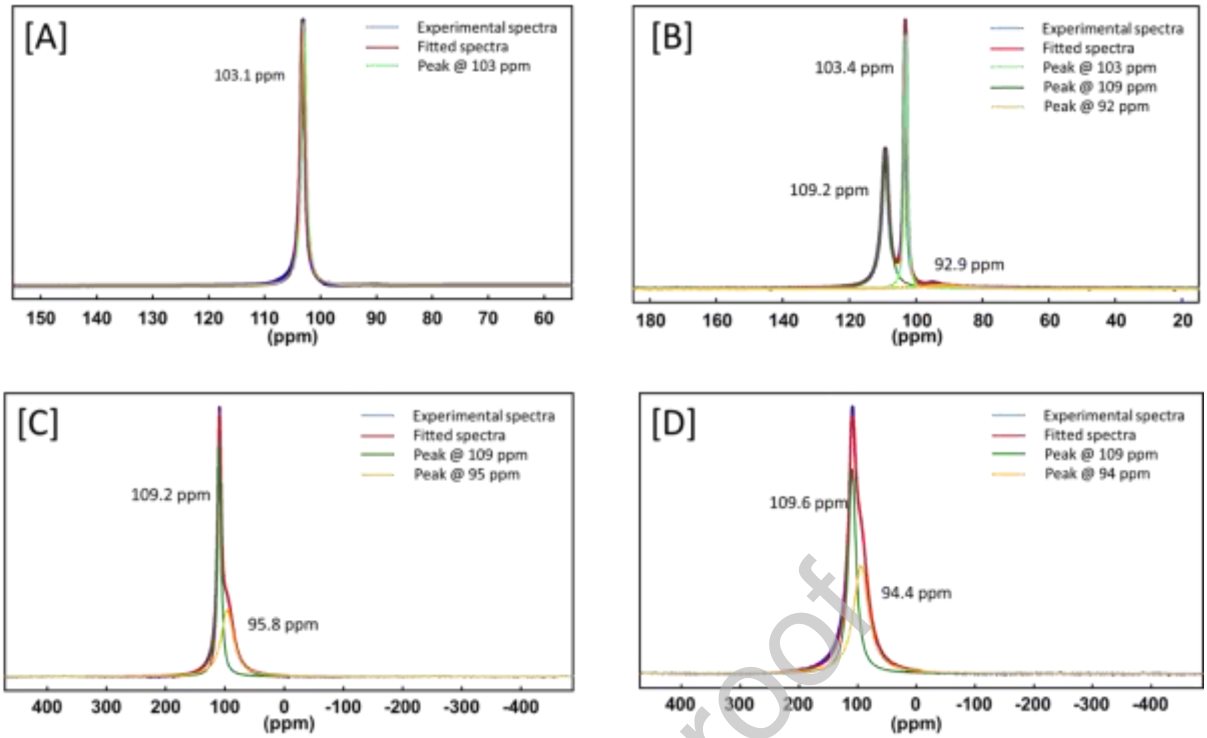


Fig 2: ^{27}Al NMR of various mole ratios of TBA and Aluminium chloride (A) 1:1 mole (B) 1:1.3 mole (C) 1:1.8 mole (D) 1:2.3 mole

Journal Pre-proof

Fig. 2 represents the ^{27}Al NMR spectra of 1:1 mole of TBA and $AlCl_3$ which shows single sharp peak at chemical shift of 103 ppm representing an adduct (TBA:$AlCl_3$) with no other peaks (Fig 2A). As the mole ratio was increased to 1.3, three clear peaks were observed (Fig 2B). Chemical shift at 103 ppm which coincides with that of the adduct was seen along with two new chemical shifts at 109 ppm and 93 ppm are detected. Out of these , the peak at 109 ppm may be assigned to the cationic aluminium as $[Al_yCl_z\ (TBA)_x]^+$, while the peak at 93 ppm can be referred to as an anionic aluminium as $(AlCl_4)^-$ anion. Further increase of aluminium chloride mole ratio to 1.8 and 2.3 moles, the peak at 109 ppm of cation becomes predominant and broadens with a shoulder around 96-94 ppm, depicting the formation of two distinct moieties. The shoulder peak has been found to shift from 93 ppm in 1.3 mole to 94-96 ppm in higher mole ratio. The shift may be attributed to the conversion of $(AlCl_4)^-$ anion to $(Al_2Cl_7)^-$ anion. The peak broadening takes place due to increase in structural in-homogeneity with increase in the concentration of aluminium chloride. There is slight change observed in chemical shifts of anion which may be due to the broadening of peak over wide range of ~10 ppm which was resulting in variation while identifying the peak maxima. It was observed that the height (Area) of the shoulder for 2.3 mole was higher than 1.8 mole, which may be attributed to more $(Al_2Cl_7)^-$ species in ionic liquid. Thus, ^{27}Al NMR shows the formation of TBA-$AlCl_3$ adduct with 1:1 mole ratio. It gets transformed to $[Al_yCl_z(TBA)_x]^+$ cation with $(AlCl_4)^-$ anion which further gets converted into $(Al_2Cl_7)^-$ anion on addition of aluminium chloride [6]. The chemical shift at 103 ppm representing adduct was clearly absent indicating complete dissociation of adduct in ionic liquid.

^{27}Al NMR spectra of chloroaluminate shows the change in chemical shift of anionic moieties with respect to the organic cation moiety in the ionic liquid. Table 2 shows the chemical shifts of cationic and anionic aluminium in various chloroaluminates.

Chloroaluminate	**Chemical shift**	**Reference**
$[C_3mpip][NTf_2]–AlCl_3$	92ppm	[17]
$[C_4mpyr][NTf_2]–AlCl_3$	94 ppm	
(EMIm)Cl - $AlCl_3$	$(Al_2Cl_7)^-$ @ 103.3 - 103.4 ppm	[18]
Urea - $AlCl_3$ Melt	$(Al_2Cl_7)^-$ @ 96.7 ppm	[19]
	$(AlCl_4)^-$ @ 101.8 ppm	
	$[AlCl_2\cdot(urea)_2]^+$ @ 71.8 ppm	
(BMIm)Cl - $AlCl_3$	$(Al_2Cl_7)^-$ @ 73.9 ppm	[20]
	$(AlCl_4)^-$ @ 79.3 ppm	
Acetamide - $AlCl_3$	$[AlCl_2(Acet)_2]^+$ @ 101.1 ppm	[13]
	$[AlCl_2(Acet)]^+$ @ 73.6 ppm	
	$(AlCl_4)^-$ @ 88.6 ppm	

Table 2: Chemical shifts of Anionic and cationic Aluminium in various chloroaluminates

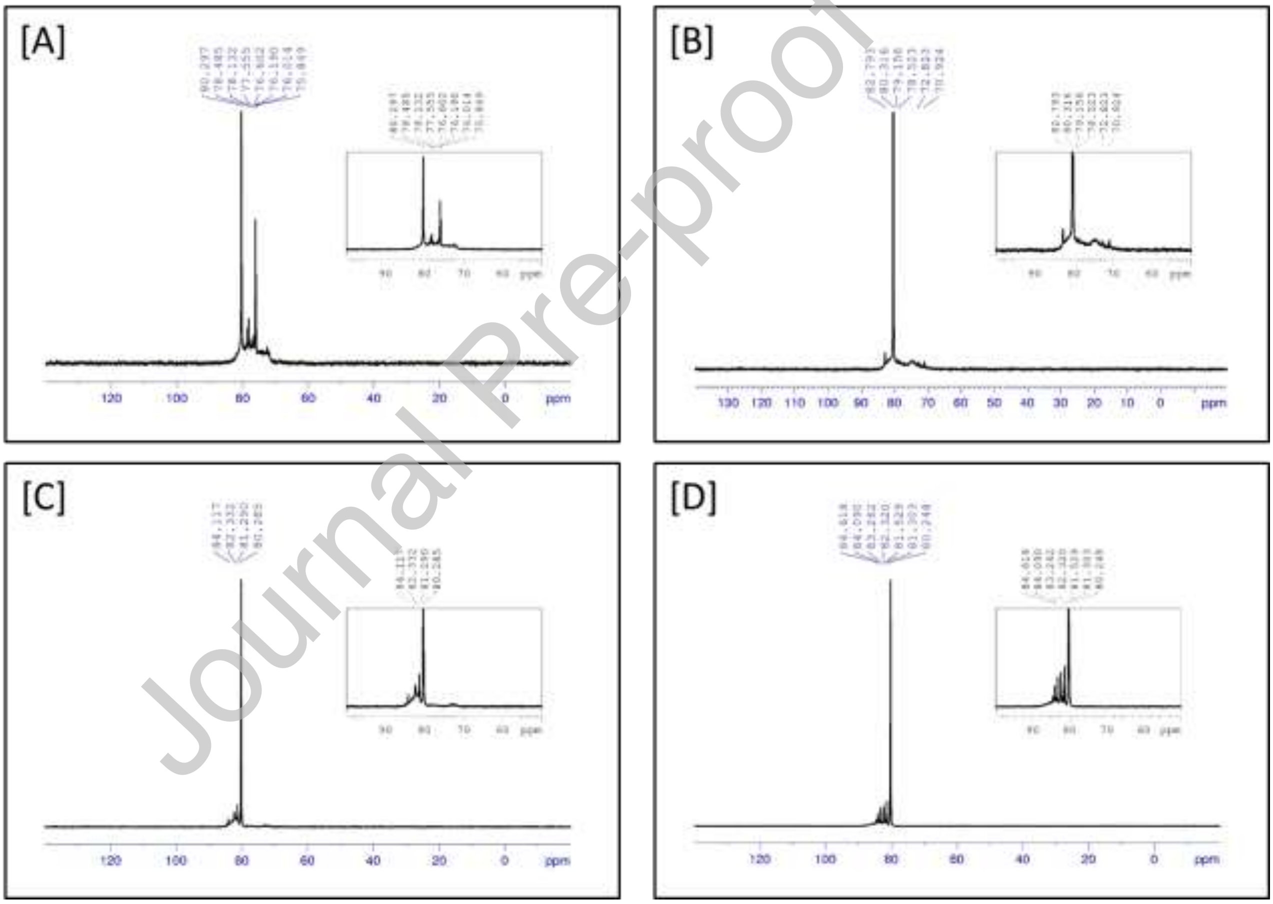
From FTIR, and ^{27}Al NMR studies and analysis, following two types compositions of ionic liquids are possible as

$$X(TBA) + nX(AlCl_3) \longrightarrow \{(TBA)_x.(Al_{(nx-n)}Cl_{(nx-4n)})\}^+.\ nAlCl_4^-$$

$$X(TBA) + nX(AlCl_3) \longrightarrow \{(TBA)_x.(Al_{(nx-2n)}Cl_{(nx-7n)})\}^+.\ nAl_2Cl_7^-$$

Journal Pre-proof

Further, for determination of Lewis acidic strength of the ionic liquids at various mole ratios, the Gutmann acceptor number was determined by ^{31}P NMR using triethyl phosphine oxide as probe molecule. Chloroaluminates are believed to possess higher acidity than that of aluminium chloride which have Gutmann acceptor number equal to 87. The chemical shift of triethyl phosphine oxide (TEPO) dissolved in ionic liquids in ^{31}P NMR is directly proportional to the Lewis acidity and can be identified and quantified as Gutmann acceptor number. ^{31}P NMR was used to measure the Lewis acidity of of freshly prepared ionic liquids using various mole ratios of TBA–$AlCl_3$



Journal Pre-proof

Fig 3: ^{31}P NMR of various mole ratios of TBA and Aluminium chloride (A) 1:1 mole (B) 1:1.3 mole (C) 1:1.8 mole (D) 1:2.3 mole

As shown in Figure 3, the sequential change in chemical shifts of TEPO were observed with modified mole ratios of TBA and $AlCl_3$. All the ionic liquids possess major peak at ~80.2-

80.4 ppm which can be assigned to the cationic Al species exhibiting equivalent Gutmann acceptor number of $AlCl_3$ i.e. 87. The higher Lewis acidity of cation than $AlCl_3$ have been reported in the amide aluminium chloride ionic liquids [5]. Many other peaks were observed at chemical shift from 75 ppm to 80 ppm for 1:1 mole ratio which possess lower Lewis acidity. Many of these less Lewis acidic peaks were diminished with increase in mole ratio to 1:1.3 with one peak emerged at 82.6 ppm which may be due to formation of $(AlCl_4)^-$. Further increase to 1:1.8 mole ratio shows two more peaks at 81.5 ppm and 83.4 ppm besides peaks of cationic species and $(AlCl_4)^-$ anionic species where 83.4 ppm chemical shift represents formation of $(Al_2Cl_7)^-$ anionic moiety. In conventional ionic liquids, a single peak at 83.48 ppm for TEPO was observed for neat Et_3NHCl– $AlCl_3$ IL in the ^{31}P NMR spectra with 1:2 molar ratio of Et_3NHCl to $AlCl_3$ indicating that neat Et_3NHCl–$AlCl_3$ IL contains only single Lewis acid moiety i.e. $[Al_2Cl_7]^-$. However, two moieties were observed at two peaks at 83.48 and 84.92 ppm for the neat N-methyl acetamide–$AlCl_3$ ionic liquid with similar molar ratio 1:2 of N-methyl acetamide to $AlCl_3$ with the addition of TEPO. The presence of various acidic moieties like $(AlCl_4)^-$, $(Al_2Cl_7)^-$, $(Al_3Cl_{10})^-$ are in equilibrium with 1:2 mole ratio of conventional ionic liquids [21, 22,11]. With TBA:$AlCl_3$ ionic liquids, the presence of various super acidic moieties was observed at 81.4 ppm, 81.6 ppm, 82.5 ppm, 83.44 ppm, 84.2 ppm and 84.7 ppm. The moiety at 83.44 coincide with the $(Al_2Cl_7)^-$. The presence of various other Lewis acid moieties along with $(Al_2Cl_7)^-$, confirms the presence in TBA -$AlCl_3$.

It is believed that the coordination of the triethyl phosphine oxide with a Lewis acid lead to change in the chemical shift with change in concentration of TEPO. Therefore, various concentration of TEPO was dissolved in chloroaluminate ionic liquid to confirm the Lewis acidity and to minimise the concentration effect. ^{31}P NMR spectra of TEPO at several small concentrations are recorded, and the chemical shift at infinite dilution was identified by

Journal Pre-proof

extrapolation. It was then compared with the infinite dilution of TEPO in hexane to identify the actual Gutmann acceptor number using formula (AN = 2.348 * $\Delta_{\text{chemical shift}}$) .

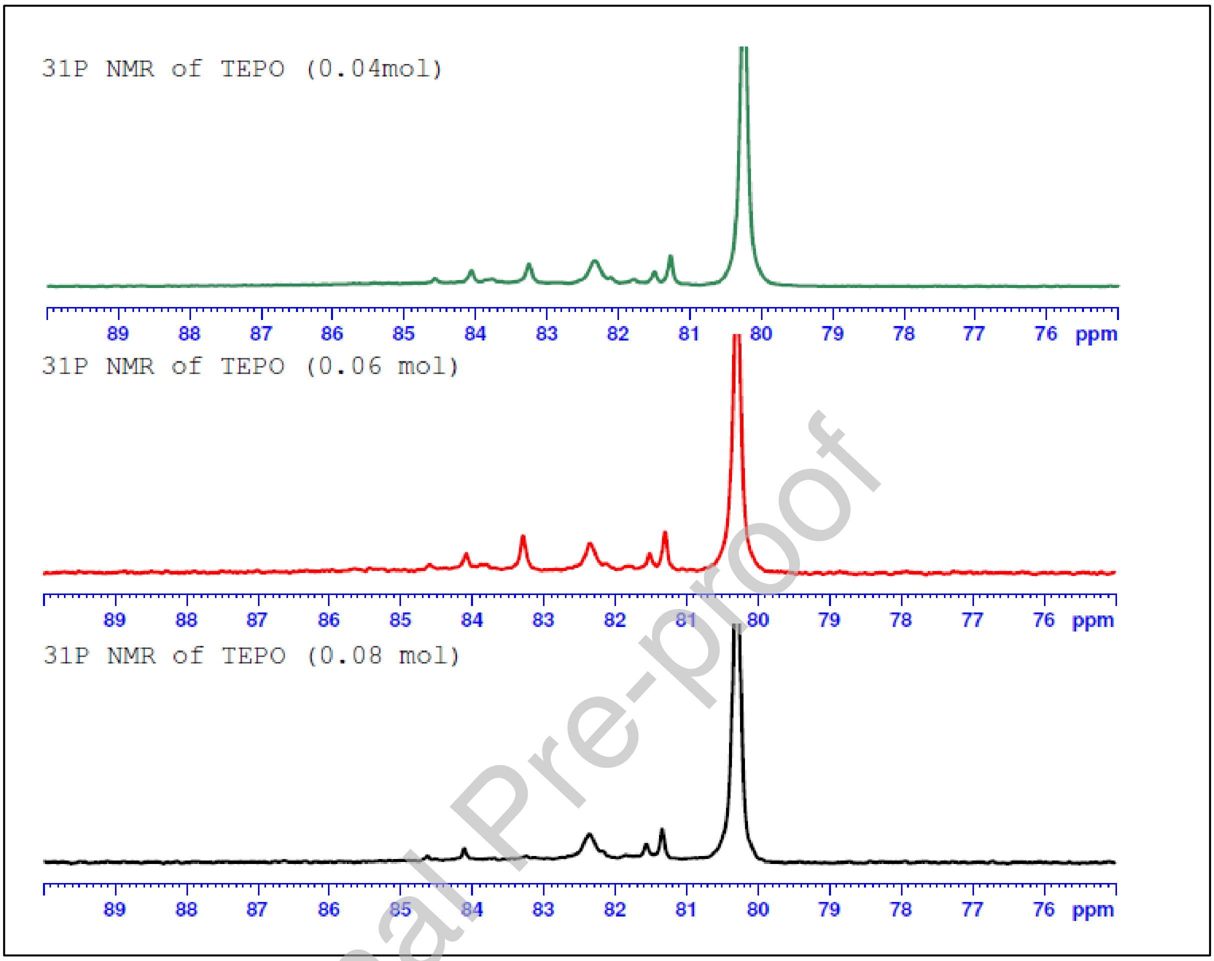


Fig 4: ^{31}P NMR of various concentration of TEPO in ionic liquid for 1:2.3 mole ratios of TBA and Aluminium chloride

Journal Pre-proof

^{31}P NMR of 1:2.3 mole ratio of TBA and AlCl$_3$, is shown in Fig. 4 wherein many acidic moieties were observed at mole ratio of 1:2.3 of TBA and AlCl$_3$ between 80.3 to 85 ppm having Gutmann acceptor number in the range 87-97, as calculated by formula for infinite dilution with respect to chemical shift at infinite dilution of hexane (AN = 2.348 * Δ_{inf}). This observation is in line with the broad shoulder observed in the FTIR spectra of this sample. This kind of strong Gutmann acceptor number provides super acidity in the sample which is required to drive the Friedel-Crafts reaction at lower catalyst concentration. Therefore, the

Lewis acidity of this chloroaluminates was supposed to be higher than aluminium chloride to make it super acidic.

Catalytic activity of ionic liquid for Friedel-Crafts reactions

Friedel–Crafts reaction has been widely studied with various chloroaluminates due to distinct advantages in Lewis acid catalysis. Therefore, to understand the catalytic properties of this chloroaluminate ionic liquid having $(Al_2Cl_7)^-$ moiety, various Friedel-Crafts reactions such as alkylation with olefins and halogenated hydrocarbons, acylation using acyl chloride and anhydrides etc were carried out and the results are mentioned in Table 3. All the reactions were carried with catalyst using benzene as solvent. However, different solvents can also be used for reactions depending upon the preferential reaction mechanisms.

chloroaluminates are active catalyst for Friedel-Crafts reaction primarily due to Lewis acidity of the chloroaluminate ionic liquid which enhance the conversion and selectivity of the desired products. $(Al_2Cl_7)^-$ moiety, which provides high Lewis acidity, has been predominantly formed when the mole fraction of $AlCl_3$ exceeds to 0.5 and has been considered to be highest at mole fraction of ~ 0.67 [23]. Also, the Gutmann Acceptor Number (AN) has been considered as a representation of the Lewis acidity. Therefore, considering the properties estimated above, the Chloroaluminate ionic liquid with 1:2.3 mole ratio of TBA to Aluminium chloride has been used for all the reactions.

Journal Pre-proof

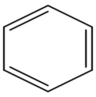
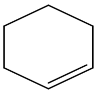
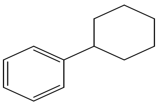
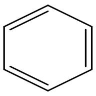
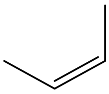
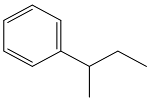
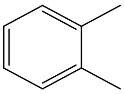
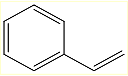
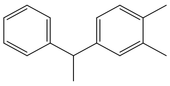
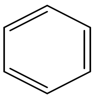
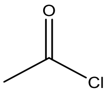
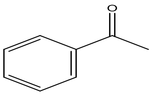
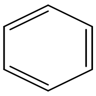
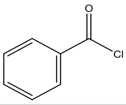
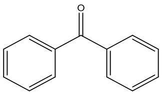
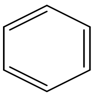
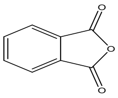
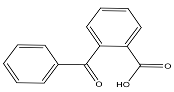
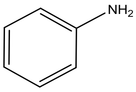
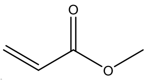
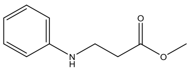
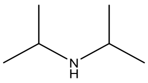
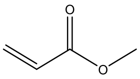
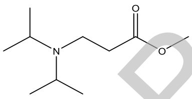
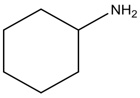
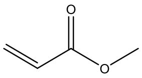
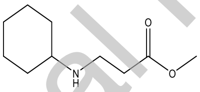
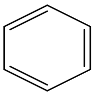
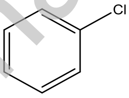
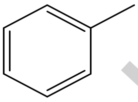
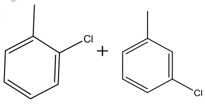
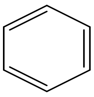
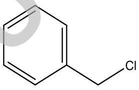
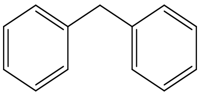
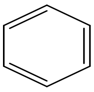
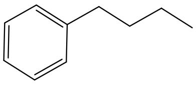
a= GC	b= NMR	c = FTIR	d= MS	e = GC MS			
Reactant A	**Reactant B**	**Product**	**Reaction Temparature**	**Mole Ratio**	**Cat Conc. % w/v**	**Yield**	**Analysis Method**
			Room temp (~25 °C)	6:1	2%	80%	a
			Room temp (~25 °C)	10:1	2%	90%	a
			Room temp (~25 °C)	10:1	2%	71%	a
			Room temp (~25 °C)	6:1	2%	95%	a
			50 °C)	6:1	10%	56%	a
			70 °C	5:1	As given in Procedure	93%	b,d
			Room temp (~25 °C)	2:1	5%	92%	a,c,e
			Room temp (~25 °C)	2:1	5%	85%	a
			Room temp (~25 °C)	2:1	5%	90%	a
	Cl_2		Room temp (~25 °C)	2:1	2%	92%	a,e
	Cl_2		Room temp (~25 °C)	2:1	2%	90%	a,e
			Room temp (~25 °C)	6:1	2%	75%	a,b,e
			Room temp (~25 °C)	6:1	2%	91%	a
$C_{10}H_{20}$	$C_{10}H_{20}$	Oligomer	50 °C	-	5%	90%	a
C_4H_8	C_4H_8	Oligomer	50 °C	-	5%	92%	a

Table 3: Friedel-Crafts reactions using chloroaluminate ionic liquid

Journal Pre-proof

The yields of the product (Table 3) were determined by gas chromatographic analysis except for acylation with phthalic anhydride where actual yield was mentioned. The FTIR, ^{13}C NMR, ^{1}H NMR and Mass spectrometry analysis of products are given in supporting material (Figure S1-S11). This ionic liquid has provided equivalent or better yields compared to other available technologies for various Friedel-Crafts reactions.

Alkylation of aromatic compounds with olefins and chlorinated hydrocarbons showed higher conversion, selectivity, and good yields in short duration of time. Alkylation of benzene with cyclohexene showed 80% selectivity towards cyclohexyl benzene with 1:6 ratio in comparison with conventional ionic liquids that has 70.5% selectivity with 1:16 mole ratio of cyclohexene to benzene [24] whereas with aluminium chloride as catalyst, selectivity was only 48.5% with 1:6 mole ratio [25]. While the reaction of benzene with cis-butene shows slightly higher yields. Reaction of *o*-xylene with styrene showed 71% yield with complete conversion of styrene without any inert solvent. Selectivity of diphenyl methane was also found to be equivalent with conventional ionic liquids after complete conversion of benzyl chloride [26]. Diphenyl methane was characterised by Mass spectra, ^{1}H NMR and ^{13}C NMR for product confirmation. Alkylation of butyl chloride also showed higher conversion to butyl benzene.

Acylation of aromatics with acid chlorides or anhydrides presented higher conversion to acetophenone but with benzoyl chloride, the benzophenone yield was found to be 56% even after longer reaction times and higher catalyst loading. Similar yields were found with conventional chloroaluminate (BMIM:$AlCl_3$) system in one hour reaction time [27].

2-benzoyl benzoic acid, a precursor for anthraquinone and its derivatives, was produced by Friedel-Crafts reaction between benzene and phthalic anhydride [28]. Benzene acylation with phthalic anhydride was performed using ionic liquid to get higher yield. The product was

Journal Pre-proof

purified, and the melting point was found to be 127 °C which is in accordance to the material safety data sheet from Sigma Aldrich (126 °C -129 °C). The mentioned products were also confirmed by Mass spectra, ^{1}H NMR and ^{13}C NMR .

Alkylation of aniline was attempted by Michael addition using methyl acrylate on supported $AlCl_3$ [29]. Aluminium chloride and the aniline forms a 1:1 complex due to their Lewis acidic and Lewis basic properties respectively, resulting in deactivation of $AlCl_3$ catalyst and terminating the reaction. Alkylation of aniline with methacrylate with this catalyst was found to be faster (20 min) and resulted in high yield (>90 %) which has been equivalent to that of supported $AlCl_3$. The formation of product was confirmed using GC-MS and FTIR analysis. FTIR of the product showed N-H band at 3366 cm^{-1} corresponding to secondary amine. It also exhibited mono-substituted aromatics peak at 690 and 746 cm^{-1}. Hence, the conversion of aniline to secondary amine by N-alkylation was confirmed. GC-MS of product shows m/z = 179 which confirms the molecular weight of desired product. Reactions with di-isopropyl amine and cyclohexyl amine also demonstrated high conversion.

Chlorination of aromatic compounds are useful for application in fungicides, insecticides, bulk drug and various other industries [30]. Monochlorinated compounds were obtained in good yields(> 90%) in short reaction time and at room temperature. The products are characterised by GC-MS. Similar high yields were achieved with conventional catalyst (BMIM:$AlCl_3$) but at 80 °C [31].

Oligomers are widely used as the base material for manufacture of lubricants [32]. Oligomerisation of olefins was carried out with high yields using ionic liquid.

Various reactions described above demonstrates the high efficiency of the chloroaluminate in important organic processes. Notably, the catalyst can be efficiently used for N-alkylation where conventional catalyst i.e. metal halides form an adduct which prevents alkylation. The

Journal Pre-proof

catalytic activity of the ionic liquid was found to be equivalent to conventional chloroaluminates whereas the yields were higher in few reactions. Chloroaluminate catalyst depict similar intrinsic properties like small catalyst quantity requirement and easy separation of catalyst in reactions as that of conventional chloroaluminates. Additionally, the major advantage is one step synthesis process for chloroaluminates which reduces the chance of moisture ingression as well as precursor impurities in ionic liquids when reactants are added in stoichiometric quantities in one step. Also, the hydrophobic ligand could help in optimising the liquid – liquid interaction which is highly desired in biphasic catalytic reactions[33]. Lower interaction could result in high reaction time and more catalyst requirement as observed in iso-propylation of naphthalene where reaction time was 3 hrs [34].

Advantages in plausible electrodeposition of Aluminium

Conventionally, aluminium deposition is performed using non-aqueous baths containing organic solvents like chlorinated solvents, comprises volatile organic solvents which are highly flammable. They have detrimental environment effects during applications and high safety measures are essential. Inorganic salt melts are better options for metal depositions requiring high temperature and eventually having high energy requirements besides the loss of aluminium. Ionic liquids (Chloroaluminates) can be easily employed at much lower temperatures with less safety concerns for electrodeposition and are environment friendly. Higher current density was observed at high temperature and high mole ratio which is due to more electroactive $(Al_2Cl_7)^-$ ions. Higher temperature have been required to moderate high viscosity resulting in a faster kinetic process and high diffusivity which can lead to higher current densities for Al plating and stripping [35]. This would also increase the conductivity of electrolyte resulting into higher deposition rate of aluminium on the cathode as the concentration of the electrolyte play prominent role [36]. Aromatic solvent used as co-solvent also resulted significant improvement in quality of deposit and enhanced diffusivity of the Lewis acidic chloroaluminate ionic liquids [37,38].

The conventional chloroaluminate ionic liquids are made from quaternary ammonium halide salts which have high cost and hygroscopic in nature which limit its application in aluminium deposition. Therefore, use of hydrophobic ‘‘neutral’’ ligands in development of chloroaluminate ionic liquid was significant for the practical electroplating of Al [7]. Therefore, Tributyl amine with aluminium chloride is the ideal molecule with properties like hydrophobicity, and neutral ligand.

The electrochemical behaviour of TBA:$AlCl_3$ chloroaluminate as electrolyte was assessed using cyclic voltammetry (CV) and is shown in Figure 5. The CV of ionic liquid mixture (1:1.8mol) at 300K was carried out using a three electrode system with glassy carbon as the working electrode (W.E), Pt as counter and Ag/AgCl as reference electrode. The electrode potential was scanned in the range of 0.0 – 0.6V at a scan rate of 10 mVs^{-1}. A small broad cathodic peak was observed at 0.235V which indicated the reduction potential of aluminium ($Al_2Cl_7^-$) in the ionic liquid [39].

Journal Pre-proof

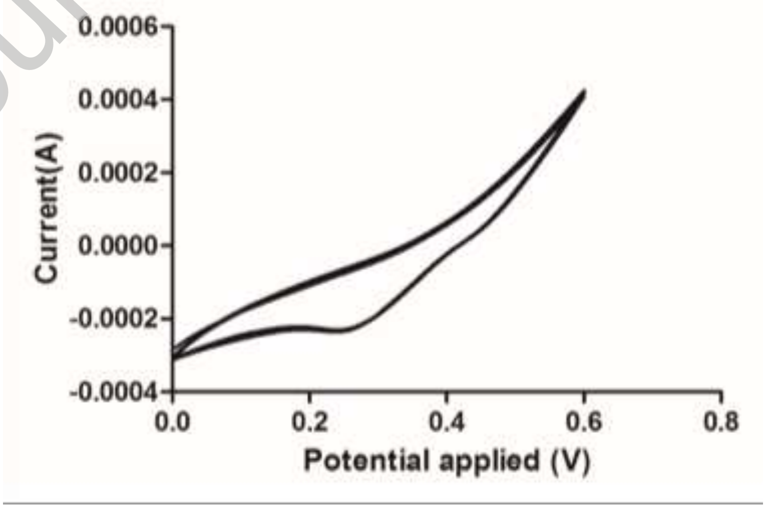


Fig 5: Cyclic voltammogram of TBA:$AlCl_3$ chloroaluminate (1:1.5 molar ratio)

Preliminary experiments on electrodeposition of aluminium from TBA:$AlCl_3$ chloroaluminate were conducted and the results are shown in Figure 6. Chronoamperometric experiments have been performed to study the nucleation process of aluminium from ionic liquid electrolyte system 1:1.8 mol at 300K. Figure 6 shows the current-time transient obtained at 300mV (set potential) using a current density of 10mA.cm^{-2}. A sharp decay of current was observed due to the electrodeposition of aluminium from the ILs on the copper surface. The deposition further thickens due to nucleation and growth of aluminium on the Cu anode [40].

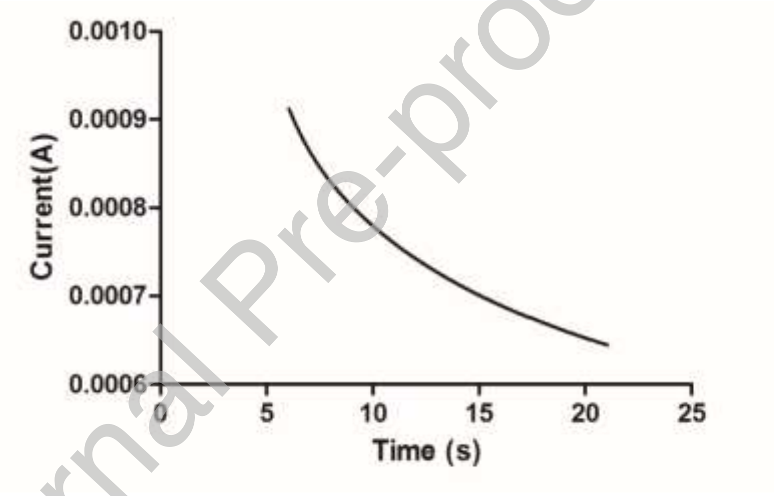


Fig 6: Current-time transient obtained using copper-copper-electrode system in 1:1.5mol at 300K. Chronoamperometric deposition at a current density of 10mA.cm^{-2} for 25 minutes.

A plausible reaction mechanism of electrodeposition of aluminium may be represented as below:

Over all reaction: $4Al_2Cl_7^- + 3e^- \rightarrow Al^0 + 7AlCl_4^-$

Anodic Reaction: $Al_2Cl_7^- + 3e^- \rightarrow Al^0 + AlCl_4 + 3Cl^-$

Cathodic Reaction: $3Cl^- + 3Al_2Cl_7^- \rightarrow 6AlCl_4^-$

Journal Pre-proof

A schematic representation of the electrochemical cell and the proposed mechanism is given in Figure 7.

Another advantage of TBA:AlCl$_3$ chloroaluminate is aromatic solvents which accelerates the ionic liquid formation and used in synthesis process itself which also reduce its viscosity significantly. Ionic liquid with higher concentration of aluminium chloride will provide aluminium deposition by cationic Al as well the anionic species $(Al_2Cl_7)^-$.

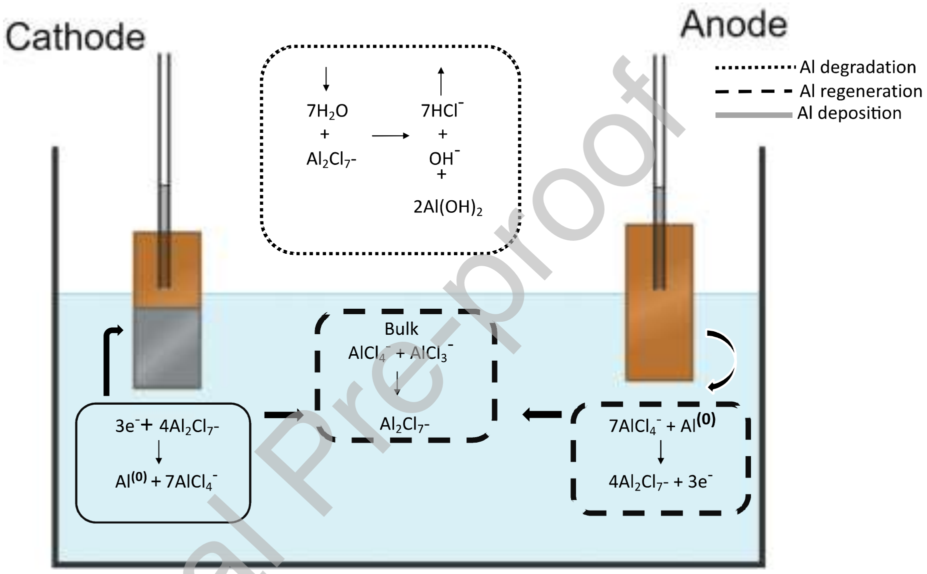


Fig 7: Schematic representation of the electrochemical cell and the process of electrodeposition of aluminium

Thus, the TBA:AlCl$_3$ chloroaluminate possesses many desired properties for electrodeposition of aluminium such as low viscosity, aromatic solvent, minimum safety risk and desired hydrophobic ligand in cation. Conventional ionic liquids are comparatively more viscous, more hygroscopic and do not contain aromatic solvent. Therefore, this chloroaluminate is a better fit for aluminium deposition than that of conventional chloroaluminates.

Conclusions

This paper reveals the compositional changes of ionic liquids at various mole ratios. The study confirms the adduction of amine – AlCl$_3$ and step wise change over to ionic liquid. This

Journal Pre-proof

sequential changes in cationic as well as anionic moieties were authenticated by ESI-MS, FTIR and ^{27}Al NMR. The multiple super Lewis acidic sites in chloroaluminate were confirmed by ^{31}P NMR for its use in catalysis.

Chloroaluminate ionic liquid was found to be highly active and selective catalyst for many Friedel-Crafts reaction. The catalyst meets the advantageous properties of conventional chloroaluminate catalyst like lower catalyst requirement and biphasic reaction systems in alkylation reactions. Pertinent to combined advantages in synthetic process of this chloroaluminate and its high catalytic activity make it an appealing replacement in many Friedel-Crafts reaction for industrial application. Due to its inherently beneficial properties of this chloroaluminate, the aluminium moiety containing hydrophobic ligand can be employed in aluminium deposition as well.

Journal Pre-proof

Term	**Definition**
Conceptualization	Sharad Lande, Sudeshna Chandra, Vishnupriya Bhakthavatsalam
Methodology	Mangesh Sakhalkar, Jeevan Pradhan, Rudra Prosad Choudhury
Validation	Mangesh Sakhalkar
Formal analysis	Mangesh Sakhalkar, Jeevan Pradhan, Rudra Prosad Choudhury, Vishnupriya Bhakthavatsalam
Investigation	Mangesh Sakhalkar, Jeevan Pradhan, Rudra Prosad Choudhury,
Resources	Sunandan Divatia School of Science, SVKM's NMIMS (Deemed to be) University, Reliance Industries Limited, Mumbai
Data curation	Mangesh Sakhalkar
Writing-original draft	Mangesh Sakhalkar
Writing-Review & Editing	Sudeshna Chandra, Sharad Lande
Visualization	Mangesh Sakhalkar, Sudeshna Chandra, Sharad Lande, Vishnupriya Bhakthavatsalam
Supervision	Sudeshna Chandra, Sharad Lande
Project administration	Sudeshna Chandra, Sharad Lande

Term	Definition
Funding acquisition	Reliance Industries Ltd. Mumbai

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Journal Pre-proof

References

[1] S.T. Handy, **Room Temperature Ionic Liquids: Different Classes and Physical Properties**, Current Organic Chemistry, 9 (2005), pp 959-988.

[2] V. I. Parvulescu, C. Hardacre, **Catalysis in Ionic Liquids**, Chemical Reviews, 107 (2007), pp 2615-2665.

[3] L. P. Zhang, Z. W. Ge, X. J. Yu, Z. D. Zhao, Y. H. Dong, **Al electrodeposition from chloroaluminate ionic liquid**, Canadian Metallurgical Quarterly, 52 (2013), pp 398-404.

[4] M. Walter, K.V. Kravchyk, C. Bofer, R. Widmer, M.V. Kovalenko, **Polypyrenes as High-Performance Cathode Materials for Aluminium Batteries**, Advanced Materials, 30 (2018), pp 1705644.

[5] H. Pengcheng, J. Wei, L. Zhong, S.F. Zhou, **Determination of the Lewis acidity of amide–$AlCl_3$ based ionic liquid analogues by combined in situ IR titration and NMR methods**, RSC Advances, 8 (2018), pp 13248–13252.

[6] G. Pulletikurthi, B. Bodecker, A. Borodin, B. Weidenfeller, F. Endresn, **Electrodeposition of Al from a 1-butylpyrrolidine-$AlCl_3$ ionic liquid**, Progress in Natural Science: Materials International 25 (2015), pp 603–611.

[7] Y. Fang, X. Jiang, X.G. Sun, S. Dai, **New ionic liquids based on the complexation of dipropyl sulfide and $AlCl_3$ for electrodeposition of aluminium**, Chemical Communication, 51 (2015), pp 13286-13289.

[8] M. Rueping, B.J. Nachtsheim, **A review of new developments in the Friedel–Crafts alkylation – From green chemistry to asymmetric catalysis**, Beilstein Journal of Organic chemistry, 6 (2010), pp 1-27.

[9] H. Olivier-Bourbigou, L. Magna, D. Morvan, **Ionic liquids and catalysis: Recent progress from knowledge to applications**, Applied Catalysis A: General, Volume 373, Issues 1–2, (2010), pp 1-56

[10] M. Sakhalkar, P. Aduri, S. Lande, S. Chandra, **Single step synthesis of Novel Chloroaluminate Ionic Liquid for Green Friedel-Crafts Alkylation Reaction**, Clean Technologies and Environmental Policy, 22 (2020), pp 59–71.

[11] R.J. Gale, R.A. Osteryoung, **Infrared investigation of room temperature aluminium chloride: Butyl pyridinium chloride melts**, Inorganic Chemistry, 19 (1980), pp 2240–2242.

[12] L.Yate, J.C. Caicedo, A.H. Macias, F.J. Espinoza-Beltrán, G. Zambrano, J. Muñoz-Saldaña, P. Prieto, **Composition and mechanical properties of AlC, AlN and AlCN thin films obtained by r.f. magnetron sputtering**, Surface & Coatings Technology, 203 (2009), pp 1904–1907.

Journal Pre-proof

[13] H. M.A. Abood, A. P. Abbott, A. D. Ballantyne, K. S. Ryder, **Do all ionic liquids need organic cations? Characterisation of [$AlCl_{2n}$Amide]$^+$$AlCl_4$ and comparison with imidazolium-based systems**, Chemical Communication, 47 (2011), pp 3523–3525.

[14] Y.X. Fang, K. Yoshii, X.G. Jiang, X. G. Sun, T. Tsuda, N. Mehio, S. Dai, **An $AlCl_3$ based ionic liquid with a neutral substituted pyridine ligand for electrochemical deposition of aluminium**, Electrochimica Acta, 160 (2015), pp 82–88.

[15] P. Abbott, R.C. Harris, Y.T. Hsieh, K.S. Rydera, I.W. Sun, **Aluminium electrodeposition under ambient conditions**, Physical Chemistry Chemical Physics, 16 (2014), pp 14675–14681.

[16] L. C. Brown, J. M. Hogg, M. Swadzba-Kwasny, **Lewis Acidic Ionic Liquids**, Topics in Current Chemistry (Z), 375 (2017), 78

[17] T. Rodopoulos, L. Smith, M.D, Horne, T. Ruther, **Speciation of Aluminium in Mixtures of the Ionic Liquids [C_3mpip][NTf_2] and [C_4mpyr][NTf_2] with $AlCl_3$: An Electrochemical and NMR Spectroscopy Study**, Chemistry - A European Journal, 16 (2010), pp 3815 – 3826.

[18] S. Takahashi, M.L. Saboungi, R.J. Klingler, M. J. Chen, J.W. Rathke, **Dynamics of room-temperature melts: nuclear magnetic resonance measurements of dialkylimidazolium haloaluminates**, Journal of the Chemical Society, Faraday Transactions, 89 (1993), pp 3591-3595.

[19] M. Angell, C.J. Pan, Y. Rong, C. Yuan, M.C. Lin, B.J. Hwang, H. Dai, **High Coulombic efficiency aluminium-ion battery using an $AlCl_3$-urea ionic liquid analog electrolyte**, Proceedings of the National Academy of Sciences, 114 (2017), pp 834-839.

[20] S.J. Nara, J.R. Harjani, M.M. Salunkhe, **Friedel−Crafts Sulfonylation in 1-Butyl-3-methylimidazolium Chloroaluminate Ionic Liquids**, Journal of Organic Chemistry, 66 (2001), pp 8616–8620

[21] M.M. Zhang, V. Kamavarum, R. Reddy, **New electrolytes for aluminium production: Ionic liquids**, The Journal of The Minerals, Metals & Materials Society, 55 (2003), pp 54–57.

[22] A. K. Abdul-Sada, A. M. Greenway, K. R. Seddon, T. Welton, **A fast Atom Bombardment Mass Spectrometric Study of Room-temperature -Ethyl-3-methyllithium**

Journal Pre-proof

Chloroaluminate(III) Ionic Liquids. Evidence for the Existence of Decachloroaluminate(III) anion, Organic Mass Spectrometry, 28 (1993), pp 759-765.

[23] L. C. Brown, J. M. Hogg, M. Swadźba-Kwaśny, **Lewis Acidic Ionic Liquids**, Topics in Current Chemistry, 375, (2017), 78.

[24] Y. Wang, J. Li, H. Chun, T Wang, **Alkylation of Benzene and Cyclohexene Catalyzed by Room-temperature Ionic Liquid**, Advances in Fine Petrochemicals, 2008-10.

[25] Md Ashaduzzaman, M. Hosssain, S. Saha, M. Saha, **A study of alkylation of benzene with cyclohexene**, Bangladesh Journal of Scientific and Industrial Research, 40 (2005), pp 103-106.

[26] D.S. Kim, W.S. Ahn, **Diphenylmethane Synthesis Using Ionic Liquids as Lewis Acid Catalyst**, The Korean Journal of Chemical Engineering, 20 (2003), pp 39−43.

[27] C. Li, W. Liu, Z. Zhao, **Efficient synthesis of benzophenone derivatives in Lewis acid ionic liquids**, Catalysis Communications, 8 (2007), pp 1834–1837.

[28] R.V.Jasra, **Solid Acid Catalysts for Acylation of Aromatics**, Bulletin of the catalysis Society of India, 2 (2003), pp 157–183.

[29] M.R. Saidi, Y. Pourshojaei, F. Aryanasab, **Highly Efficient Michael Addition Reaction of Amines Catalyzed by Silica-Supported Aluminum Chloride**, Synthetic Communications, 39 (2009), pp 1109-1119.

[30] S.K. Sharma, **Chlorination of Aromatic Compounds in Aqueous Media using N-Chlorosuccinimide**, Research Journal of Chemical Sciences, 5 (2015), pp 54−73.

[31] A. Wang, X. Zhu, H. Yin, Y. Fu, X. Hou, Chlorination of Toluene to o-Chlorotoluene Catalyzed by Ionic Liquids, Catalysts 8 (2018), 532.

[32] C. Fehér, E. Kriván, Z. Eller, J. Hancsók, R. Skoda-Földes, **In Oligomerization of Chemical and Biological Compounds**; Claire Lesieur, Intech Open, 2014.

[33] D. Zhao, M. Wu, Y. Kou, E. Min, **Ionic liquids: applications in catalysis**, Catalysis Today, 74 (2002), pp 157–189

Journal Pre-proof

Journal Pre-proof

[34] Li Chenmin; Qi Xin; Tang Xiangyang; **Synthesis of 2-Isopropyl Naphthalene Catalyzed by $Et_3NHCl-AlCl_3$ Ionic Liquids**; China Petroleum Processing and Petrochemical Technology, 16 (2014), pp 60-65.

[35] M. Zhang, J. S. Watson, R. M. Counce, P. C. Trulove,T. A. Zawodzinski Jr., **Electrochemistry and Morphology Studies of Aluminium Plating/Stripping in a Chloroaluminate Ionic Liquid on Porous Carbon Materials**, Journal of The Electrochemical Society, 161 (2014), pp D163-D167.

[36] T. Melton, J. Joyce, J. T. Maloy, J. A. Boon, J. S. Wilkes, **Electrochemical Studies of Sodium Chloride as a Lewis Buffer for Room Temperature Chloroaluminate Molten Salts**, Journal of the Electrochemical Society, 137 (1990), pp 3865.

[37] Q Liao, W.R. Pitner, G. Stewart, C. L. Hussey, G. R. Stafford, **Electrodeposition of Aluminum from the Aluminum Chloride- 1- Methyl- 3- ethylimidazolium Chloride Room Temperature Molten Salt + Benzene**, Journal of the Electrochemical Society, 144 (1997), pp 936-943.

[38] S. Prabu, H.W. Wang, **Factors Affecting the Electrodeposition of Aluminum Metal in an Aluminum Chloride–Urea Electrolyte Solution**, Journal of Chinese Chemical Society, 64 (2017), pp 1467-1477.

[39] E. Berretti, A. Giaccherini, S. M. Martinuzzi, M. Innocenti, T. J. S. Schubert, F. M. Stiemke, S. Caporali, **Aluminium Electrodeposition from Ionic Liquid: Effect of Deposition Temperature and Sonication**, Materials, 9 (2016), 719 (14pp)

[40] Y. Zheng, C. Peng, Y. Zheng, D. Tian, Y. Zuo, **Low-temperature Electrolysis of Aluminium from 1-Butyl-3-methylimidazolium Chloroaluminate Ionic Liquids with Inert Anode**, International Journal of Electrochemical Science, 11 (2016), pp 6095 – 6109.

Journal Pre-proof