An Attempt to Chlorinate Copper Phthalocyanine Blue using Ionic Liquid

By

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An Attempt to Chlorinate Copper Phthalocyanine Blue using Ionic Liquid

Project

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Declaration

This is to certify that

1. The Thesis comprises my Original work towards the Degree of Master of Technology in Chemical Engineering (Environmental Process Design) at Nirma University and has not been Submitted elsewhere for a Degree.
2. Due Acknowledgment has been made in the text to all other material used.

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Undertaking for the Originality of the work

I, Ajinkya Apte, 13MCHE01, give undertaking that the Project entitled **"An Attempt to Chlorinate Copper Phthalocyanine Blue using Ionic Liquid"** submitted by me, towards the partial fulfillment of the requirements for the degree of Master in Chemical Engineering (Environmental Process Design) of Nirma University, Ahmedabad is the original work carried out by me and I give assurance that no attempt of plagiarism had been made.

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Abstract

Copper Phthalocyanine blue is an important pigment of the colour family. Numerous shades of blue can be made using this basic blue pigment. It is also called as monastral blue, phthalo blue and helio blue. This pigment finds its applications in paints, plastics and dyes. Copper Phthalocyanine is the highest volume pigment produced in the world.

The chlorination of this pigment is done to produce Copper Phthalocyanine Green. This green pigment helps to produce a variety of green shades. Thus, the chlorination process is very vital to obtain totally different green-colour pigments from the original blue-coloured pigments. The chlorination done traditionally involves the use of organic petroleum-derived solvents like dichloromethane, hexane, toluene, ethyl benzene etc. These organic solvents are potential carcinogens along with being non-renewable at the same time. Also, the traditional chlorinating agents include sulfonyl chloride, thionyl chloride, sulphur monochloride etc. which are costly as well as harmful.

Ionic liquids are made up of ions and ion pairs. These have very low melting points and are mostly liquids at room temperatures. They have good selectivity for water and organics. Moreover, these can be synthesised in the laboratory as per the requirement by varying the cation and anion combinations thereby enabling them to be tailored to suit a given application. Easy recovery and recycle at the end of the process as well as good solubilities have accelerated the use of ionic liquids as solvents in recent past.

Following research sheds light on the use of the ionic liquids 1-butyl-3-methyl imidazolium bromide [BMIm][Br] and 1-butyl-3-methyl imidazolium tetrafluoroborate [BMIm][BF_4] as solvents for the chlorination of Copper Phthalocyanine Blue pigment. The process involves the synthesis of the ionic liquids as stated in the literature and their characterisation, as well as the application of the synthesised liquid for chlorination.

Keywords: [BMIm][Br], [BMIm][BF_4], Copper Phthalocyanine Blue, Copper Phthalocyanine Green, chlorination

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Ajinkya Apte

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Chapter 1

Introduction

1.1 Ionic Liquids

Ionic liquids have a wide application range and as such have attracted great interest in the last decade. Nowadays, ionic liquids with more targeted species are synthesised and as such the ionic liquid family is now extended to include these as well. A number of reviews on the physico-chemical properties and mode of application (liquid phase, multiphase, immobilised on supports) have been reported due to this expanding interest.

In addition to the fact that they are now commercially available, there is a now a better understanding of the chemical and physical properties and also the effect of ionic liquids. In consequence, ionic liquids are now used with better process control. The introduction of structural functionalities on the cationic or anionic part has made it possible to design new ILs with targeted properties. Recently, a lot of publications have been aimed at better understanding of these solvents, their physic-chemical properties and use in diversified applications such as batteries, fuel cells, plasticizers, lubricants, capacitors, thermal fluids, extractants, ionogels, sensors and solvents in analysis, synthesis, catalysis and separation processes.

Newer applications like pharmaceutical ionic liquids are emerging now. ILs are used more than just as “green” solvents. Their unique ionic character and structure differs them from molecular solvents. This peculiar structure leads to specific effects. They are generally made up asymmetric and flexible ions, the components being of highly different sizes and shapes, and involve different types of interactions.

These materials are tuneable and are used for multipurpose tasks. They act as multifunctional compounds like solvents and ligands, solvents and catalysts, stabilising agents for the catalysts or intermediates along with performing the single function of a solvent. The implementation methodology of ionic liquid determines its function. They play specific roles and can be utilised in very different ways: homogeneous,

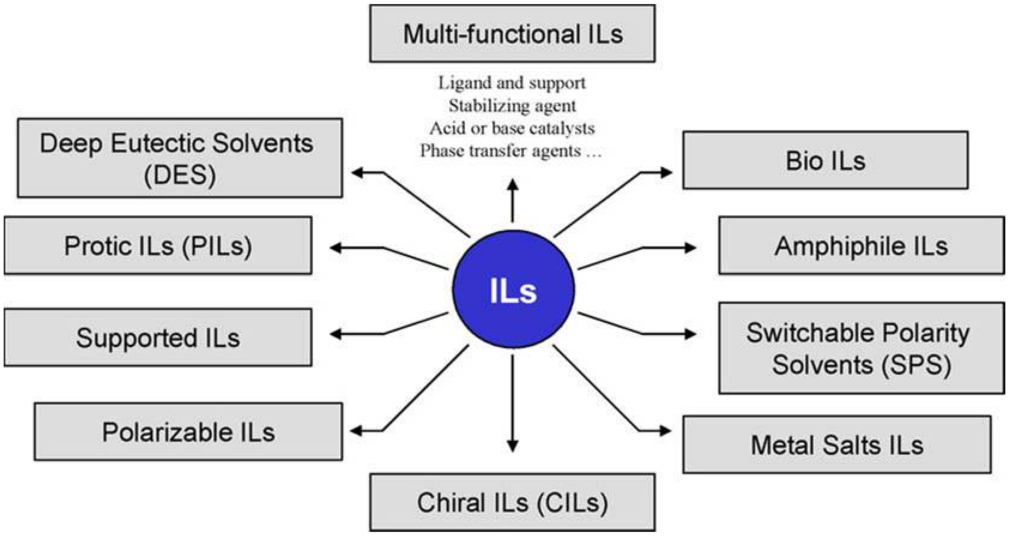


Figure 1.1: Types of Ionic Liquids

Table 1.1: General properties of ionic liquids

A salt	Cation and or anion quite large
Freezing point	Mostly $< 100^{o}$C
Liquid range	Often $> 200^{o}$C
Thermal stability	Usually high (degradation usually occurs at about 450^{o}C)
Viscosity	Normally $<$ 100cP
Dielectric constant	Implied $< =$ 30
Polarity	Moderate
Specific conductivity	Usually $<$ 10mS cm $^{-1}$
Molar conductivity	$<$ 10 cm^{2} mol^{-1}
Electrochemical window	Greater than 2V (except for Bronsted acid system)
Vapour pressure	Usually negligible

multiphase, heterogeneous, in bio transformations or in organo-catalysis.

1.2 Modern day ionic liquids

The properties of a modern day ionic liquid are summarized below. Particularly significant are:

- Mostly low vapour pressure in contrast to volatile organic solvents.
- Moderate specific conductivities, usually in the same range as those of aqueous electrolytes. Many of these are used in electro-deposition[1].

1.2.1 General properties of ionic liquids

The general properties of ionic liquids are as shown in Table 1.1

Table 1.2: Properties of Various liquids

Compound	Temp (° C)	Molarity (mol/lit)	Specific Conductivity (S/cm)	Molar Conductivity (S cm^2 / mol)	Viscosity cP	Reference
NaCl	900	25.3	3.88	154	1.05	[2]
LiCl	780	35	7.59	217		[2]
$NaNO_3$	450	21.4	0.72	34	6.9	[2]
Na_2SiO_3	1750	18	4.8	270		[2]
$AlCl_3$ (63%)- NaCl	175	5.8	0.24	41	3.85	[3]
LiCl-KCl	450	29.7	1.57	53	2.44	[4]
$[(CH_3)_3S][HBr_2]$	25	7.3	0.034	4.7	20.5	[4]
[EMIm][Cl] (60%)-$AlCl_3$	25	5.3	0.0065	1.2	47	[4]
[EMIm][Al_2 Cl_7]	25	3.4	0.015	4.4	14	[4]
[BMIm][CF_3CO_2]	20	5.1	0.0032	0.6	73	[4]
[BuPy][BF_4]	25	5.5	0.0019	0.3	103	[4]
[EMIm] [$(CF_3SO_2)_2$ N]	25	3.7	0.0057	1.5	31	[4]
H_2O	25	55.3	$4*10^{-8}$	$7*10^{-7}$	0.895	[2]
0.1 M KCl	25	0.1	0.013	129	0.9	[2]
Na	100	40.4	$1.04*10^{5}$	$2.6*10^{6}$	1.058	[2]
H_2SO_4	25	0.049	0.0104	212	24.55	[5]
CH_3COOH	25	17.5	$8*10^{-9}$	$4.6*10^{-7}$	1.056	[6]
HF	0	50.1	$1*10^{-6}$	$2*10^{-5}$	0.256	[5]

(EMIm= ethyl methyl imidazolium, BMIm= butyl methyl imidazolium, BuPy= butyl pyridinium)

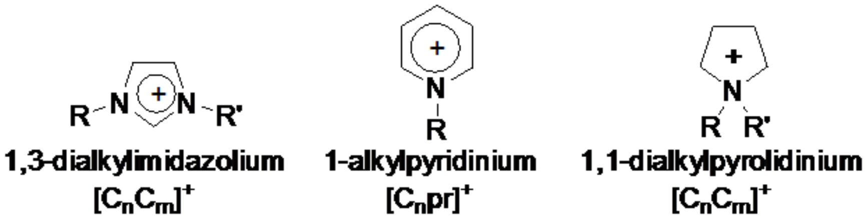


Figure 1.2: Common cations used for ionic liquids

1.2.2 Relative properties of various liquids

The cations of the ionic liquids are generally bulky and asymmetric (phosphonium and ammonium salts or hetero-aromatics) with low charge densities, low symmetry and weak intermolecular interactions (figure 1.2). The 1,3-dialkylimidazolium salts are investigated the maximum but other affordable salts are also now being studied. 1,3-dialkylimidazolium salts are used as starting materials for synthesising low melting salts. Typically, the anions are inorganic and include $[PF_6]^-$, $[BF_4]^-$, $[CF_3SO_3]^-$ and $[(CF_3SO_2)_2N]^-$, although organic anions (e.g. $[RCO_2]^-$) have also been introduced more recently. The cation and anion, both, determine the physical and chemical properties of the ionic liquid.

1.3 Varieties at room temperature

Room temperature ionic liquids consist of organic cations such as 1-alkyl-3-methylimidazolium, 1-alkylpyridinium, N-methyl-N-alkylpyrrolidinium and ammonium ions (which are bulky and asymmetric). As regards properties, phosphonium cations are advantageous but they are relatively uncommon. Anions can be of a wide range; they can be simple halides having high melting points or inorganic anions like tetrafluoroborate and hexafluorophosphate or large organic anions.

A wide range of anions are employed, ranging from simple halides such as bromine or chlorine which have high melting points, to inorganic anions such as tetrafluoroborate and hexafluorophosphate to large organic anions like bistriflimide, triflate or tosylate. Ionic liquids containing simple non-halogenated organic anions such as formate, alkylsulfate, alkylphosphate or glycolate also have many interesting uses. 1-butyl-3-methylimidazolium tetrafluoroborate is a colourless liquid with high viscosity at room temperature. It has a very low melting point of about −80 °C. Metal nanoparticles act as the actual catalyst or as a catalyst reservoir in many synthetic processes. ILs help in the formation and stabilization of catalytically active transition metal nanoparticles.

Ionic liquids can also be prepared to comprise of coordinating groups like the nitrile group on either the cation or the anion.

1.4 Low temperature varieties

Low temperature is advantageous in imaging long wave infrared light. This part of light comes from very distant faraway places in the universe. Hence, low temperature ionic liquids are used as fluid base in the spinning liquid mirror telescope to be sent on moon. The reflective surface shall be made up of liquid base covered with a thin metallic film. Low temperature varieties are found below 130 K. Low temperature varieties have extremely low volatility.

1.5 Advantages of ionic liquids

Ionic liquids are attractive as potential solvents for a number of reasons:

- They exhibit very low vapour pressures under ambient conditions and thus are effectively non-volatile.
- They are generally colourless liquids with relatively low viscosities.
- Ionic liquids can be found that are good solvents for a broad spectrum of

Table 1.3: Properties of Copper Phthalocyanine

Colour strength	High
Solvent-resistance	Good-excellent
Heat stability	Excellent (300°C)
Light fastness and weatherability	Very good

inorganic, organic and polymeric materials and are immiscible with numerous organic solvents.

- Applications in process intensification and as non-aqueous polar alternatives in biphasic systems are possible.
- Being composed of two parts, there is a synthetic flexibility that is not available for single component molecular solvents.

Apart from these advantages, they are also readily prepared from commercially available reagents. Hence, a variety of ionic liquids of various qualities can be synthesised as per requirement. This is particularly important in catalysis, where trace impurities can make a huge difference to the outcome of a reaction.

1.6 Phthalocyanines

Phthalocyanine (PC) group comprises of a large number of pigments. The most important of these are the Phthalocyanine Blue and the Phthalocyanine Green. Copper Phthalocyanine blue is the copper (II) complex of tetra aza tetra benzoporphine and Phthalocyanine green is its chlorinated derivative. This chlorinated derivative is familiar by the name Pigment green 7. Just as chlorination imparts a green shade, the bromination imparts a yellowish green shade. This brominated derivative is known by the name Pigment green 36.

1.6.1 Properties of Copper Phthalocyanine

Table 1.3 shows properties of copper phthalocyanine.

1.7 Phthalocyanine Blue

Phthalocyanine Blue is a bright, crystalline, synthetic blue pigment of the Phthalocyanine family. The reaction between phthalic anhydride and urea with copper yields Pigment Blue. It is a cyclic product. Its CAS number is 147-14-8. Monastral blue and phthalo blue are its other names. It is blue powder and insoluble in water and most solvents. Developed as a pigment, it is frequently used in paints and dyes. It has superior properties such as light fastness, tinting strength, covering power and resistance to the effects of alkalies and acids and hence is of high value in the pigment industry.

It was accidentally produced at an ICI phthalimide plant and was noticed as a by-product formed due to the reaction between phthalimide and trace amounts of iron from the reactor. The chemist dissolved samples of this blue into sulphuric acid and made it into a blue pigment. This pigment was converted and centered at Copper which was sold by the name of Monastral Blue. Today, the pigment is the highest volume pigment produced.

1.7.1 Synonyms and trade names

The substance is also known as:

- Monastral blue
- Phthalo blue
- Helio blue
- Winsor blue
- Phthalocyanine blue
- Pigment Blue 15:2
- Copper Phthalocyanine blue
- Copper tetrabenzoporphyrazine
- Cu-Phthaloblue
- PB-15
- PB-36 and
- C.I. 74160.
- The abbreviation 'CuPC' is also used.

1.7.2 Structure and properties

Phthalocyanine blue ($C_{32}H_{16}N_8Cu$) is a complex of copper with Phthalocyanine. Its molecular mass is 576.08 g and melting point is 600 °C (with decomposition). It is insoluble in water ($<$ 0.1 g/100 ml at 20 °C) but soluble in concentrated sulphuric acid. Density of the solid is approximately 1.6 g/cm^3. The colour is due to a π-π^* electronic transition, with λ_{max} ~ 610 nm[7]. Figure 1.3 shows structure of Copper Phthalocyanine molecule.

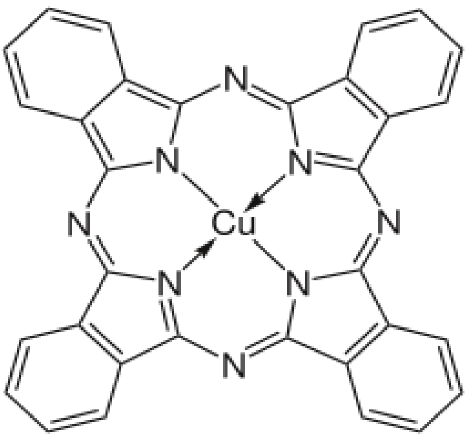


Figure 1.3: Structure of Copper Phthalocyanine Blue

Table 1.4: Difference between alpha blue and beta blue

Alpha Blue	Beta Blue
Red shade blue copper phthalocyanine	Green shade blue copper phthalocyanine
Phase stabilised by partial chlorination	stabilised towards flocculation and phase change
Denoted by 15:1 and 15:2	Denoted by 15:3
Smaller particle size	Larger particle size
Higher tinctorial strength	Lower tinctorial strength
Less stable crystal formulation	More stable crystal formulation
Available as crystallising type and non-crystallising non flocculating type	Available as non-crystallising type and non-crystallising non flocculating type

1.7.3 Types of Phthalocyanine Blue

Phthalocyanine blue is primarily of two types; alpha blue and beta blue. Initial alpha forms did not form stable dispersions in solvents (the blue pigment showed tendency to flocculate). Beta blue and newly found more stabilised alpha forms show good dispersive ability.

1.7.4 Toxicity and hazards

The compound is non-biodegradable but not toxic to fish or plants. However this compound is not associated with any specific danger. No serious effects were observed upto an oral LD_{50} of 5g per kg. At 0.2g/kg or greater, the chronic ingestion levels of concern were observed. Carcinogenic effects are not known as such. Some evidence shows birth defects in developing embryos on exposure to Phthalocyanines.

1.7.5 Applications

Ink : Due to its stability, phthalo blue is also used in inks, coatings, and many plastics. The pigment is insoluble and has no tendency to migrate in the material. It is a standard pigment used in printing ink and the packaging industry. Phthalo blue is a cool blue with a slight hue of green. It has a high tinting strength and easily dominates the mix when combined with other colours. It is a transparent staining colour and can be applied using glazing techniques.

Manufacture of Phthalocyanine Green: Phthalocyanine Blue is used as a source material for manufacture of Phthalocyanine Green.

Photovoltaics: Copper Phthalocyanine, often referred to as CuPC, is also a leading material used in organic solar cell research[8].

1.8 Phthalocyanine Green

Phthalocyanine Green is a synthetic green pigment belonging to the Phthalocyanine dye family. It is a complex of copper (II) with chlorinated Phthalocyanine. It is synthesised as a very soft and fine powder which is insoluble in water. It has the CAS numbers 1328-45-6 and 1328-53-6 on the extent of chlorination. As a result, its chemical formula ranges from $C_{32}H_3Cl_{13}CuN_8$ to $C_{32}HCl_{15}CuN_8$. It is a bright, high intensity colour. It finds its applications in oil and acrylic based artist's paints. Pigment Green is also known by the following names:

- Phthalo green
- Pigment Green 7
- Copper Phthalocyanine Green
- C.I. Pigment Green 7
- Non-flocculating Green G
- Polychloro copper Phthalocyanine

1.8.1 Production and Chemistry

Phthalocyanine green is a Phthalocyanine blue pigment with most of the hydrogen atoms replaced with chlorine. Phthalocyanine Green is produced by chlorinating Phthalocyanine Blue in a melt of sodium chloride and aluminium chloride at elevated temperatures. The electron distribution is influenced due to the chlorination as a result of which the absorption spectrum of Phthalocyanine Green is shifted as compared

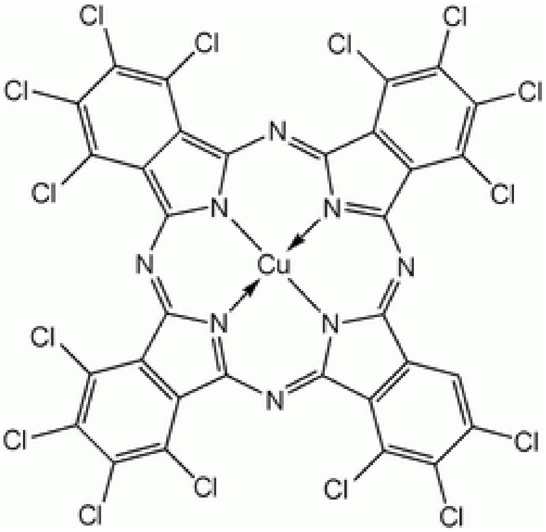


Figure 1.4: Structure of Copper Phthalocyanine Green

to that of Phthalocyanine Blue. Phthalo Green molecules are highly stable. They are resistant to alkali, acids, solvents, heat, and ultraviolet radiation. The pigment is insoluble and has no tendency to migrate in the material.

Pigment Green 7 is crystal stable chlorinated derivative of Pigment Blue and is of non-crystallising non-flocculating type. It provides a yellowish shade of green.

1.8.2 Differentiating characteristics of Pigment Green

Pigment Green are differentiated by the following characteristics:

- The particular intermediate shade of Pigment Green and Pigment Blue, which currently include Pigment Blue 15.1, Pigment Blue 15.2, Pigment Blue 15.3 and Pigment Blue 15.4;
- Crystallising type, which determines the brilliance and brightness of products;
- Non-crystallising type, which determines the ability of products to maintain their colour under all conditions; and
- Non-crystallising non-flocculating type, which determines the ability of products to spread evenly over the surfaces that they are applied on.

1.8.3 Structure

Figure 1.4 shows structure of Copper Phthalocyanine Green molecule.

1.8.4 Uses

Phthalo green is used in inks, coatings, printing inks, plastics, rubber, paints (for exterior and interior surfaces), textiles, leather and paper on account of its high stability. It is a standard pigment used in printing ink and packaging industry. It is used in some tattoos.

1.8.5 Toxicity and hazards

Developing embryos are seen to have some defects on exposure to this compound [7].

1.8.6 Aims and Objectives

The present ongoing industrial process for the manufacture of chlorinated copper phthalocyanine uses a mixture of aluminium chloride and sodium chloride. This melt has to be treated at the end of the reaction. Only cupric chloride which is used as a catalyst is recovered at the end of the process. Rest of the effluent has to be treated which increases the overall cost of the project. This treated effluent is discharged at the end. Hence, fresh melt is required for every new batch. Thus the need to find suitable alternatives as solvents. Present study focuses on the following objectives:

1) To eliminate the use of $AlCl_3$ + NaCl melt, thereby using less reagents for the reaction
2) To reduce the reaction time of the reaction
3) To eliminate the generation of any effluent as well as its treatment.
4) To provide a cleaner and economical alternative to the existing process.

Chapter 2

Literature Survey

Ghani et.al. (2012) [9] tested the solubility of unsubstituted metal Phthalocyanines with various metal atoms such as Co, Cu, Fe, Mg, Mn, Sn, Zn and Ni in conventional solvents, ionic liquids and acids. They tested two ionic liquids: 1-ethyl-3-methylimidazolium acetate (STOR) and 1-ethyl-3-methylimidazolium ethyl sulphate (EMIM). They stated that the molar absorption coefficients of the metal Phthalocyanines derived from Q-band intensities were not reliable owing to low solubility (concentration $< 10^{-4}$ mol/kg). The maximum concentration Cmax (mol/kg) for STOR was $4.71*10^{-7}$ while that for EMIM were not reliable due to low solubility (concentration $<10^{-8}$ mol/kg) and low absorption .

Tshibangu et.al. (2011) [10] carried out the density viscosity and conductivity studies of [BMIm][Br]. For this, they synthesised and characterised the ionic liquid. Results showed that the density and viscosity reduced while conductivity increased with an increase in temperature. Also, the conductivity of [BMIm][Br] was found to be more than that of water. Addition of water/ ethanol increased the conductivity while addition of methanol/ acetone /acetonitrile decreased it.

Dharaskar et. al. (2013) [11] performed the extractive desulphurisation of liquid fuel using [BMIm][BF_4]. They synthesised [BMIm][BF_4] and carried out its characterisation by FTIR and NMR. Different ratios of model liquid to Ionic liquid were taken and the effects of reaction time, reaction temperature and S-compound on removal of sulphur were noted. For diesel, they attained S-removal of 55.8% for 1:1 mass ratio at 30°C for 30 minutes and single stage extraction. For gasoline, a removal of 70% was observed.

Holtzmann et.al. (US patent 2662085) [12] prepared chlorinated CuPC using 3 parts copper phthalocyanine, 41 parts chlorsulfonic acid,1.5 parts sulphur dichloride,0.15 parts antimony trichloride and chlorine gas. The product was found to contain 45.6% chlorine with a yield of 95%

Pavlinac et.al. (2009) [13] mentioned that Lee et.al. carried out chlorination of ketones in [BMIm][BF_4] in half an hour at room temperature; Laali et.al. chlorinated aryl trifluoro methyl sulphides in [BMIm][BF_4] in 5 minutes at room temperature.

Barraclough et.al. [14] produced phthalocyanine green by reacting 17 parts of copper phthalocyanine blue with 2 parts by volume chlorosulfonic acid in 60 parts nitrobenzene as solvent. S ulfuryl chloride was used as chlorinating agent while anhydrous iron chloride or zinc chloride was used as halogen transfer agent. The maximum temperature attained was 170^o C and the overall reaction time was 13 hours. This method yielded a 94% product with 15 chlorine atoms per molecule.

Geeren et.al. [15] synthesised polychloro copper phthalocyanine by reacting 600 kg copper phthalocyanine with chlorine gas entering at 100 kg/hr. 1800 kg Aluminium chloride was used as halogen transfer agent. Sodium chloride in 25% wt ratio was also used. The reaction time was much longer of about 18 hours with the temperature being 180^{o}C. 50% weight chlorine was found in the product.

Matsuura et.al. [16] demonstrated a process for producing highly chlorinated CuPC by using a primary catalyst sulphur monochloride and an auxiliary catalyst like iodine chloride in chlorosulfonic acid as solvent. Chlorine gas was used as a chlorinating agent and was fed at 3 kg/cm2 pressure. The reaction was conducted at low temperature of 100^{o}C and at a lower reaction time of 8 hours. A brilliant yellowish green crude product was obtained in 98% yield.

Wessling et.al. [17] produced chlorinated CuPC by reacting CuPC with chlorine gas in sulfuryl chloride solvent. Aluminium chloride and sodium chloride were also used. Substitution of sodium chloride with potassium chloride or sodium bromide also yielded the same results. The reaction time was significantly high of about 20 hours. The product constituted 49% of chlorine by weight.

Stewart et.al. [18] devised a way for halogenating phthalocyanines in pyrosulfuryl acid using chlorine gas with the halogen transferring agent being aluminium chloride and sodium chloride. The reaction temperature was 200^{o}C and time being 7 hours. The product constituted 47% by weight chlorine and was readily dispersible in any organic media. In another attempt, chlorination was performed using sulfuryl chloride as a solvent with sulphur monochloride being the halogenating agent. The reaction was performed in 6 hours at 160^{o}C. The chlorinated product comprised 14.5 chlorine atoms per molecule but was free from any combined sulphur.

Pepoy et. al.[19] performed chlorination of 1 part CuPC in 10 parts sulfuryl chloride using 3 parts aluminium chloride and 0.5 part cuprous chloride. The reaction was carried at 10 bar pressure with the time varied between 1-5 hours at maximum pressure. The yield of the product was 98% with 12.5 atoms substituted.

Caliezi et.al.[20] chlorinated CuPC in chlorosulfonic acid with aluminium chlo-

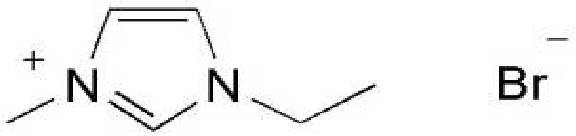


Figure 2.1: Structure of [BMIm][Br]

ride and sodium chloride at 160°C for 6 hours with pure green pigment product of 49% by weight chlorine.

Randall et. al [21] demonstrated chlorination of CuPC in sulfuryl chloride with chlorine gas and aluminium chloride. Hydrochloric acid was also used for this process which was performed at 180°C for 4 hours. The final product had a yellow trace and a darker tone and constituted 48.6% chlorine by weight.

Segawa et.al. [22] successfully chlorinated copper phthalocyanine blue using the catalysts iodine and sulphur monochloride. 1,1,2,2-tetrachloroethane containing 3 weight % chlorosulfonic acid was used as solvent. Chlorine acid was used as chlorinating agent and 2% aqueous sulphuric acid was added to the solvent. The reaction was carried out at 140°C temperature for 10 hours at 5 kg/cm^2 gauge pressure. The product obtained was yellowish green crude with a yield of 100% and 14.8 chlorine atoms per molecule.

2.1 Selection of Ionic Liquids

Based on the literature review, we have chosen two ionic liquids. These particular ionic liquids have been chosen as they have been highly exploited. Looking at the procedure of experimentation, we have chosen the ionic liquids [BMIm][Br] [BMIm][BF_4] which are hydrophilic in nature.

2.2 1-butyl-3-methylimidazolium bromide, [BMIm][Br]

2.2.1 Structure

Figure 2.1 shows structure of [BMIm][Br]

2.2.2 Identification

Also known as [BMIm][Br], 1-Butyl-3-methylimidazolium bromide. Its chemical formula is $C_8H_{15}N_2Br$ and the CAS number is 85100-77-2. It is also irritant to eyes and skin.

Table 2.1: Properties of [BMIm][Br]

Formula	C_8 H_{15} N_2Br
Molecular weight	219.12
Glass transition temperature	-65 ^{0}C (208 K)
Refractive index	1.42 (298.15K)
Specific density (Kg/m^3)	1298 (298.15K)
Viscosity (Pa.s)	0.23 (293.15K)

2.2.3 Physical and chemical properties

- Physical state: Solid
- Density: 1.298(g/cc)
- Melting point/range: 75°C to 78°C
- Boiling point/range: Not available
- Vapour pressure: Not available
- Flash point: Not available
- Soluble in water, acetonitrile and methanol.
- Appearance: colourless to yellow viscous liquid, no characteristic odour.

Some more properties of [BMIm][Br] are shown in Table 2.1

2.2.4 Stability and reactivity

No particular stability concerns are found. Also, no data is available on materials to be avoided when using this substance. Contact should be avoided with strong oxidizers and bases. High temperatures generate corrosive gases/fumes of CO_2, carbon monoxide (CO), NO_x etc.

2.2.5 Toxicological information

Data on toxicity of this product are not available.

2.2.6 Uses

[BMIm][Br] is used as a solvent and reaction media. It is also used for the synthesis of [BMIm][BF_4]

2.3 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIm][BF_4]

2.3.1 Structure

Figure 2.2 shows structure of [BMIm][BF_4]

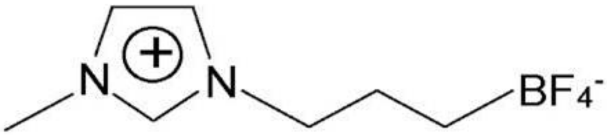


Figure 2.2: Structure of [BMIm][BF_4]

Table 2.2: Properties of [BMIm][BF_4]

Formula	C_8 H_{15} BF_4 N_2
Molecular weight	226.03
Glass transition temperature (K)	176.1
Heat capacity at constant pressure (J/(mol K))	364.71(298.15K)
Refractive index	1.42 (298.15K)
Specific density (kg/m^3)	1120 (298.15K)
Speed in sound (m/s)	1570.23 (100kPa, 293.15K)
Thermal conductivity (W/(m K))	0.186 (300K)
Viscosity (Pa.s)	0.154 (293.15K)

2.3.2 Identification

Also known as [BMIm] [BF_4], 1-Butyl-3-methyl-1H-imidazolium tetrafluoroborate. Its Chemical formula is $C_8H_{15}N_2$ BF_4 and CAS number 174501-65-6. It is harmful if swallowed and is irritant to eyes. The NFPA rating on a scale of 0-4 for health is 2; fire is 1 and instability is 0.

2.3.3 Physical and chemical properties

- Physical state: Liquid [23]
- Density: 1.22 [23]
- Melting point/range: -71°C to -75°C [23]
- Boiling point/range: Not available [23]
- Vapour pressure: Not available [23]
- Flash point: Not available [23]
- Soluble in water but insoluble in most common organic solvents [23]
- Appearance: Colourless to yellow viscous liquid, no characteristic odour [23]

Some more properties of [BMIm][BF_4] are stated in Table 2.2 [23]

2.3.4 Stability and reactivity

It is stable at normal conditions. No data is available on particular materials that are to be avoided with its usage. Also, no data is available on the conditions to be avoided. Its hazardous polymerization will not occur but at the same time, no data is available on any hazardous decomposition products.

2.3.5 Toxicological information

Acute toxicity:

- Oral LD_{50} for rat : 300 - 500 mg/Kg
- Dermal LD_{50} for rat : 2000 mg/Kg
- Dermal irritation for rabbit: Not irritant
- Eye irritation for rabbit: Mild irritant
- Effects of overexposure: Irritant to eyes

Chronic toxicity: No data available

2.3.6 Uses

[BMIm][BF_4] is used in many different fields, for example, in chromatography, chemical synthesis, enzyme media or biological catalyst [24]. This material is intended primarily for use as a solvent in the Pharmaceutical and other Fine Chemical Industries.

2.3.7 Mixture of [BMIm][BF_4] in water

The most important effects are summarized below:

- Significant cation-cation aggregation
- C-H→F hydrogen bonds cause ion pairing
- Water acts as hydrogen bond competitor: C-H→F, so the cation-cation interactions are progressively replaced.

2.4 Relative solubilities of Copper Phthalocyanine in various solvents

Table 2.3 shows copper phthalocyanine solubilities in various solvents

2.5 Advantage

CuPC is hardly soluble in any of the solvents as shown in Figure 2.3. A normal Q-band is observed in the spectra of CuPC dissolved in conventional solvents. CuPC only dissolves in one of the ionic liquids, STOR, although with a very low concentration and with a somewhat distorted spectrum. It dissolves with high concentrations

Table 2.3: Relative solubilities of Copper Phthalocyanine

Solvent	Solubility	Reference
Trifluoroacetic acid	$2*10^{-3}$ (mol/kg)	[11]
[EMIm][Ac]	$4.71*10^{-7}$(mol/kg)	[11]
Anisole	$4.57*10^{-7}$(mol/kg)	[11]
Benzene	$2.61*10^{-7}$(mol/kg)	[11]
Dioxane	$4.42*10^{-7}$(mol/kg)	[11]
Tetrahydrofuran	$9.1*10^{-6}$ (mol/kg)	[11]

only in TFA where it becomes protonated and new bands appear in the absorption spectrum [25]

Figure 2.3 shows maximum concentration of CuPC in different solutions (left) and their corresponding normalised Q-band spectra (right)

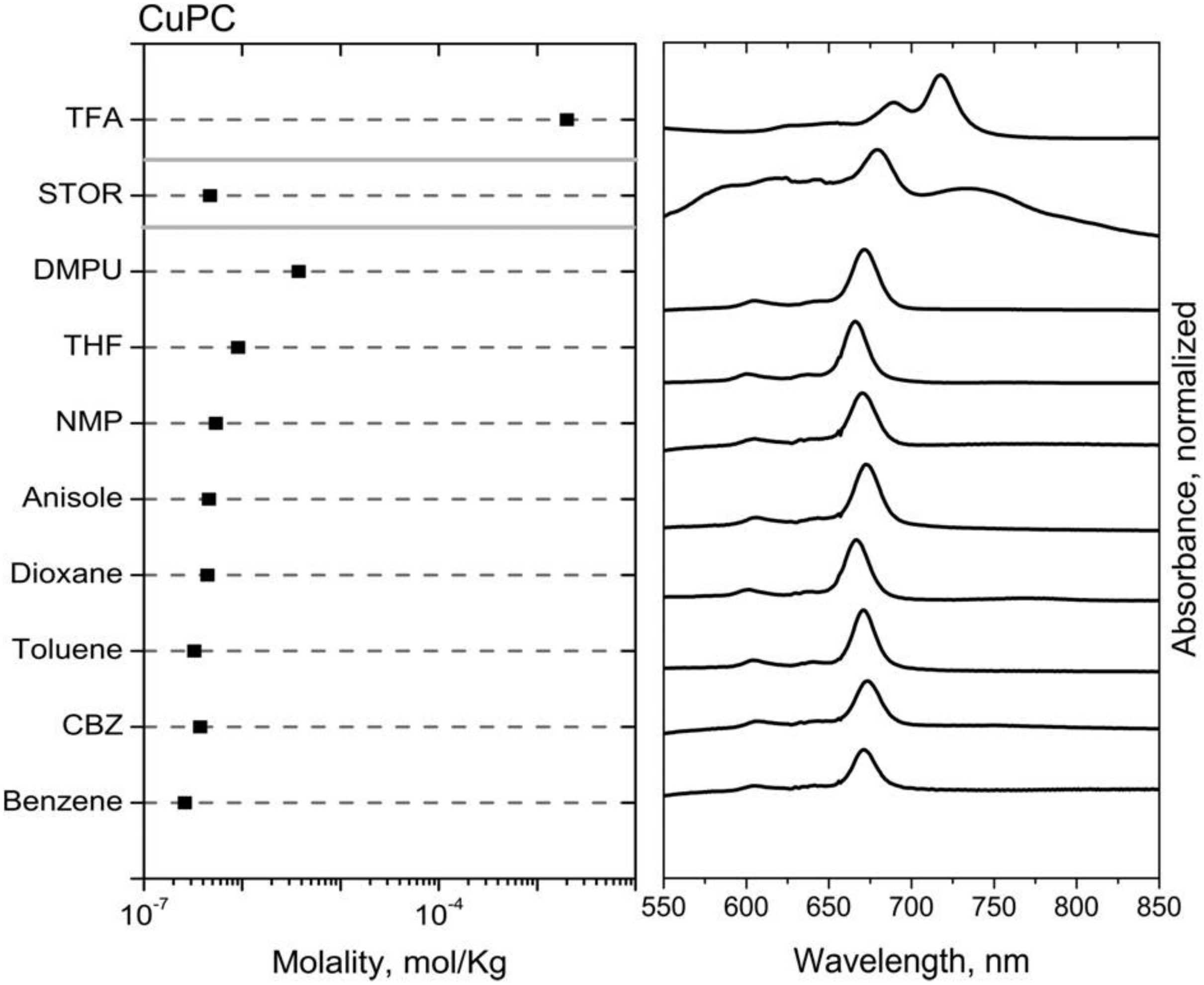


Figure 2.3: Maximum concentration of CuPC in different solutions

Chapter 3

Materials and Methods

3.1 Chemicals for synthesising ionic liquids

1-bromobutane (500 gm, LR, National Chemicals), 1-methyl imidazole (500 gm, Spectrochem), ethyl acetate (500 ml, LR, Rankem), acetone (500 ml, LR, Rankem), Sodium tetrafluoroborate (500 gm, Spectrochem) have been used as supplied.

3.2 Chemicals for chlorination

Freshly prepared ionic liquids [BMIm][Br] and [BMIm][BF_4], cupric chloride ($CuCl_2$), 15.1 CuPC blue, $AlCl_3$ and molecular chlorine gas have been used. These were procured from plant itself.

3.3 Chlorination set-up

Figure 3.1 shows chlorination set-up. It consists of a 500 ml beaker (Schott-Duran) equipped with a glass stirrer and Teflon agitator. The set-up has an arrangement to pass the HCl vapours formed into a scrubbing solution of NaOH. The beaker is kept in a heating mantle having a temperature range upto 250^o C. An inlet continuously supplies demoistened chlorine gas.

3.4 Experimental Procedure

Each experiment was carried out in a round bottom flask at temperatures above 100^{o}C. The reactants were added in stoichiometric proportions on the basis of preliminary studies and the observations were recorded at 15 minute time intervals. Chlorine was added through a sparger. It was demoisturised first to ensure no moisture content, as that would lead to the formation of HCl gas during process. As chlorine

Figure 3.1: Chlorination setup

gas is hazardous to health and also irritant, all due precautions are taken during its usage. The heating was controlled with a heating mantle. The agitator speed was kept around 200 RPM during all experiments.

3.4.1 Synthesis of 1-butyl-3-methyl-imidazolium bromide

1) 1.25 moles of 1-bromobutane are added to 1 mole of 1-methyl imidazole maintained at 0°C over a period of 30 minutes under vigorous stirring.
2) The flask is then covered with aluminium foil and the ice bath is maintained for 4 hours after which it is allowed to melt to room temperature.
3) The mixture is then stirred for 3 days at 40°C until there is formation of two phases.
4) The upper phase contains the unreacted reagents which is decanted.
5) Ethyl acetate, about half the volume of the lower phase is added under comprehensive stirring. Washing with ethyl acetate is carried out thrice with intermediate decantation.
6) Any remaining ethyl acetate is removed by heating the solution to 70°C and stirring to room temperature [10].
7) On carrying out the experiment, we obtained 78 ml of [BMIm][Br] after vacuum filtration.
8) The ionic liquid was characterised with FT-IR spectra analysis.

The process of replacing one anion with another anion is called ‘anion metathesis’. [BMIm][BF_4] is synthesised using the same.

3.4.2 Synthesis of 1-butyl-3-methyl-imidazolium tetrafluoroborate

1) Equimolar composition of [BMIm][Br] and $NaBF_4$ are added to a definite amount of acetone (used as a solvent).
2) The reaction mixture is stirred vigorously for 10 hours at 400°C.
3) The precipitate obtained is vacuum filtered and removed.
4) The filtrate is washed with Dichloromethane to remove any impurities.
5) It is then heated in an oven for 2 hours at 80°C to remove dichloromethane [11].
6) The ionic liquid was characterised with FT-IR spectra analysis.

3.4.3 Chlorination with ionic liquids

The process for chlorinating Copper Phthalocyanine using chlorine gas was as follows[12]:

1) Dissolution of CuPC in ionic liquid: The ionic liquid and CuPC were stirred together for sufficient time.
2) Increase the temperature to above 100°Celsius: The dissolution increased when the temperature is elevated above 100°Celsius. A higher temperature favours chlorination.
3) Add chlorine gas: Chlorine gas was then bubbled through the solution.
4) Carry out the reaction until required chlorination: Take intermediate samples on a plate and observe the greenness of the sample. Chlorination should be done until required greenness is induced.
5) Cool the reaction mass: The reaction mass is then cooled to 60°Celsius
6) Drown in water: The entire mass is then drowned in water where copper phthalocyanine precipitates out.
7) Filter: The separated CuPC was then filtered
8) Washing: It was then washed with water.
9) Dry: Drying wasdone in an oven.
10) Recycling of the ionic liquid. After filtering out CuPC, the hydrophilic ionic liquid and water shall be left behind as a mixture. These were separated using normal distillation operation whereby water was recovered as a distillate. The ionic liquid was removed from the bottoms due to its non-volatile nature.

3.5 Analytical Procedure

Fourier Transform Infrared Spectroscopy (FT-IR): After the synthesis of ionic liquids, the functional groups were determined by FT-IR spectrometer (Spectrum One^{TM}, Perkin Elmer, USA) using KBr pellet method. Spectra was recorded over the range of 600-4000 cm^{-1} wavenumber having 4 cm^{-1} resolution.

Nuclear Magnetic Resonance Spectroscopy (NMR): Samples were analysed using a Varian, USA Mercury Plus 300 MHz NMR spectrometer. ^{1}H NMR spectra was obtained on this instrument using a $CDCl_3$ solvent.

Chapter 4

Results and Discussions

4.1 Characterisation of synthesised ionic liquids

FTIR and NMR spectroscopy techniques were used for characterisation.

4.1.1 4.1.1 FT-IR spectra analysis of [BMIm][Br]

Figure 4.1 shows the FT-IR graph

FT-IR analysis (Transmission against Wavelength, v/cm^{-1}) of neat liquid gave the following result:

Br (3426.397 cm^{-1}), aliphatic C-H stretch (2955 cm^{-1}), imidazolium ring stretch (1570.786 cm^{-1}), imidazolium H-C-C and H-C-N bending (1167.836 cm^{-1}), out of plane imidazolium ring bending (757.2194 cm^{-1}), imidazole C-N-C bending (621.0546 cm^{-1}). This spectrum conforms with the literature [25].

4.1.2 NMR spectra analysis of [BMIm][Br]

Following figure 4.2 shows ^{1}H-NMR spectra of [BMIm][Br]. This spectrum conforms with the standard spectrum on ChemBioOffice 14 software.

4.1.3 FT-IR spectra analysis of [BMIm][BF$_4$]

Figure 4.3 shows the FT-IR graph

FT-IR analysis (Transmission against Wavelength, v/cm^{-1}) of neat liquid gave the following result:

Aliphatic asymmetric C-H stretching vibration (2978.095 cm^{-1}), Aliphatic symmetric C-H stretching vibration (2840 cm^{-1}), in-plane bending vibration due to methyl group (1170 and 1158.02 cm^{-1}), C=C stretching (1655 cm^{-1}), C-N stretching vibration (618.755 cm^{-1}) .This spectrum conforms with the literature [11].

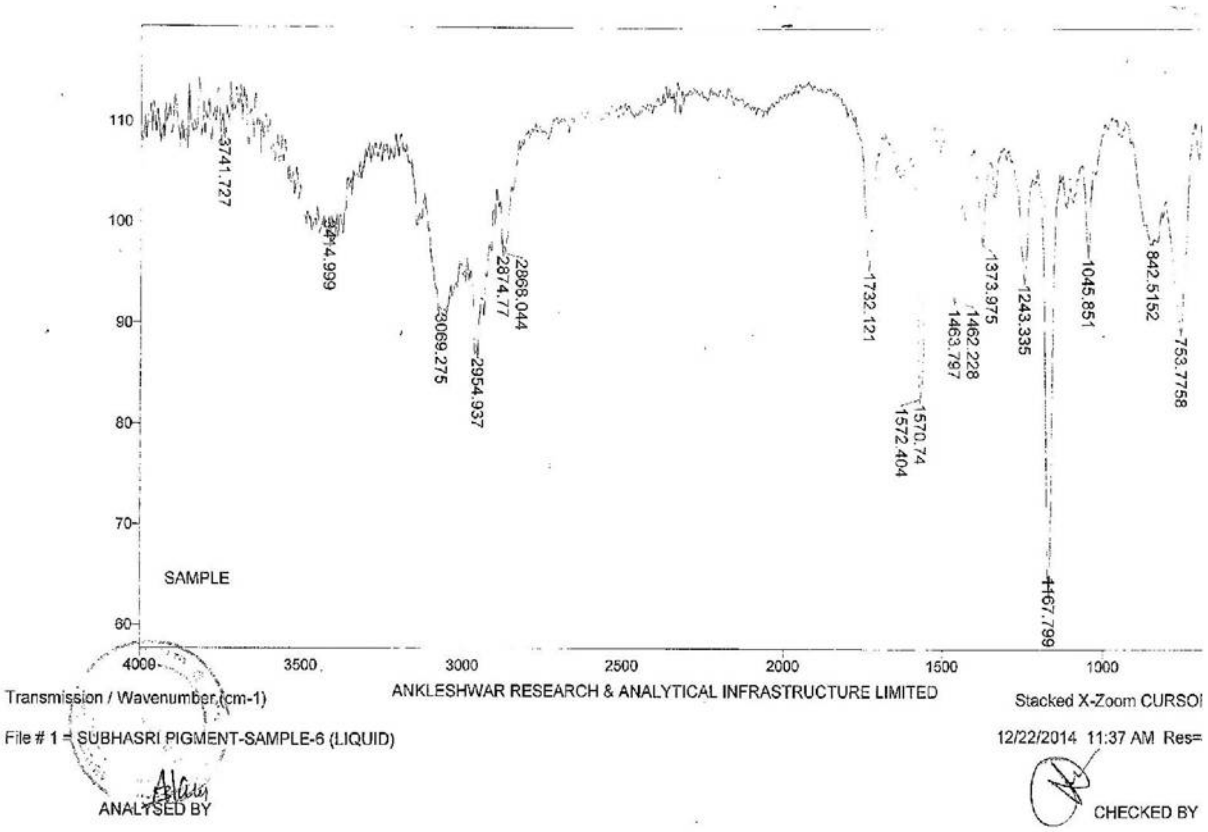
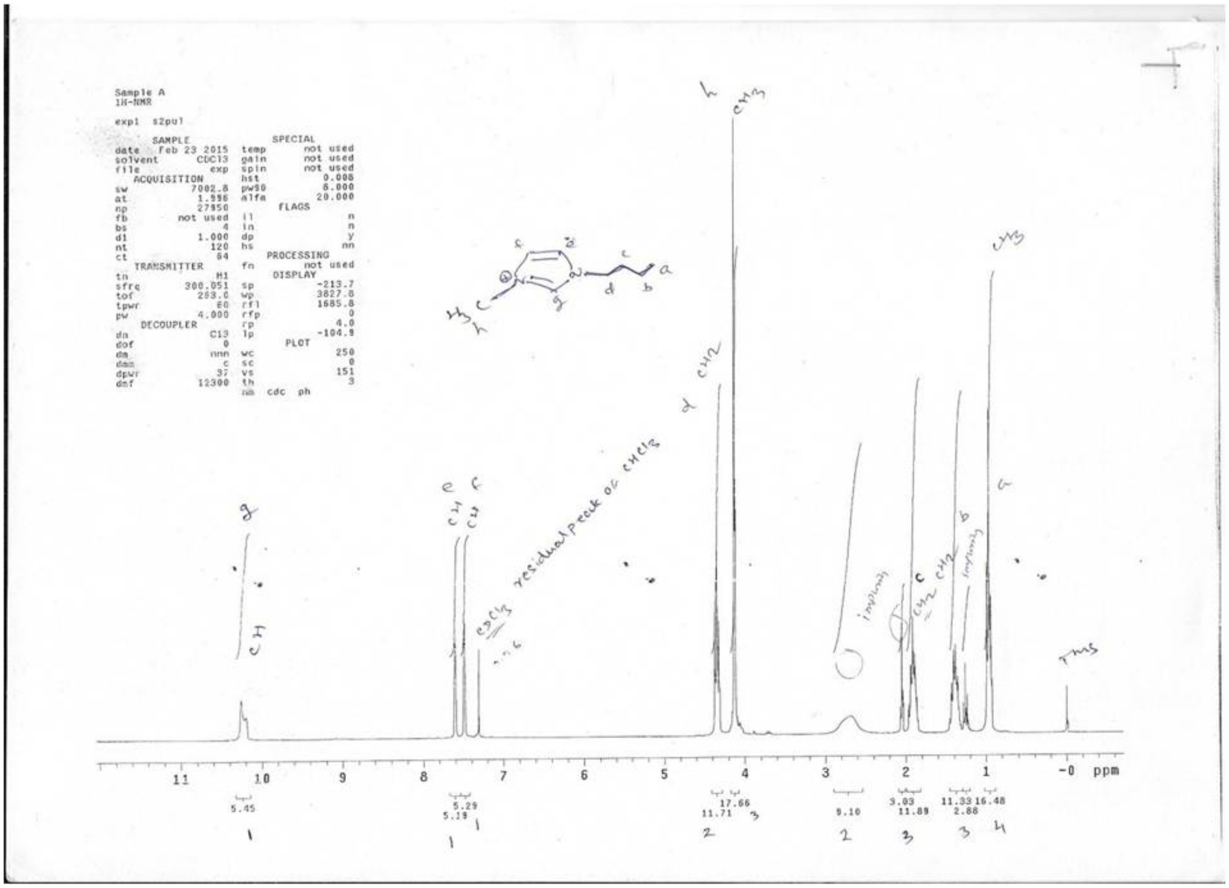


Figure 4.1: FTIR spectrum of [BMIm][Br]



```
Sample A
1H-NMR

exp1  s2pul

     SAMPLE                   SPECIAL
date   Feb 23 2015  temp        not used
solvent       CDCl3  gain        not used
file            exp  spin        not used
   ACQUISITION       hst            0.008
sw           7002.8  pw90           8.000
at            1.996  alfa          20.000
np            27950        FLAGS
fb         not used  il                 n
bs                4  in                 n
d1            1.000  dp                 y
nt              120  hs                nn
ct               64       PROCESSING
   TRANSMITTER       fn          not used
tn               H1        DISPLAY
sfrq        300.051  sp            -213.7
tof           283.0  wp            3827.8
tpwr             60  rfl           1685.8
pw            4.000  rfp                0
    DECOUPLER        rp               4.0
dn              C13  lp            -104.9
dof               0          PLOT
dm              nnn  wc               250
dmm               c  sc                 0
dpwr             37  vs               151
dmf           12300  th                 3
                     nm   cdc   ph
```

Figure 4.2: NMR spectrum of [BMIm][Br]

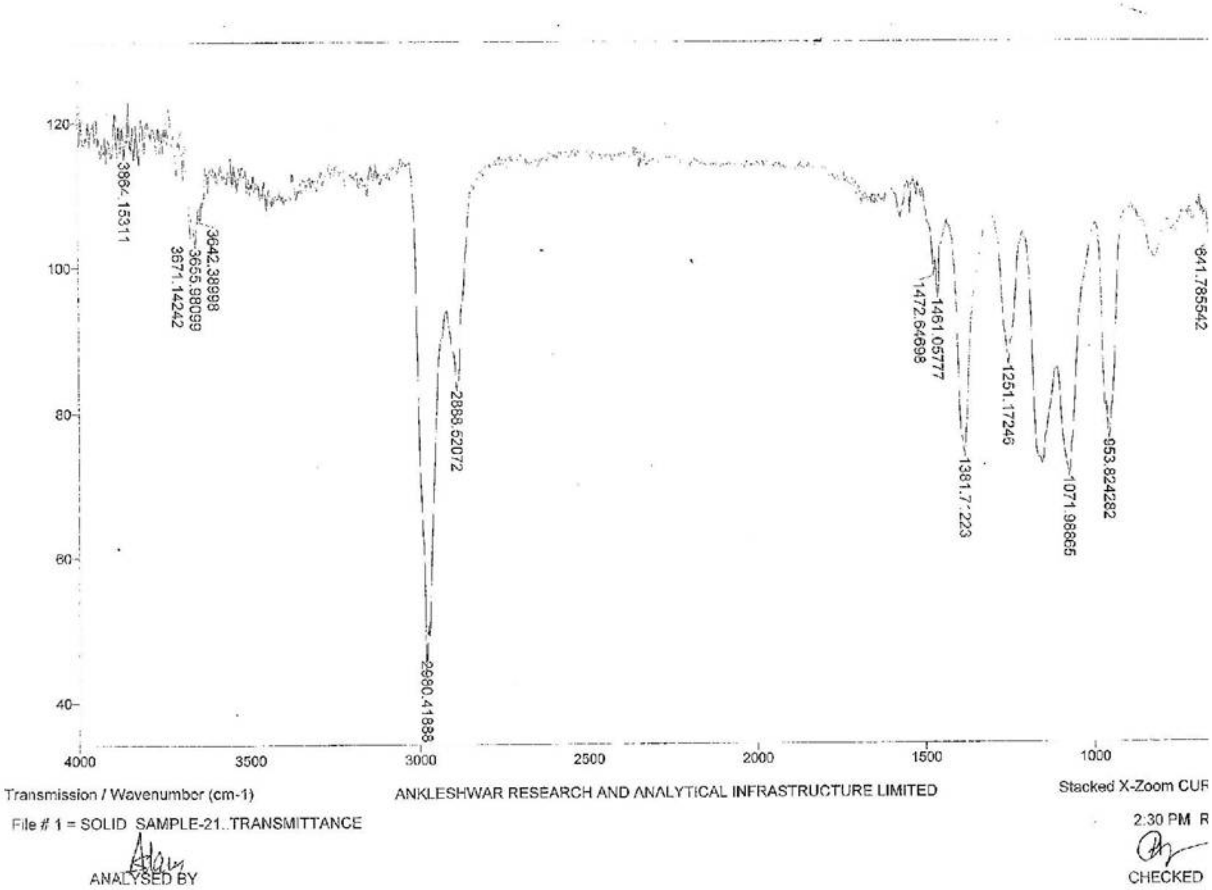
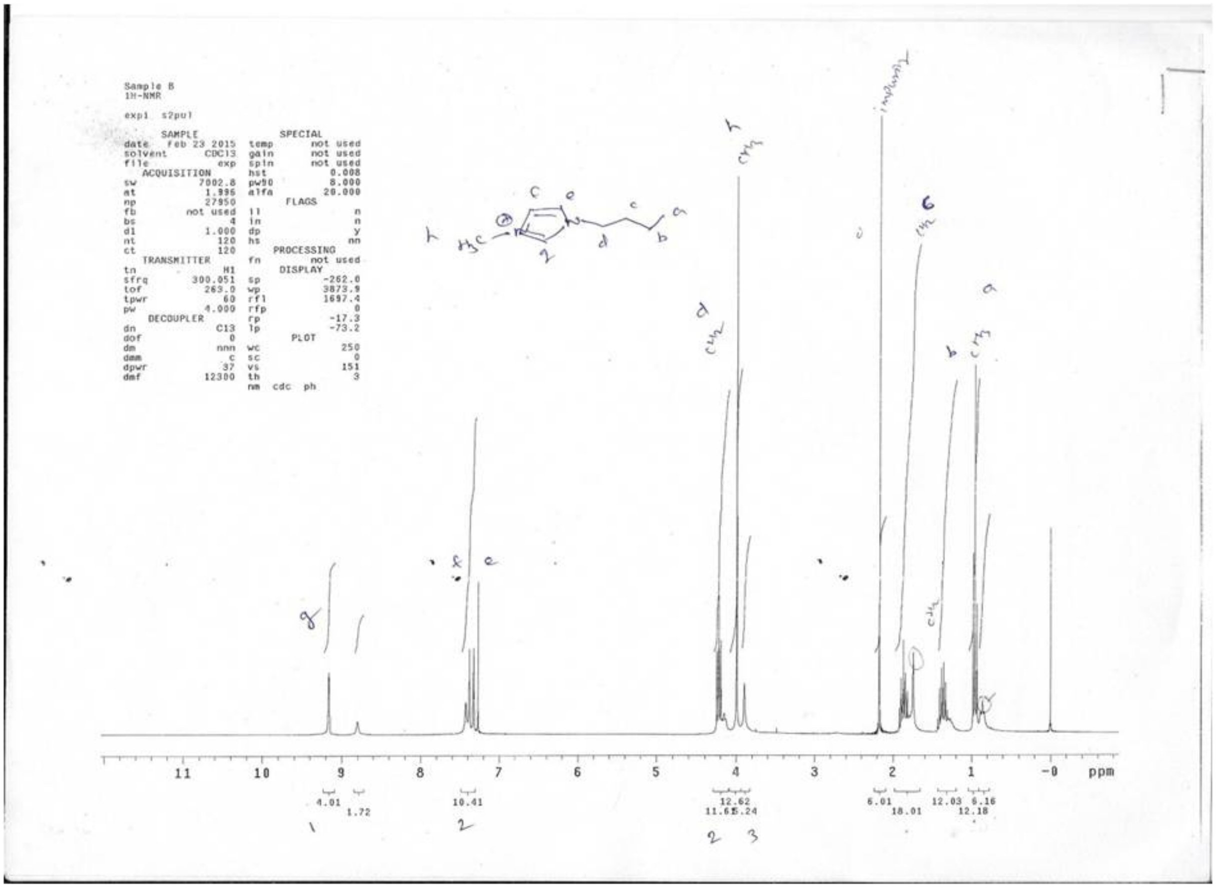


Figure 4.3: FTIR spectrum of [BMIm][BF_4]



```
Sample B
1H-NMR

expl  s2pul

      SAMPLE               SPECIAL
date   Feb 23 2015   temp        not used
solvent      CDCl3   gain        not used
file           exp   spin        not used
   ACQUISITION       hst            0.008
sw          7002.8   pw90           8.000
at           1.996   alfa          20.000
np           27950          FLAGS
fb        not used   il                 n
bs               4   in                 n
d1           1.000   dp                 y
nt             120   hs                nn
ct             120        PROCESSING
   TRANSMITTER       fn          not used
tn              H1          DISPLAY
sfrq       300.051   sp            -262.0
tof          263.0   wp            3873.9
tpwr            60   rfl           1697.4
pw           4.000   rfp                0
    DECOUPLER        rp             -17.3
dn             C13   lp             -73.2
dof              0           PLOT
dm             nnn   wc               250
dmm              c   sc                 0
dpwr            37   vs               151
dmf          12300   th                 3
                     nm  cdc  ph
```

Figure 4.4: NMR spectrum of [BMIm][BF_4]

Table 4.1: Stoichiometry of trial 1 with [BMIm][Br]

Quantities	[BMIm][Br]	CuPC blue	$CuCl_2$
Theoretical	233.64 g (180 ml)	11.6828 g	0.5982 g
Practical	233.64 g (180 ml)	11.683 g	0.5982 g

4.1.4 NMR spectra analysis of [BMIm][BF_4]

Figure 4.4 shows ^{1}H-NMR spectra of [BMIm][BF_4]. This spectra conforms with available literature [11]

4.2 Chlorination with [BMIm][Br]

4.2.1 Trial 1

Figure 4.5, 4.6 and 4.7 shows the relevant graphs.

The batch process was performed for longer time interval (10 hrs) and at higher temperature (170°C). This was done with a view to provide sufficient contact time for the chlorine gas to impart green colour to CuPC blue sample. The mean RPM

Table 4.2: Reaction details of Trial 1 with [BMIm][Br]

Time (t, min)	Temperature (T, °C)	RPM	Chlorine rate (L/hr)
0	26	220	-
15	42	218	-
30	65	220	0.35
45	40	216	0.35
60	60	218	0.40
75	100	216	0.40
90	120	218	0.35
105	140	220	0.40
120	170	222	0.40
135	172	220	0.40
150	173	220	0.40
165	173	222	0.35
180	173	220	0.35
195	175	220	0.40
210	175	220	0.40
225	175	218	0.40
240	175	220	0.40
255	175	222	0.35
270	175	222	0.35
285	175	220	0.35
300	175	220	0.35
315	175	222	0.35
330	175	220	0.40
345	175	219	0.40
360	175	218	0.40
375	175	218	0.35
390	175	218	0.40
405	175	220	0.40
420	175	220	0.40
435	175	218	0.35
450	175	220	0.35
465	175	220	0.35
480	175	220	0.35
495	175	218	0.35
510	175	222	0.40
525	175	220	0.35
540	175	219	0.40
555	175	219	0.35
570	175	219	0.35
585	175	220	0.40
600	175	220	0.35
	Mean T = 170	Mean RPM = 220	Mean flow = 0.37

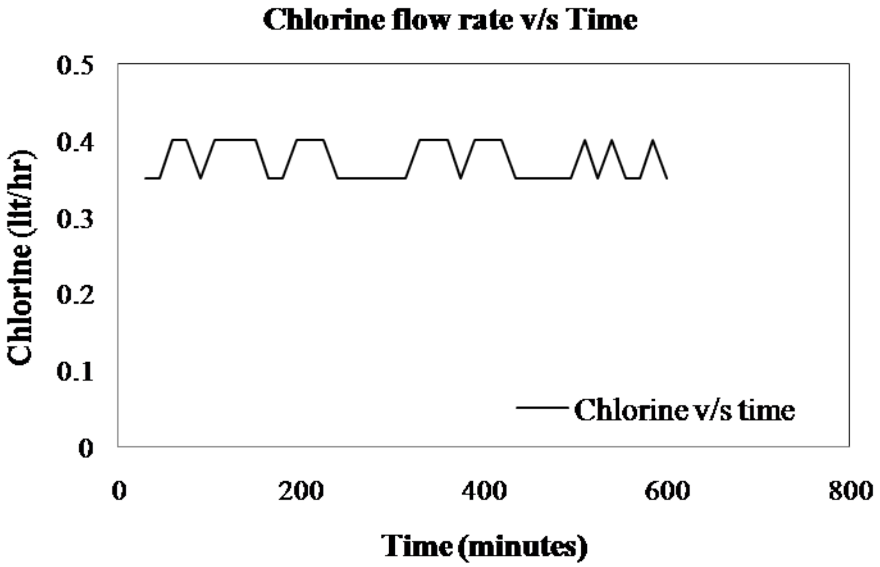


Figure 4.5: Chlorine flow rate v/s Time for trial 1 with [BMIm][Br]

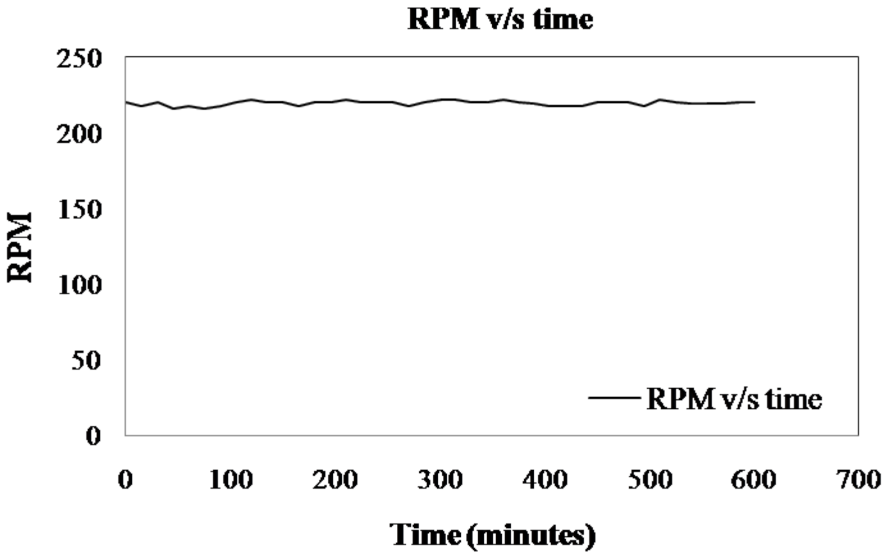


Figure 4.6: RPM v/s Time for trial 1 with [BMIm][Br]

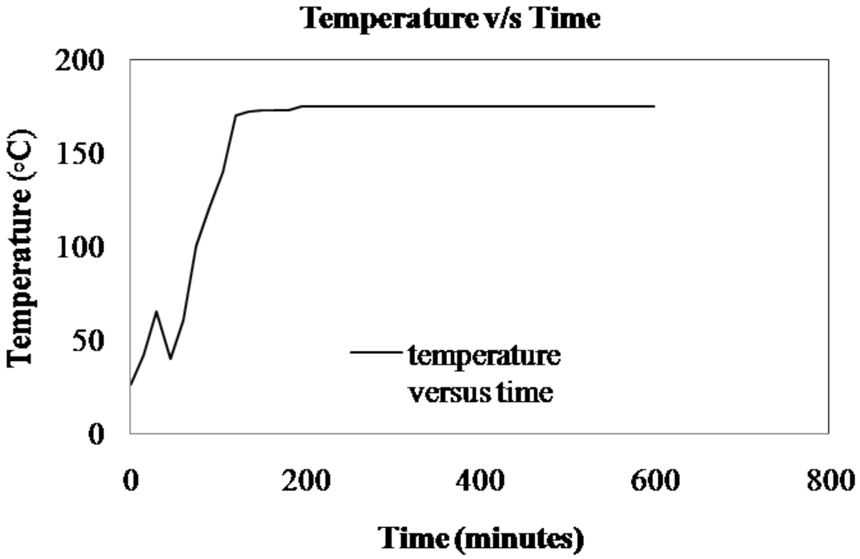


Figure 4.7: Temperature v/s Time for trial 1 with [BMIm][Br]

Table 4.3: Stoichiometry of trial 2 with [BMIm][Br]

Quantities	[BMIm][Br]	CuPC blue	$CuCl_2$
Theoretical	246.62 g (190 ml)	12.3310 g	0.6165 g
Practical	246.62 g (190 ml)	12.3310 g	0.6166 g

was maintained at 220 and mean flow at 0.37 litres/hr. The total chlorine that was introduced into the system was around 3.5 litres. The product obtained was not green in colour (as initially expected) but was bluish-black in appearance. Figure 4.8 shows sample after chlorination with [BMIm][Br].

4.2.2 Trial 2

Figure 4.9, 4.10, 4.11 shows the relevant graphs.

The batch process was performed for a time interval of 4 hrs and at a higher temperature (170°C). The earlier experiment was performed for 10 hrs which did not yield the expected results. Hence, the reaction time was lowered to 4 hours. The mean RPM was maintained at 216 and mean higher chlorine flow rate (0.95 litres/hr). The total chlorine that entered the system was about 3.3 litres. The obtained product was blue in colour. Figure 4.12 shows sample after chlorination with [BMIm][Br]

4.2.3 Trial 3

Figures 4.13,4.14 and 4.15 show the relevant graphs.

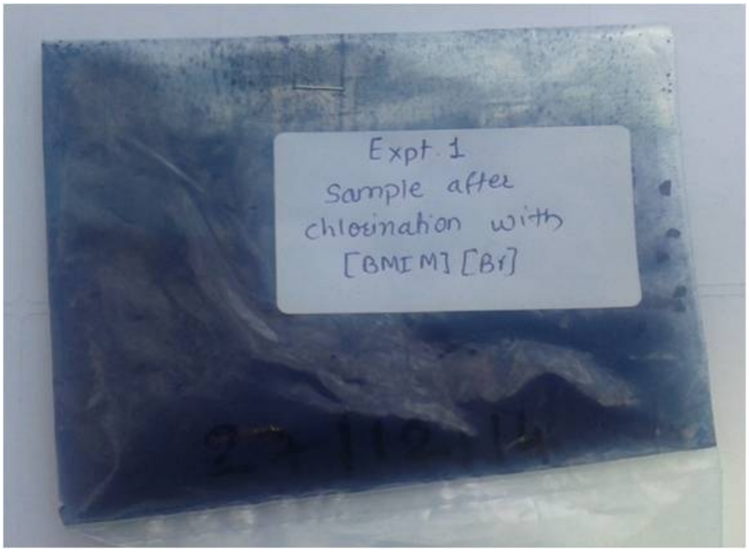


Figure 4.8: Sample 1 after chlorination with [BMIm][Br]

Table 4.4: Reaction Details of trial 2 with [BMIm][Br]

Time (t, min)	Temperature (T,°C)	RPM	Chlorine rate (L/hr)
0	26	219	-
15	110	210	-
30	148	208	0.75
45	160	212	0.80
60	175	212	0.75
75	178	213	0.75
90	179	210	0.95
105	178	212	0.95
120	190	219	0.95
135	173	221	1.10
150	171	218	1.00
165	170	220	0.85
180	180	221	1.10
195	168	216	1.00
210	180	220	0.95
225	181	220	1.10
240	178	220	1.10
	Mean temp = 170	Mean RPM = 216	Mean Flow = 0.95

Table 4.5: Stoichiometry of trial 3 with [BMIm][Br]

Quantities	[BMIm][Br]	CuPC blue	$CuCl_2$
Theoretical	343.97 g (265 ml)	17.1985 g	0.8599 g
Practical	343.97 g (265 ml)	17.1986 g	0.8600 g

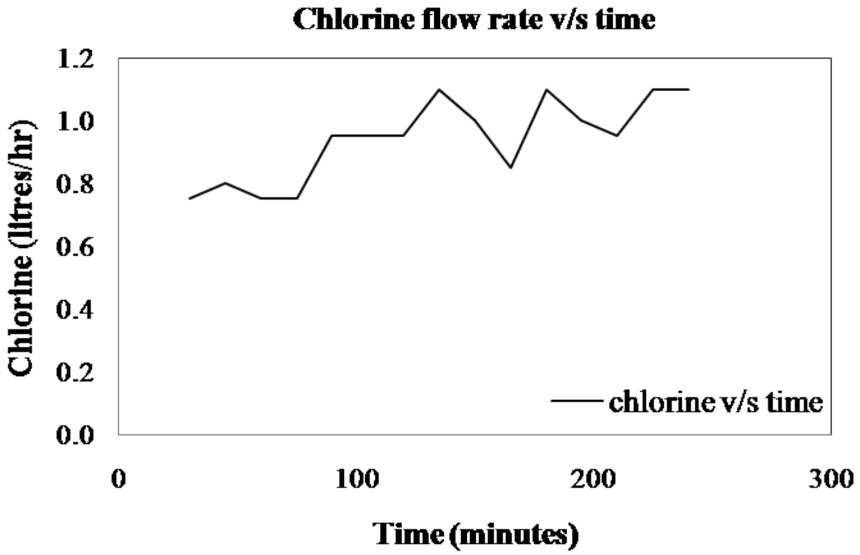


Figure 4.9: Chlorine flow rate v/s time for trial 2 with [BMIm][Br]

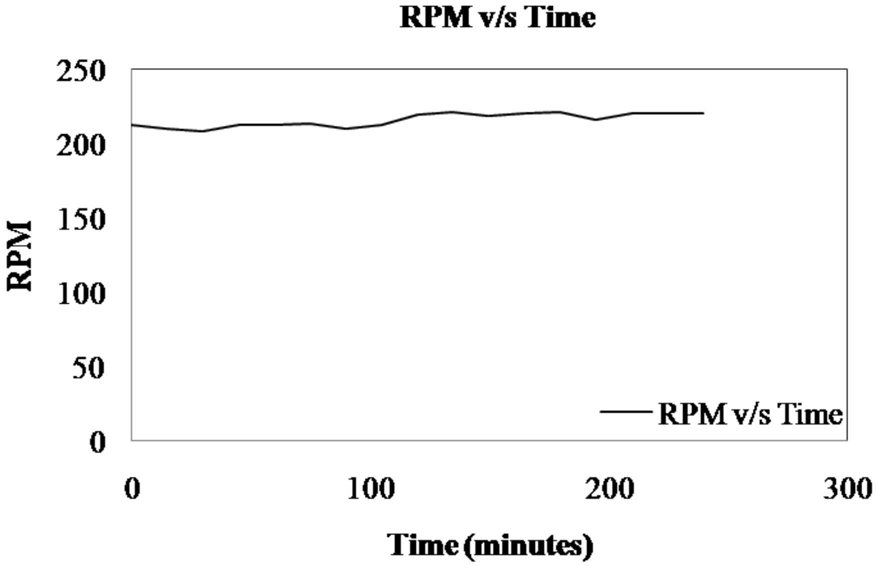


Figure 4.10: RPM v/s Time for trial 2 with [BMIm][Br]

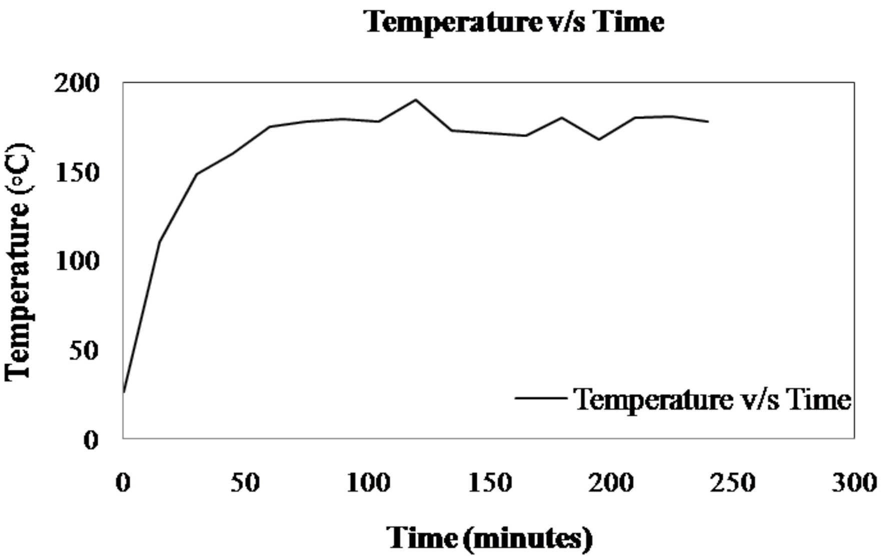


Figure 4.11: Temperature v/s Time for trial 2 with [BMIm][Br]

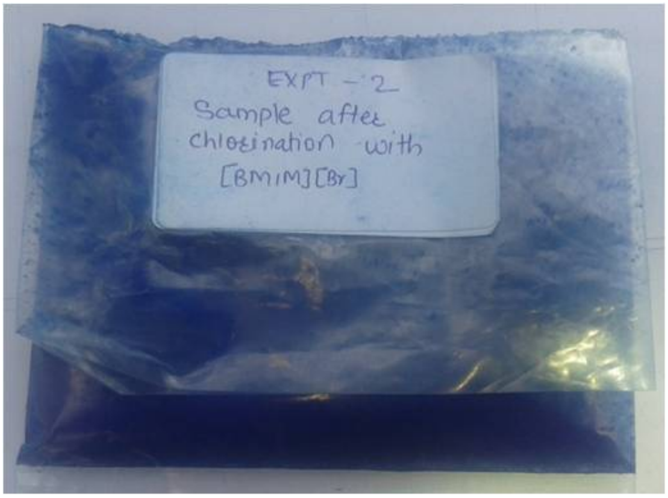


Figure 4.12: Sample 2 after chlorination with [BMIm][Br]

Table 4.6: Reaction Details of trial 3 with [BMIm][Br]

Time (t, min)	Temperature (T,ºC)	RPM	Chlorine rate (L/hr)
0	26	200	-
15	100	206	-
30	138	212	0.95
45	165	210	0.80
60	170	212	1.00
75	168	220	0.95
90	173	202	1.10
105	174	216	0.85
120	166\8	212	0.75
135	168	208	1.10
150	172	207	0.65
165	171	208	0.75
180	175	211	1.00
195	168	210	0.80
210	180	212	0.95
	Mean temp = 164	Mean RPM = 210	Mean flow = 0.90

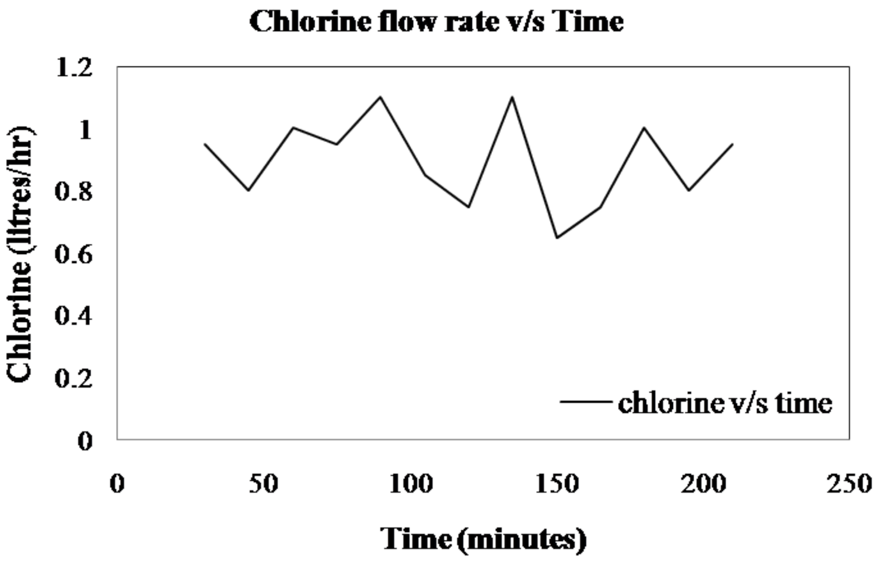


Figure 4.13: Chlorine flow rate v/s time for trial 3 with [BMIm][Br]

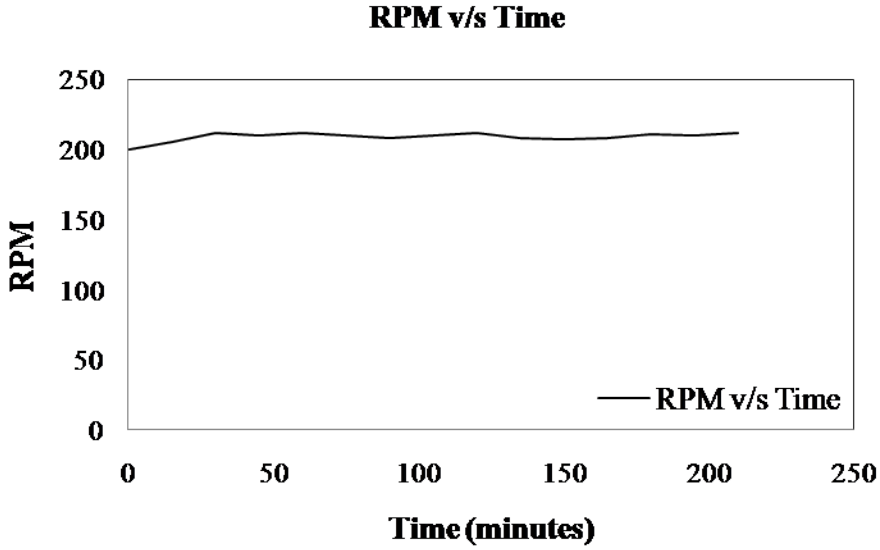


Figure 4.14: RPM v/s Time for trial 3 with [BMIm][Br]

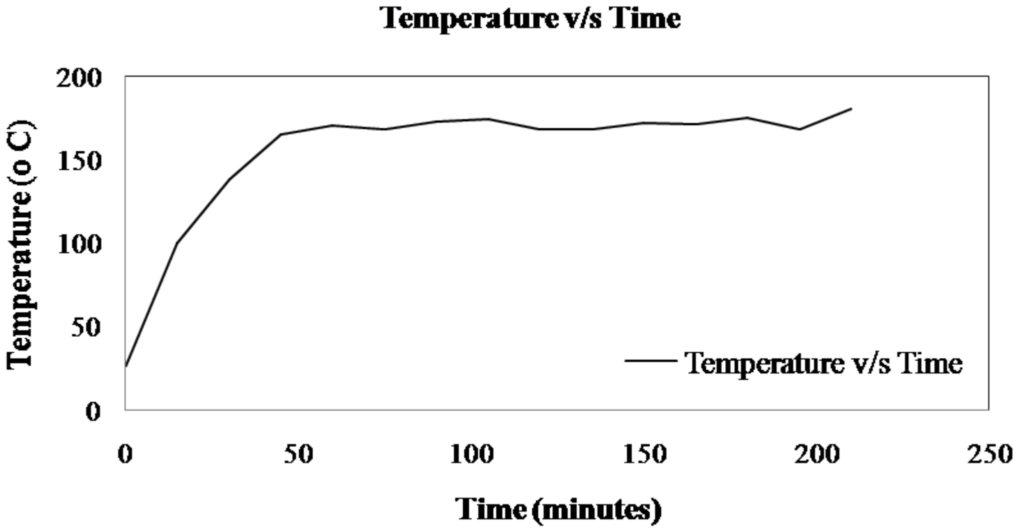


Figure 4.15: Temperature v/s Time for trial 3 with [BMIm][Br]

Figure 4.16: Sample 3 after chlorination with [BMIm][Br]

Table 4.7: Stoichiometry of trial 4 with [BMIm][Br]

Quantities	[BMIm][Br]	CuPC blue	$CuCl_2$
Theoretical	233.64 g (180 ml)	11.6820 g	0.5982 g
Practical	233.64 g (180 ml)	11.6823 g	0.5990 g

The batch process was performed with more stoichiometric quantities of the reactants. The time duration for the process was 3.5 hrs and at moderate temperature (164°C). The mean RPM was maintained at 210 and mean flow rate at 0.9 litres/hr of chlorine. The total chlorine entering the system was about 2.7 litres. The obtained product was blue in colour with no appearance of any green shade seen. Figure 4.16 shows sample after chlorination with [BMIm][Br].

4.2.4 Trial 4

Figures 4.17, 4.18 and 4.19 represent the relevant graphs of the trial.

The time duration for the process was short 2.5 hrs and at moderate temperature (163°C). The mean RPM was maintained at 220 and a high mean flow of 0.9 litres/hr of chlorine. Almost 2 litres of chlorine was fed. The obtained product was almost the same as the initial reactant that was fed. Figure 4.20 shows sample after chlorination.

4.2.5 Trial 5

Figures 4.21, 4.22 and 4.23 represent the relevant graphs of the trial.

The time duration for the process was 4 hrs and at a lower temperature (138°C). This variation was done to see if any change occurred due to variation in temperature. The mean RPM was maintained at 174 and low mean flow rate at 0.55 litres/hr of

Table 4.8: Reaction Details of trial 4 with [BMIm][Br]

Time (t, min)	Temperature (T,°C)	RPM	Chlorine rate (L/hr)
0	26	220	-
15	100	218	-
30	120	220	0.95
45	142	220	0.95
60	168	222	0.85
75	180	221	0.85
90	183	221	0.90
105	185	221	0.85
120	185	220	0.85
135	185	220	0.85
150	185	220	0.85
	Mean Temp = 163	Mean RPM = 220	Mean flow = 0.90

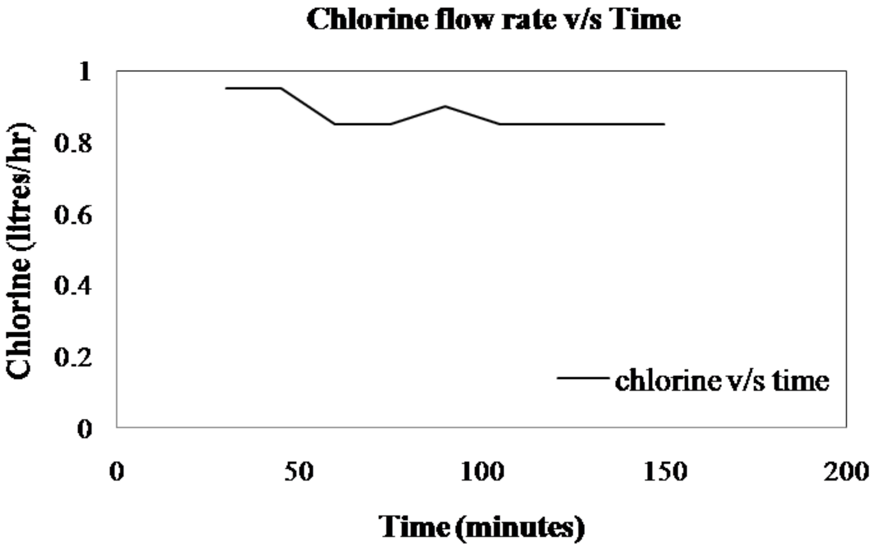


Figure 4.17: Chlorine flow rate v/s time for trial 4 with [BMIm][Br]

Table 4.9: Stoichiometry of trial 5 with [BMIm][Br]

Quantities	[BMIm][Br]	CuPC blue
Theoretical	233.64 g (180 ml)	11.6820 g
Practical	233.64 g (180 ml)	11.6823 g

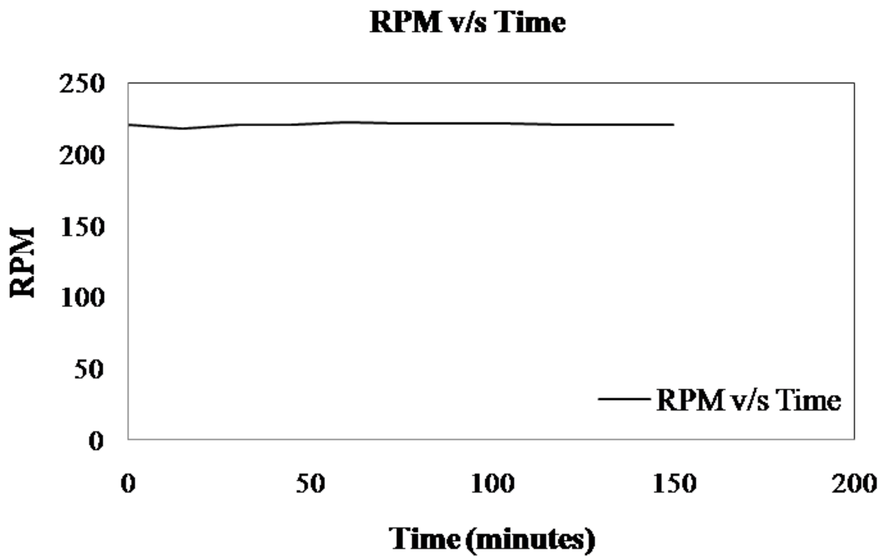


Figure 4.18: RPM v/s Time for trial 4 with [BMIm][Br]

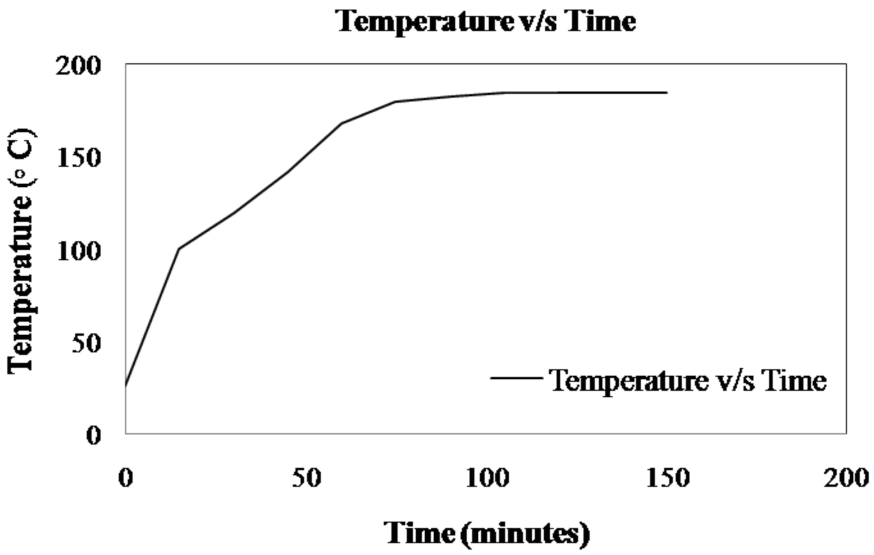


Figure 4.19: Temperature v/s Time for trial 4 with [BMIm][Br]

Figure 4.20: Sample 4 after chlorination with [BMIm][Br]

Table 4.10: Reaction Details of trial 5 with [BMIm][Br]

Time (t, min)	Temperature (T,°C)	RPM	Chlorine rate (L/hr)
0	26	170	-
15	57	172	0.60
30	105	173	0.65
45	111	173	0.60
60	123	173	0.60
75	128	171	0.50
90	133	172	0.45
105	134	172	0.45
120	140	176	0.50
135	145	175	0.50
150	148	177	0.60
165	150	175	0.60
180	150	175	0.60
195	150	175	0.65
210	150	174	0.65
225	150	174	0.60
240	150	174	0.50
	Mean temp = 138	Mean RPM = 174	Mean flow = 0.55

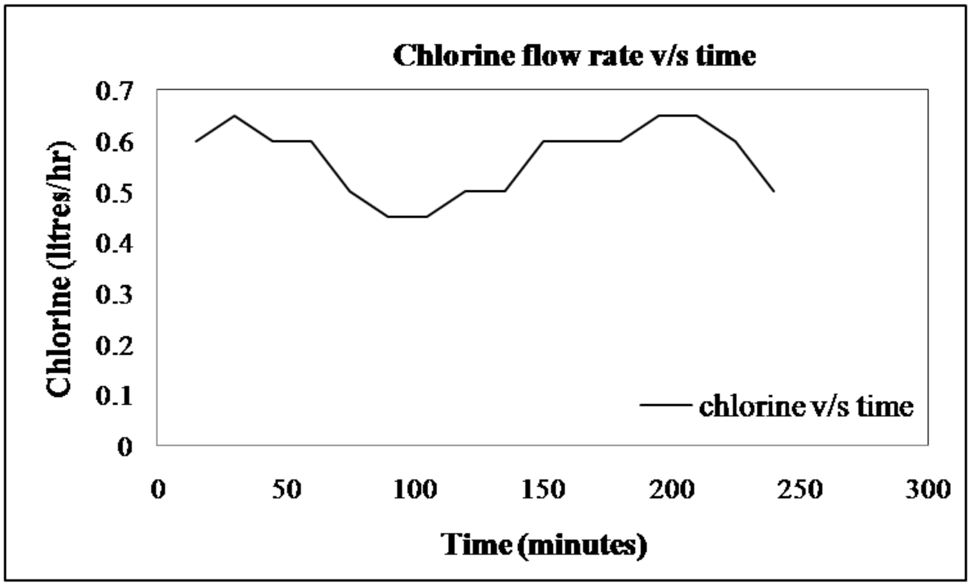


Figure 4.21: Chlorine flow rate v/s time for trial 5 with [BMIm][Br]

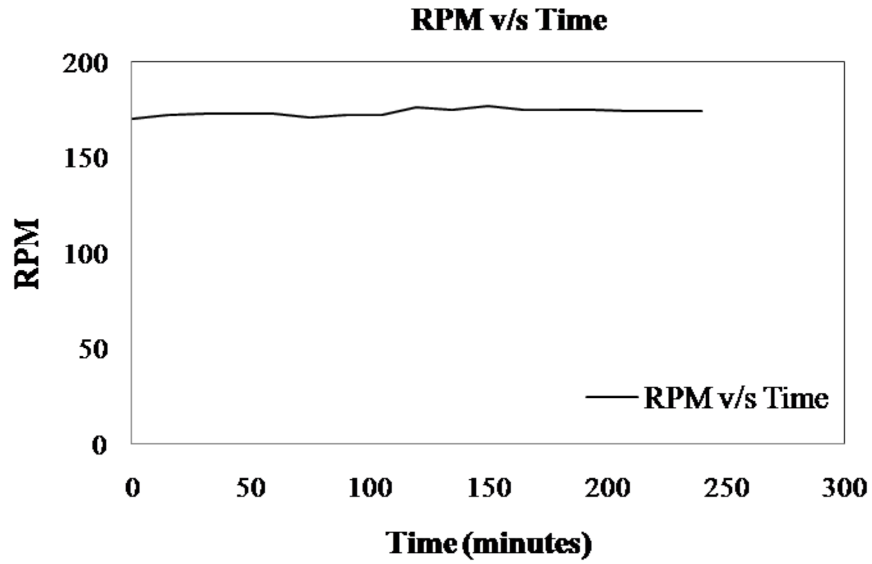


Figure 4.22: RPM v/s Time for trial 5 with [BMIm][Br]

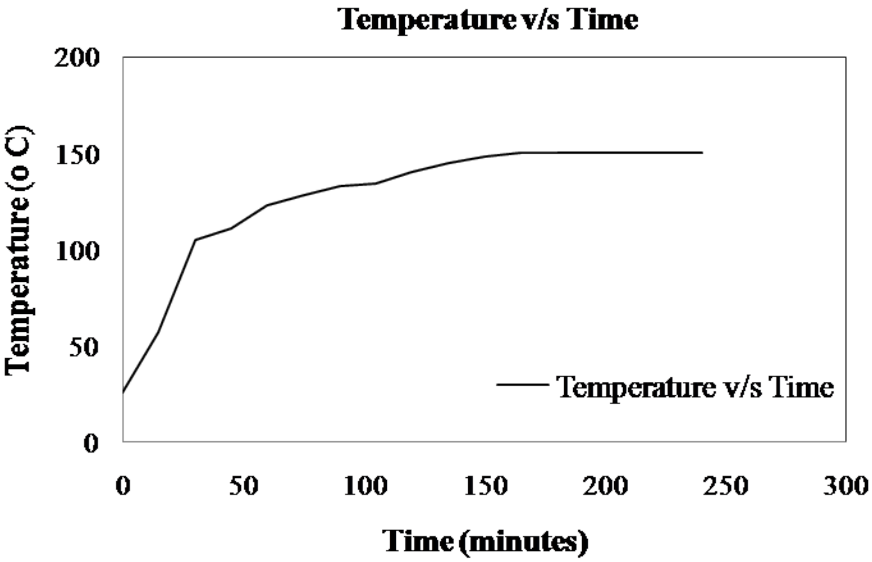


Figure 4.23: Temperature v/s Time for trial 5 with [BMIm][Br]

Table 4.11: Stoichiometry of trial 6 with [BMIm][Br]

Quantities	[BMIm][Br]	CuPC blue	$CuCl_2$	$AlCl_3$
Theoretical	233.64 g (180 ml)	11.6820 g	0.5982 g	46.728 g
Practical	233.64 g (180 ml)	11.6828 g	0.5985 g	46.730 g

chlorine with about 2 litres of chlorine being fed into the system until the reaction was stopped. This reaction was conducted without the use of catalyst. This trial also yielded the same results as before. Even the slightest change was not seen. Figure 4.24 shows sample after reaction.

4.2.6 Trial 6

Figures 4.25, 4.26 and 4.27 shows the graphs for the trial.

The time duration for the process was 5.5 hrs and at a higher temperature (171°C). The mean RPM was maintained at 211 and low mean flow at 0.42 litres/hr of chlorine. The low flow rate of chlorine along with higher time durations accounted for a sufficient amount of chlorine entering the system. The reaction was conducted with the use of $AlCl_3$ as a supporting chlorinating agent. The introduction of $AlCl_3$ resulted in white colour fumes which flooded the reaction mixture for a while. Even the use of $AlCl_3$ did not yield the expected results. Figure 4.28 shows sample after reaction.

Figure 4.24: Sample 5 after chlorination with [BMIm][Br]

Table 4.12: Reaction details of trial 6 with [BMIm][Br]

Time (t, min)	Temperature (T,^{o}C)	RPM	Chlorine rate (L/hr)
0	26	200	-
15	71	206	-
30	128	209	0.50
45	136	200	0.50
60	156	199	0.55
75	165	197	0.45
90	175	202	0.45
105	176	200	0.45
120	181	213	0.45
135	179	216	0.35
150	178	217	0.35
165	179	217	0.35
180	178	214	0.40
195	179	217	0.40
210	179	216	0.40
225	176	212	0.40
240	174	216	0.40
255	170	214	0.40
270	169	212	0.40
285	170	220	0.40
300	176	218	0.40
315	173	222	0.40
330	175	220	0.40
	Mean temp = 171	Mean RPM = 211	Mean flow = 0.42

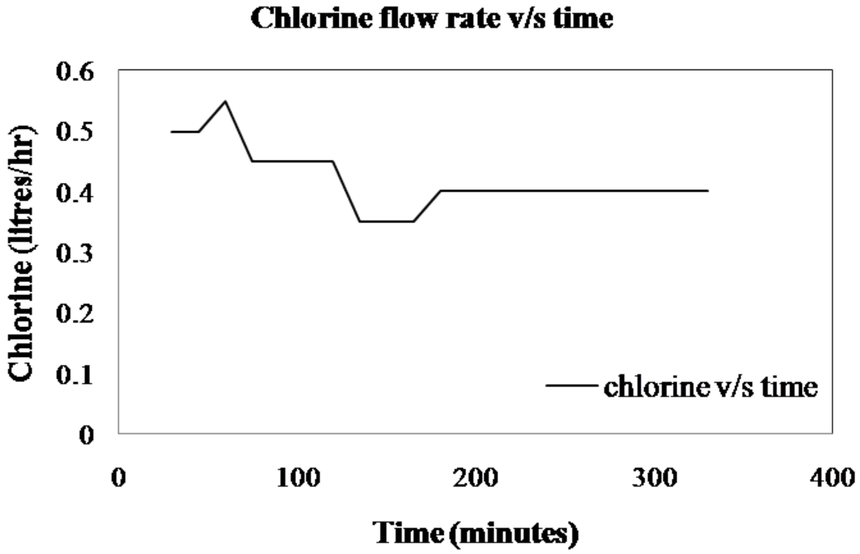


Figure 4.25: Chlorine flow rate v/s time for trial 6 with [BMIm][Br]

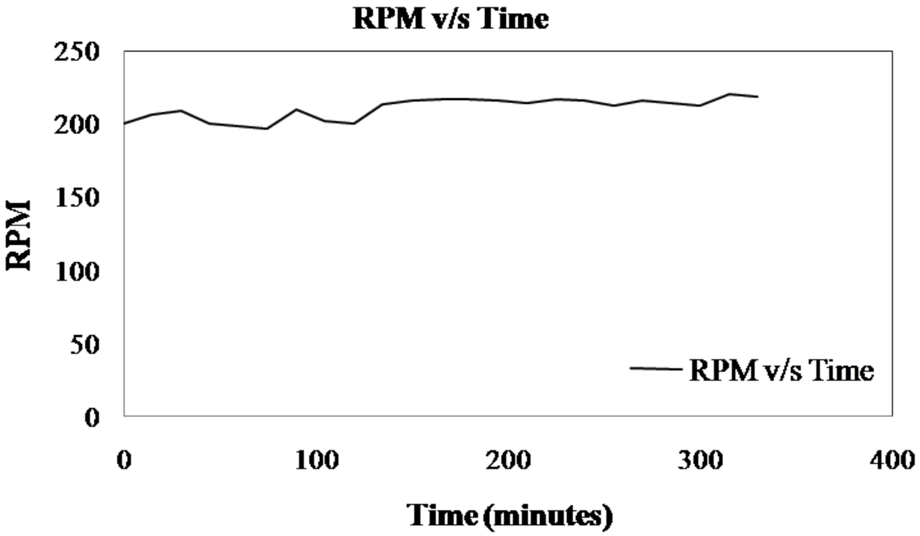


Figure 4.26: RPM v/s Time for trial 6 with [BMIm][Br]

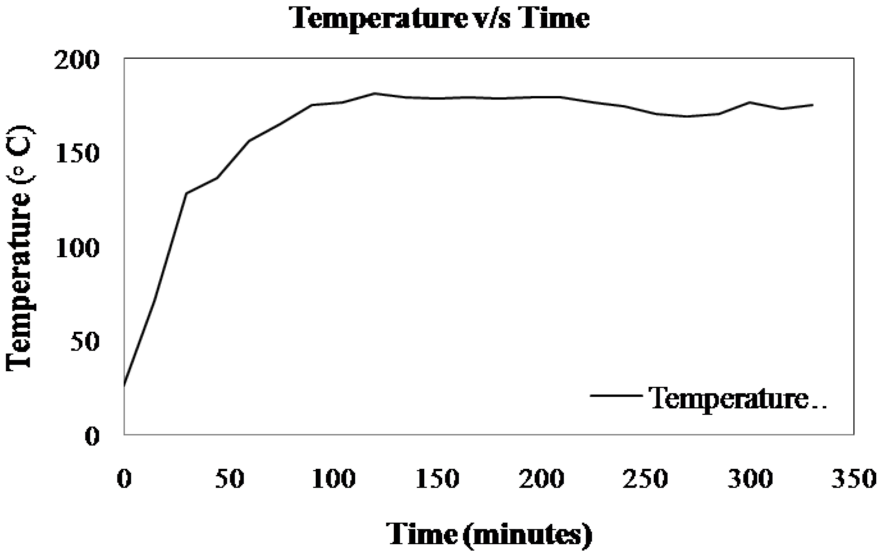


Figure 4.27: Temperature v/s Time for trial 6 with [BMIm][Br]

Figure 4.28: Sample 6 after chlorination with [BMIm][Br]

Table 4.13: Stoichiometry of trial 1 with [BMIm][BF_4]

Quantities	[BMIm][BF_4]	CuPC blue	$CuCl_2$
Theoretical	183 g (150 ml)	9.1500 g	0.4575 g
Practical	183 g (150 ml)	9.1510 g	0.4576 g

Table 4.14: Reaction details of Trial 1 with [BMIm][BF_4]

Time (t, min)	Temperature (T,°C)	RPM	Chlorine rate (L/hr)
0	26	210	-
15	68	208	-
30	125	209	0.40
45	135	208	0.40
60	154	206	0.50
75	167	207	0.45
90	177	206	0.45
105	179	206	0.45
120	181	205	0.45
135	180	206	0.35
150	179	207	0.35
165	179	207	0.35
180	179	204	0.40
195	179	207	0.40
210	179	206	0.40
225	178	204	0.40
240	178	204	0.40
	Mean Temp = 170	Mean RPM = 206	Mean Flow = 0.40

4.3 Chlorination with [BMIm][BF_4]

4.3.1 Trial 1

Figures 4.29, 4.30 and 4.31 show the graphs of chlorine flow rate, RPM and temperature versus time respectively.

The time duration for the process was 4 hrs and at a higher temperature (170°C). The mean RPM was maintained at 206 and low mean flow at 0.40 litres/hr of chlorine. About 1.6 litre chlorine was fed into the system. The experiment however, did not yield any desired result.

4.3.2 Trial 2

Figure 4.33, 4.34 and 4.35 show the graphs for the trial.

Table 4.15: Stoichiometry of trial 2 with [BMIm][BF_4]

Quantities	[BMIm][BF_4]	CuPC blue	$CuCl_2$
Theoretical	244 g (200 ml)	12.2000 g	2.4400 g
Practical	244 g (200 ml)	12.2010 g	2.4408 g

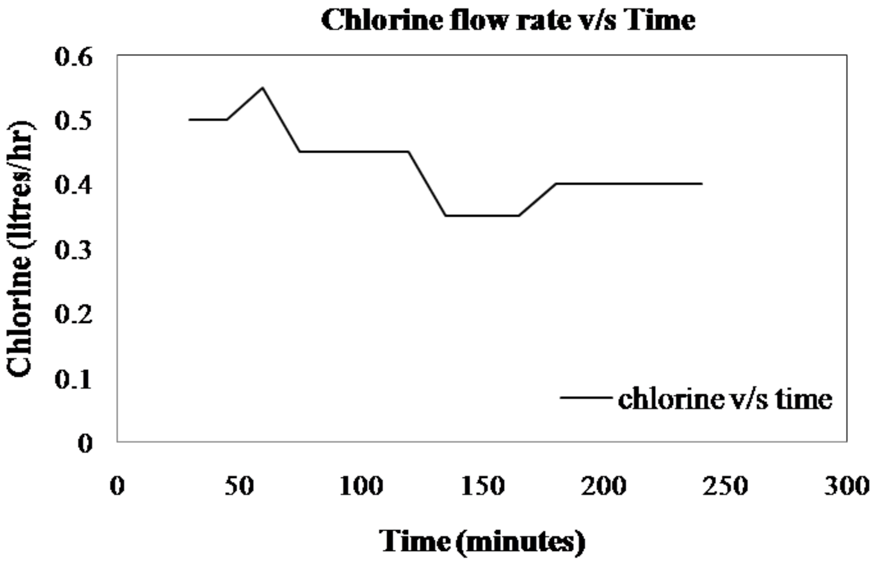


Figure 4.29: Chlorine flow rate v/s time for trial 1 with [BMIm][BF_4]

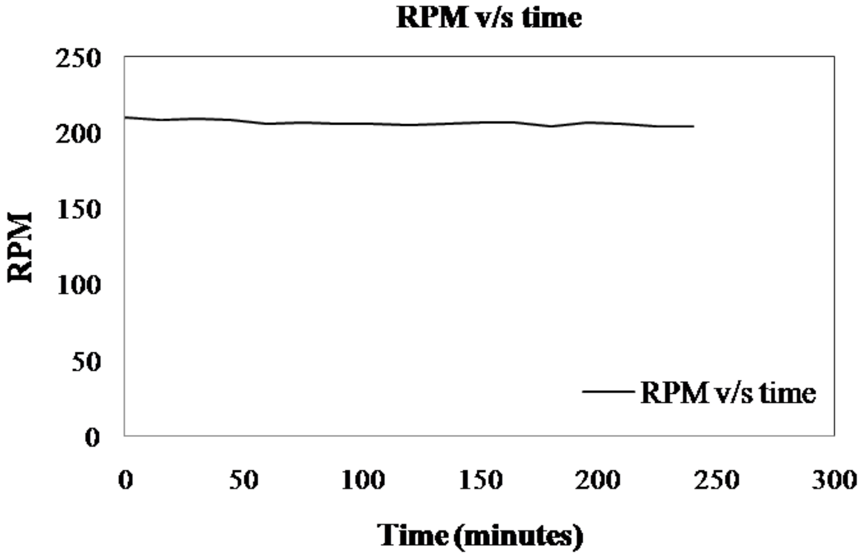


Figure 4.30: RPM v/s Time for trial 1 with [BMIm][BF_4]

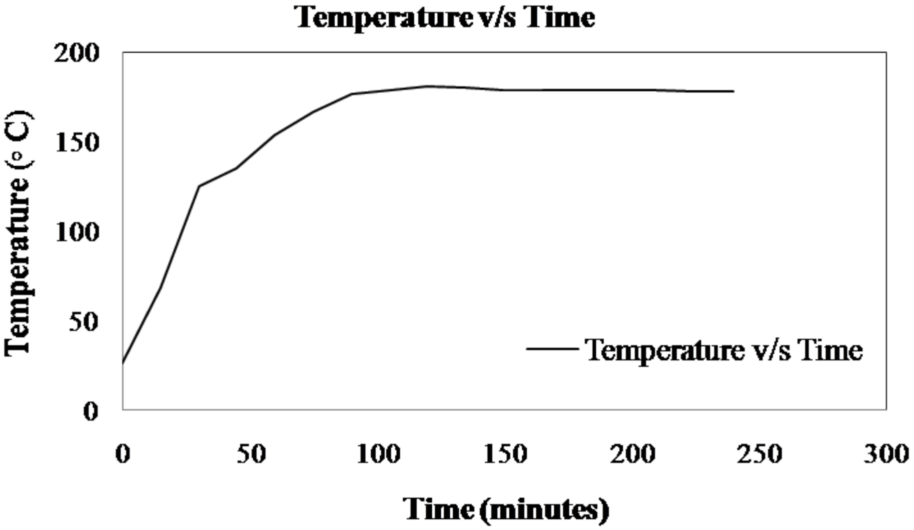


Figure 4.31: Temperature v/s time for trial 1 with [BMIm][BF_4]

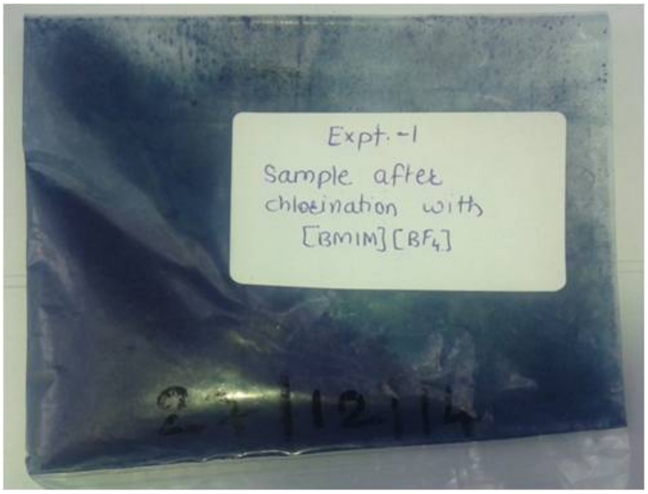


Figure 4.32: Sample 1 after chlorination with [BMIm][BF_4]

Table 4.16: Reaction details of Trial 2 with [BMIm][BF_4]

Time (t, min)	Temperature (T,°C)	RPM	Chlorine rate (L/hr)
0	26	200	-
15	57	202	-
30	105	202	0.75
45	135	204	0.75
60	154	203	0.70
75	167	202	0.70
90	177	202	0.75
105	179	203	0.70
120	180	201	0.70
135	181	203	0.65
150	180	202	0.70
165	180	202	0.70
180	179	203	0.70
195	180	204	0.75
210	180	202	0.75
225	179	202	0.75
240	179	202	0.75
	Mean temp = 169	Mean RPM = 202	Mean flow = 0.72

Table 4.17: Stoichiometry of trial 3 with [BMIm][BF_4]

Quantities	[BMIm][BF_4]	CuPC Blue	$CuCl_2$
Theoretical	183 g (150 ml)	9.1500 g	1.8300 g
Practical	183 g (150 ml)	9.1520 g	1.8350 g

The time duration for the process was 4 hrs and at a higher temperature (169°C). The duration is selected as 4 hours as normally, the prior experiments conducted with ionic liquids have attained completion in the range of 5 minutes to half an hour [15]. Hence, 4 hours were selected to provide sufficient time for the reaction to occur. The mean RPM was maintained at 202 and moderate mean flow at 0.72 litres/hr of chlorine. The reaction was performed with higher stoichiometric amounts of reactants. This was done to ensure sufficient quantities of reactants into the system. Expected results were not yielded. Figure 4.36 shows the same.

4.3.3 Trial 3

Figure 4.37, 4.38 and 4.39 depict the graphs of the experiment.

The time duration for the process was short 2 hrs and at a higher temperature (170°C). The mean RPM was maintained at 220 and moderate mean flow at 0.87 litres/hr of chlorine. The total chlorine inlet was 1.75 litres. The obtained product was blue in colour. Figure 4.40 shows the same.

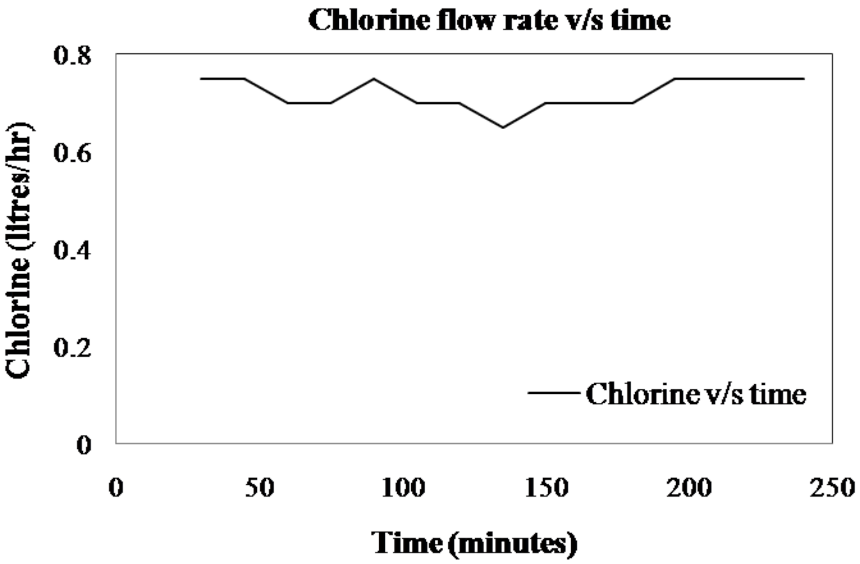


Figure 4.33: Chlorine flow rate v/s time for trial 2 with [BMIm][BF_4]

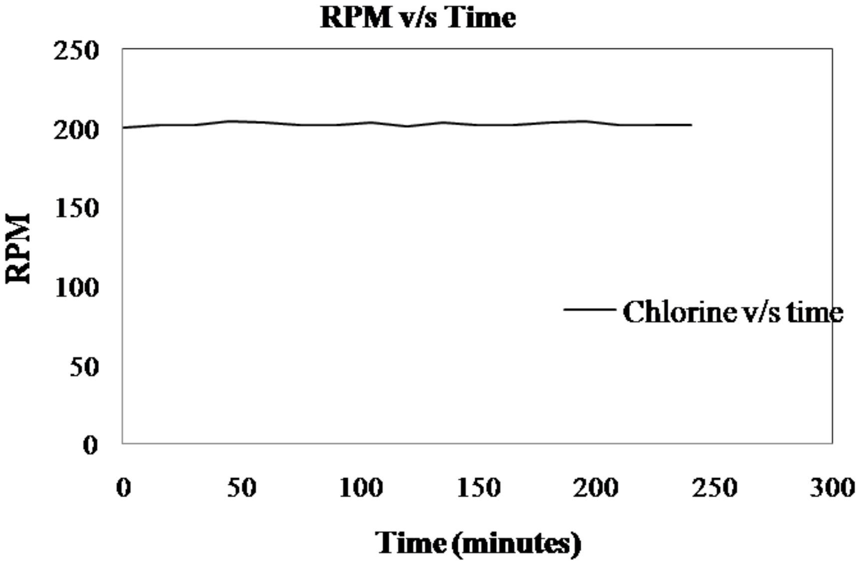


Figure 4.34: RPM v/s Time for trial 2 with [BMIm][BF_4]

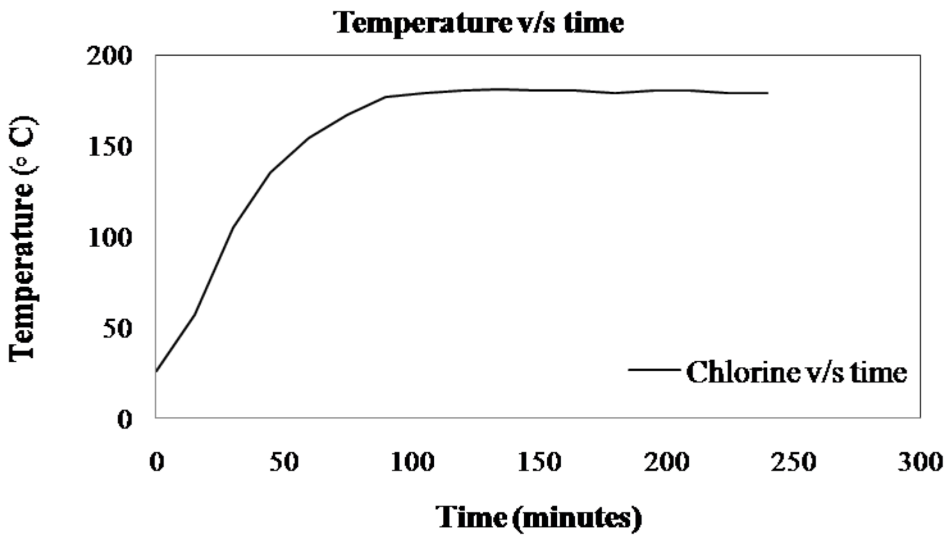


Figure 4.35: Temperature v/s time for trial 2 with [BMIm][BF_4]

Figure 4.36: Sample 2 after chlorination with [BMIm][BF_4]

Table 4.18: Reaction details of Trial 3 with [BMIm][BF_4]

Time (t, min)	Temperature (T,°C)	RPM	Chlorine rate (L/hr)
0	26	220	-
15	120	218	-
30	141	220	0.90
45	162	220	0.90
60	185	222	0.85
75	185	221	0.85
90	187	221	0.90
105	188	221	0.85
120	188	220	0.85
	Mean temp = 170	Mean RPM = 220	Mean flow = 0.87

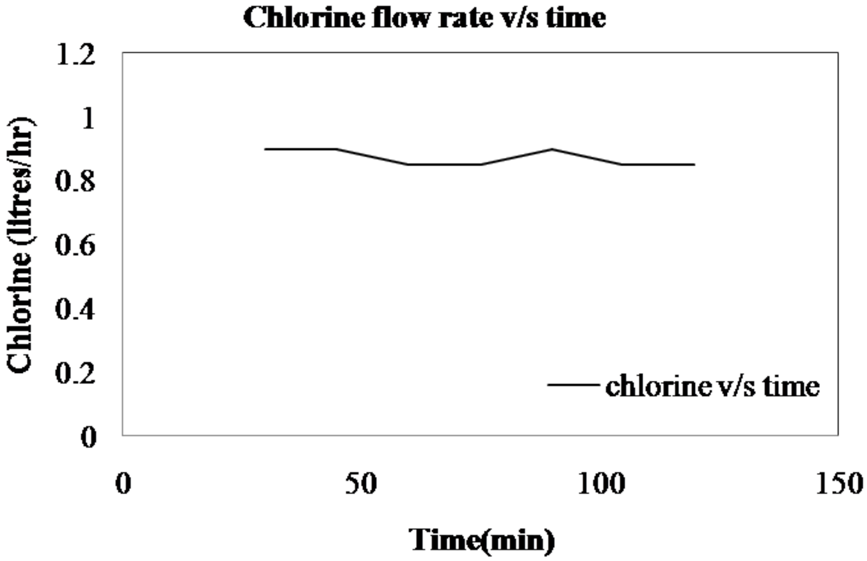


Figure 4.37: Chlorine flow rate v/s time for trial 3 with [BMIm][BF_4]

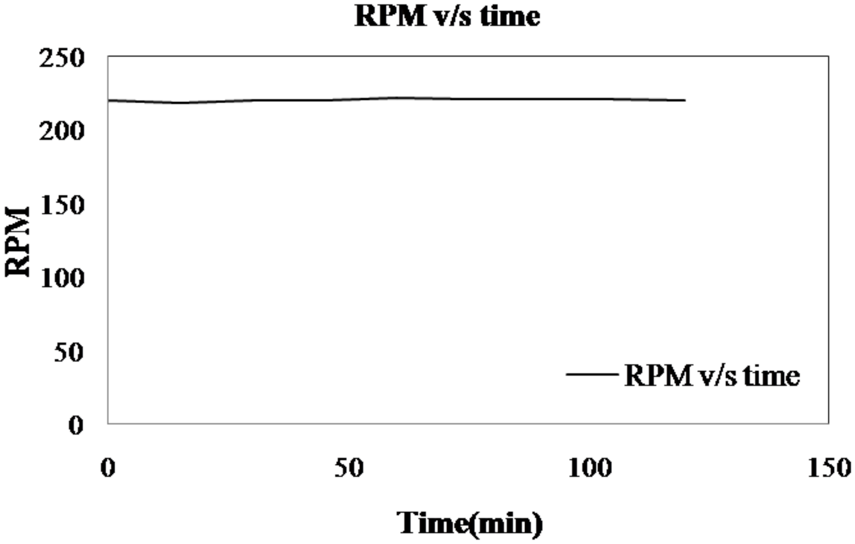


Figure 4.38: RPM v/s Time for trial 3 with [BMIm][BF_4]

Table 4.19: Stoichiometry of trial 4 with [BMIm][BF_4]

Quantities	[BMIm][BF_4]	CuPC blue	$CuCl_2$
Theoretical	183 g (150 ml)	9.1500 g	1.8300 g
Practical	183 g (150 ml)	9.1520 g	1.8310 g

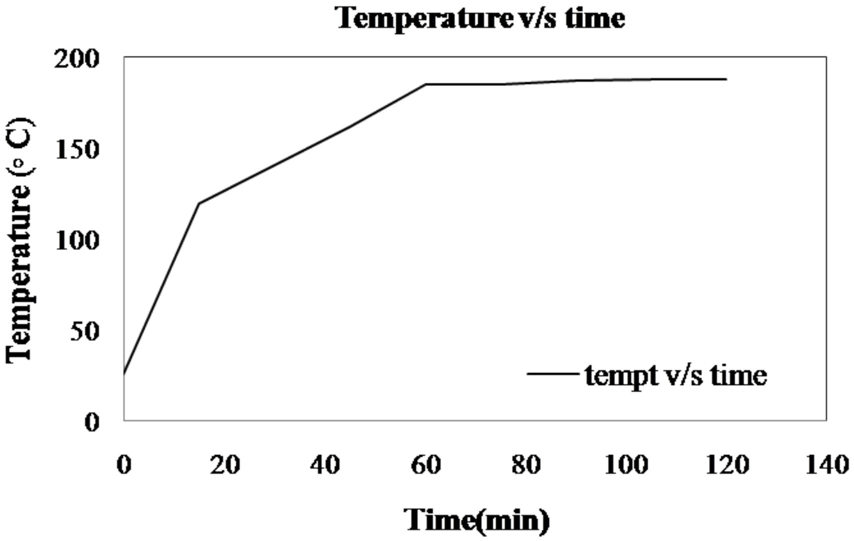


Figure 4.39: Temperature v/s time for trial 3 with [BMIm][BF$_4$]

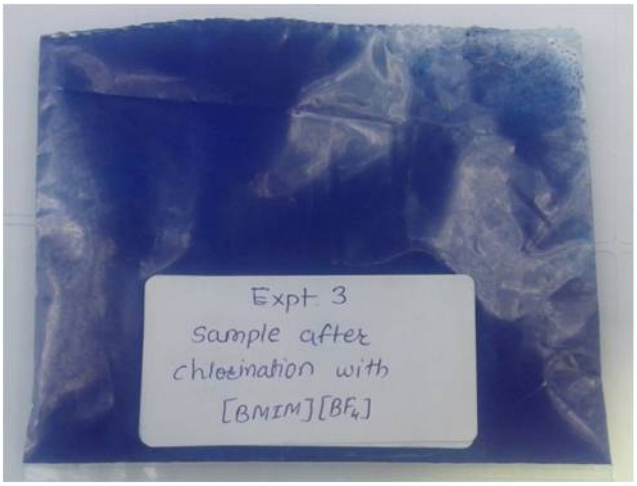


Figure 4.40: Sample 3 after chlorination with [BMIm][BF$_4$]

Table 4.20: Reaction details of Trial 4 with [BMIm][BF_4]

Time (t, min)	Temperature (T,°C)	RPM	Chlorine rate (L/hr)
0	26	220	-
15	57	218	-
30	73	220	0.40
45	91	216	0.40
60	102	218	0.40
75	115	216	0.40
90	132	218	0.35
105	154	220	0.40
120	170	222	0.40
135	171	220	0.40
150	172	220	0.40
165	172	218	0.35
180	173	220	0.35
195	175	220	0.40
210	175	222	0.40
225	175	220	0.40
240	176	220	0.35
255	176	220	0.35
270	176	218	0.35
285	176	220	0.35
300	176	222	0.35
315	176	222	0.35
330	175	220	0.40
345	175	220	0.40
360	175	222	0.40
375	175	220	0.40
390	175	219	0.40
	Mean Temp = 166	Mean RPM = 204	Mean flow = 0.42

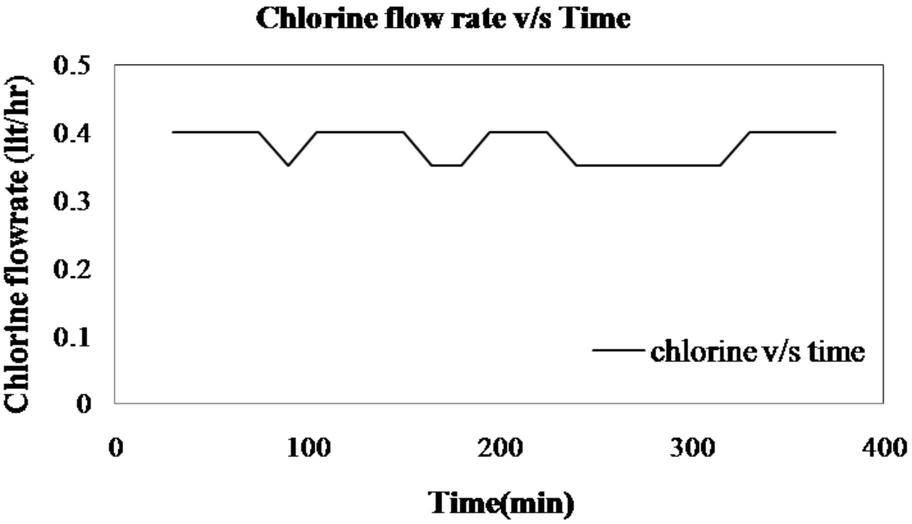


Figure 4.41: Chlorine flow rate v/s time for trial 4 with [BMIm][BF_4]

Table 4.21: Stoichiometry of trial 5 with [BMIm][BF_4]

Quantities	[BMIm][BF_4]	CuPC blue	$CuCl_2$
Theoretical	183 g (150 ml)	9.1500 g	1.8300 g
Practical	183 g (150 ml)	9.1525 g	1.8376 g

4.3.4 Trial 4

Figure 4.41, 4.42 and 4.43 shows the graphs for chlorine flow rate, RPM and Temperature versus Time respectively.

The time duration for the process was high (6.5 hrs) and at a higher temperature (166°C). The mean RPM was maintained at 204 and low mean flow at 0.42 litres/hr of chlorine. An attempt was made to chlorinate CuPC blue using a low flowrate of 0.42 litres/hr (i.e. 2.5 litres in 6 hours). The results however, did not comply with the expected. figure 4.44 shows the resultant product.

4.3.5 Trial 5

Figures 4.45, 4.46 and 4.47 represent the graphs for the trial.

The time duration for the process was high (4.5 hrs) and at a higher temperature (169°C). The mean RPM was maintained at a low of 113 and moderate mean flow at 0.64 litres/hr of chlorine (about 2.5 litres chlorine during the reaction course). A low RPM was kept to simulate the actual industrial agitator speed of an average of 100 RPM. The attempt failed to yield the desired results. Figure 4.48 shows the obtained result.

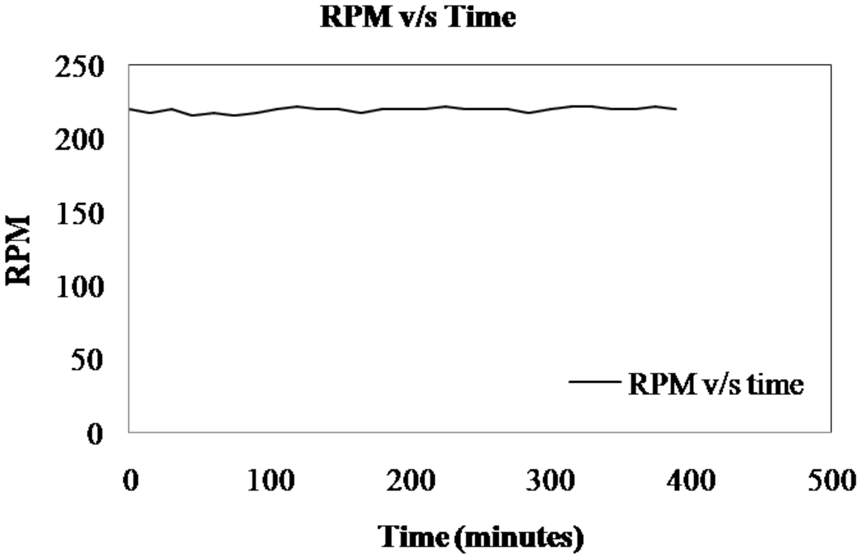


Figure 4.42: RPM v/s Time for trial 4 with [BMIm][BF_4]

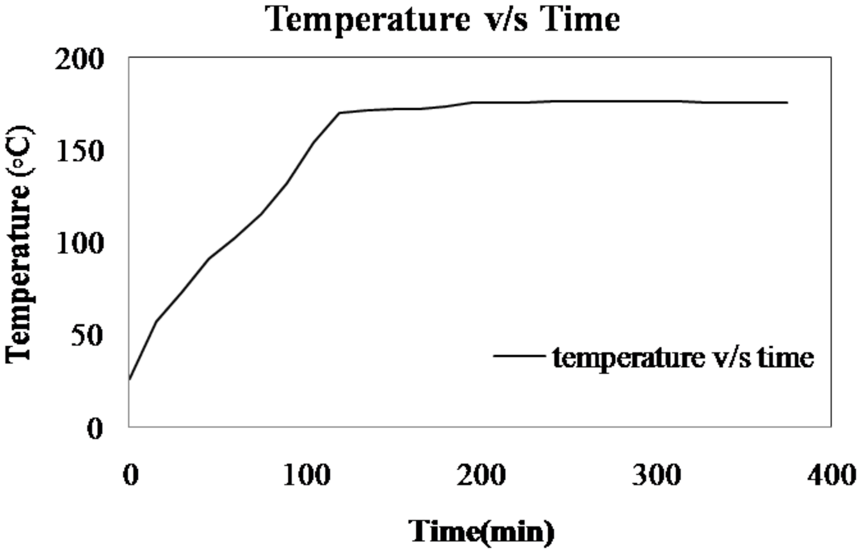


Figure 4.43: Temperature v/s time for trial 4 with [BMIm][BF_4]

Figure 4.44: Sample 4 after chlorination with [BMIm][BF$_4$]

Table 4.22: Reaction details of Trial 5 with [BMIm][BF$_4$]

Time (t, min)	Temperature (T,°C)	RPM	Chlorine rate (L/hr)
0	26	110	-
15	112	110	-
30	160	112	0.60
45	168	112	0.60
60	168	114	0.60
75	170	116	0.65
90	170	116	0.65
105	172	114	0.65
120	172	114	0.65
135	174	114	0.65
150	174	114	0.70
165	175	112	0.65
180	175	112	0.65
195	175	112	0.70
210	175	112	0.65
225	175	112	0.60
240	176	114	0.60
255	176	114	0.60
270	176	114	0.60
	Mean temp = 169	Mean RPM = 113	Mean flow = 0.64

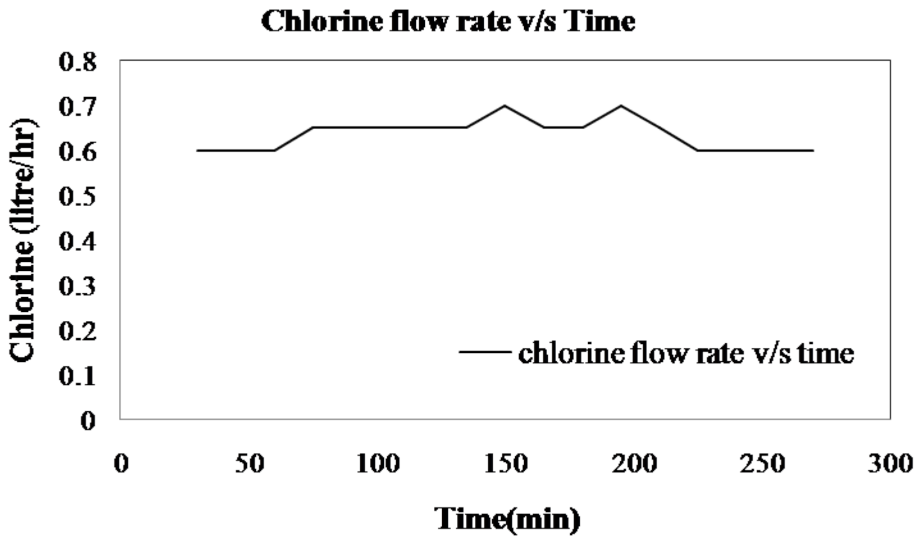


Figure 4.45: Chlorine flow rate v/s time for trial 5 with [BMIm][BF_4]

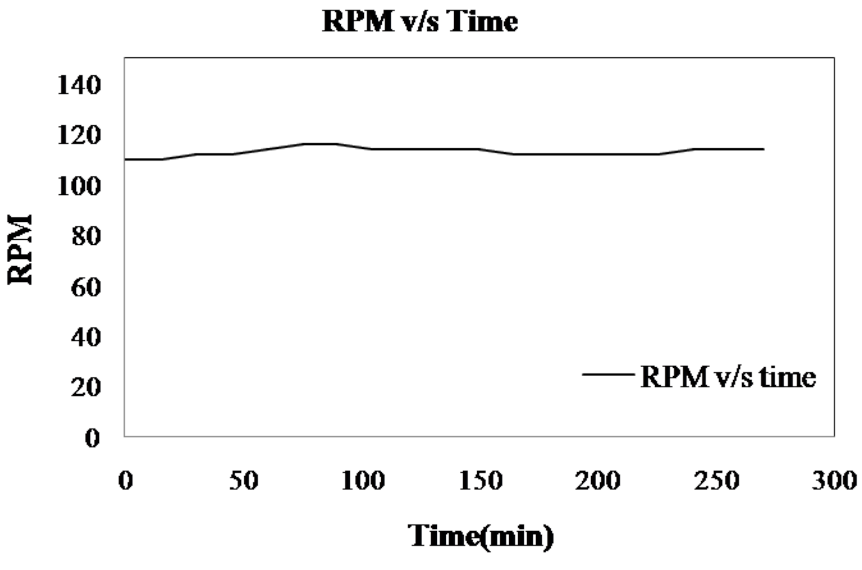


Figure 4.46: RPM v/s Time for trial 5 with [BMIm][BF_4]

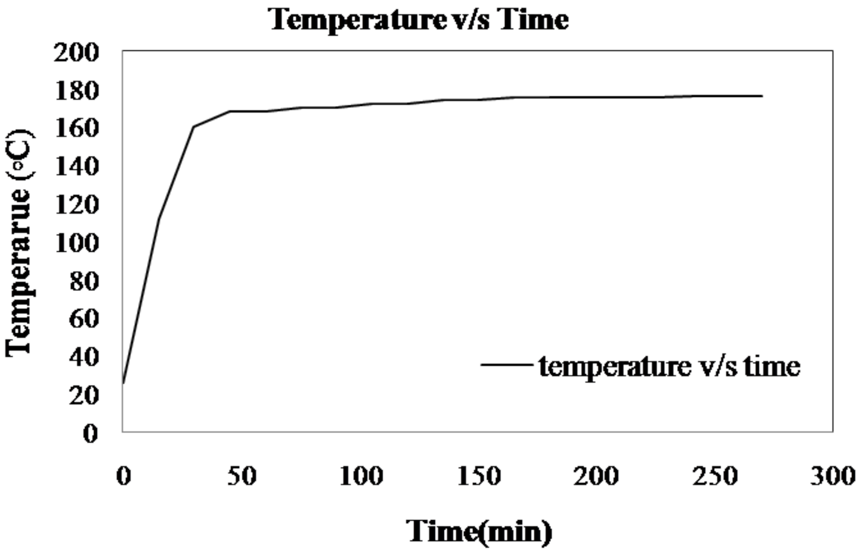


Figure 4.47: Temperature v/s time for trial 5 with [BMIm][BF_4]

Figure 4.48: Sample 5 after chlorination with [BMIm][BF_4]

Table 4.23: Stoichiometry of trial 6 with [BMIm][BF_4]

Quantities	[BMIm][BF_4]	CuPC blue	$CuCl_2$
Theoretical	183 g (150 ml)	9.1500 g	3.6600 g
Practical	183 g (150 ml)	9.1527 g	3.6620 g

Table 4.24: Reaction details of Trial 6 with [BMIm][BF_4]

Time (t, min)	Temperature (T,°C)	RPM	Chlorine rate (L/hr)
0	26	220	-
15	110	218	-
30	148	220	1.00
45	160	216	1.00
60	175	218	0.95
75	178	216	0.95
90	179	218	0.95
105	178	220	0.95
120	177	222	0.95
135	175	220	0.95
150	173	220	0.95
165	173	218	0.95
180	175	220	1.00
195	174	220	1.00
210	174	222	1.00
225	173	220	1.00
240	172	220	1.00
255	172	220	0.95
270	172	218	0.95
	Mean temp = 169	Mean RPM = 220	Mean flow = 0.97

4.3.6 Trial 6

Figures 4.49, 4.50 and 4.51 show the graphical representation of chlorine flow rate, RPM and temperature against time respectively.

The time duration for the process was high (4.5 hrs) and at a higher temperature (169°C). The mean RPM was maintained at 220 and high mean flow at 0.97 litres/hr of chlorine. The total amount of chlorine that entered the system was about 3.9 litres. The attempt did not yield any CuPC green product as shown in figure 4.52

4.4 Recycling of ionic liquids

The ionic liquids were recycled upto three cycles. The recycling process is later explained.

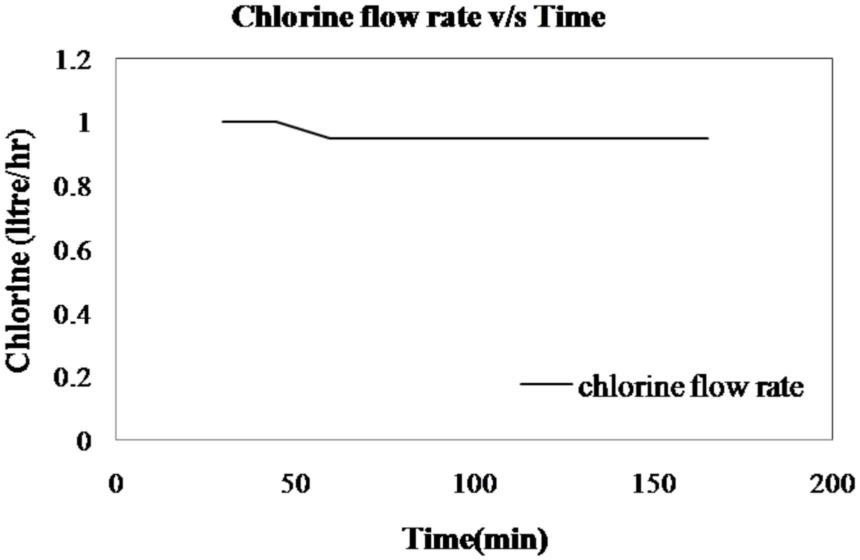


Figure 4.49: Chlorine flow rate v/s time for trial 6 with [BMIm][BF_4]

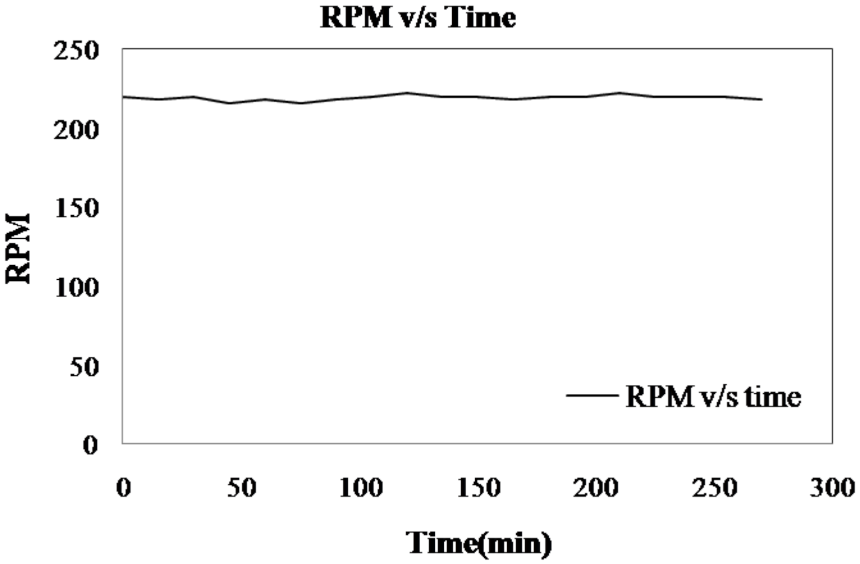


Figure 4.50: RPM v/s Time for trial 6 with [BMIm][BF_4]

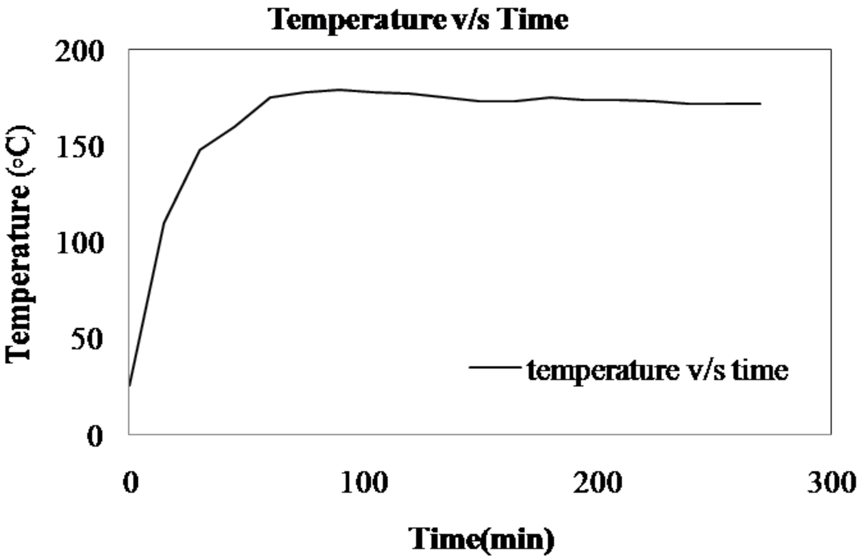


Figure 4.51: Temperature v/s time for trial 6 with [BMIm][BF_4]

Figure 4.52: Sample 6 after chlorination with [BMIm][BF_4]

Figure 4.53: Air purging set up

4.4.1 Air Purging

After the reaction was stopped, the solution was air purged. This was done to remove the residual chlorine that was left in the solution. Air was introduced through a pipe into the mixture and the residual chlorine was removed along-with it. This step is essential as chlorine, if present in the solution, tends to create problems during distillation of the solution and recovery of the ionic liquid. Moreover, as the reaction did not yield the desired products, much of the chlorine that was passed into the system, remained in the system. Hence, this process was performed once the reaction was stopped. The entire chlorine that could be removed was removed and the chlorine-free solution was further distilled.

Figure 4.53 shows the setup that was used for air purging.

4.4.2 Distillation

4.4.2.1 Distillation of [BMIm][Br]

The reaction mixture, after air purging, was diluted in water. The amount of water taken was 10 times the weight of ionic liquid taken, say if 200 gms of ionic liquid is reacted then 2000 gms (i.e. 2000 ml) of water is taken for dilution. Copper Phthalocyanine being insoluble in water, floats on the surface and can be removed with filtration. For this, the entire water drowned solution was introduced in a vacuum filtration unit and the blue pigments were collected on the filter paper. These pigments were washed thoroughly with water to maintain the acidity. The washed pigments were dried in an oven for 2 hours to obtain completely dry powder. After removing the pigments, the filtrate was distilled.

Figure 4.54: Distillation set up for [BMIm][Br]

The filtrate was introduced in a round bottom flask and heated upto 102°C. Water starts distilling as the temperature approaches 90°C. Distillation of water continues for about 4 hours. After four hours, water seems to stop being distilled. The solution left behind in the round bottom flask is the mixture of ionic liquid [BMIm][Br] and catalyst $CuCl_2$. This mixture need not be separated as the same could be and was used for further experiments.

4.4.2.2 Distillation of [BMIm][BF_4]

The procedure adopted for the distillation of solution of [BMIm][BF_4] is the same as that adopted for [BMIm][Br]. The solution obtained after removal of CuPC blue pigments was distilled. Water continued to be distilled for about 4 hours after which it ceased. The resultant solution contained the ionic liquid [BMIm][BF_4] and $CuCl_2$ catalyst.

4.5 Sodium Hypochlorite formation

Sodium hydroxide (5% solution) was prepared to absorb the HCl formed on substitution of hydrogen (H) atoms by chlorine (Cl) atoms due to the supply of molecular chlorine gas. As in our reaction, CPC green was not formed as expected, which in-turn means H atoms were not substituted by Cl atoms, there seemed to be no formation of NaCl salt. This is by the chemistry:

$NaOH + HCl \rightarrow NaCl + H_2O$

Also, some of the free chlorine gas directly entered the scrubbing solution of NaOH and formed Sodium Hypochlorite (NaOCl) which imparted a yellowish colour

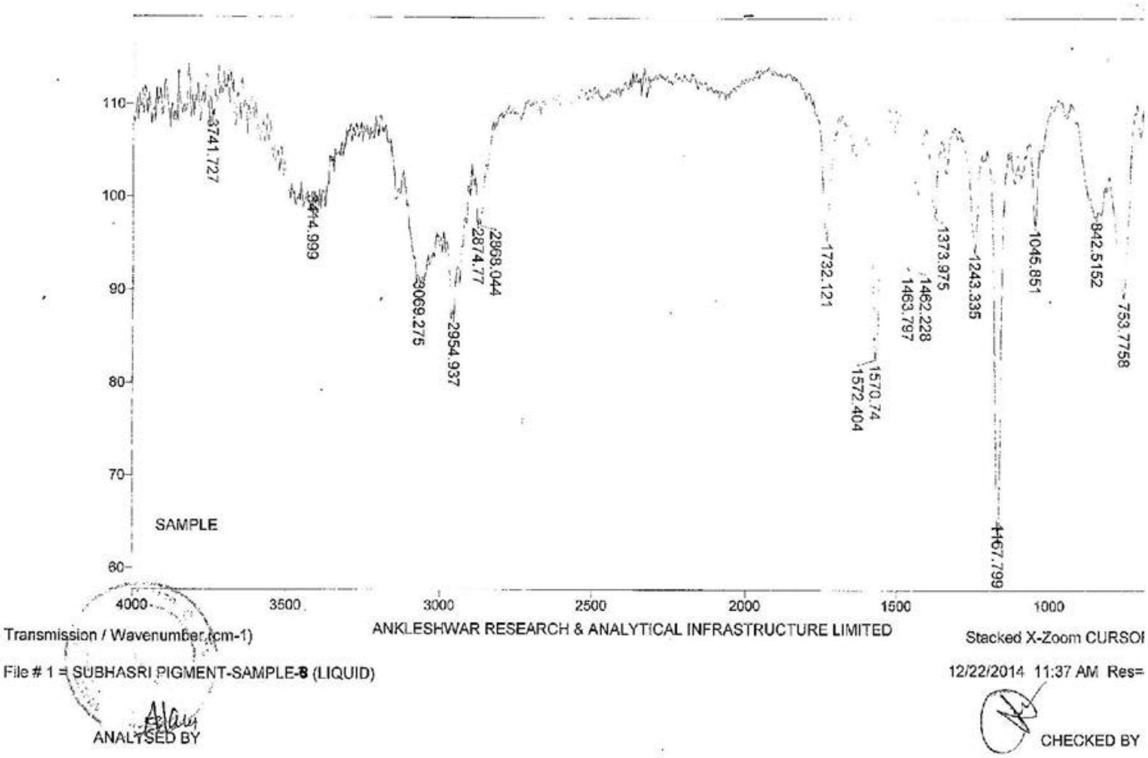


Figure 4.55: FTIR spectrum of [BMIm][Br] after distillation

Figure 4.56: Distillation set up for [BMIm][BF_4]

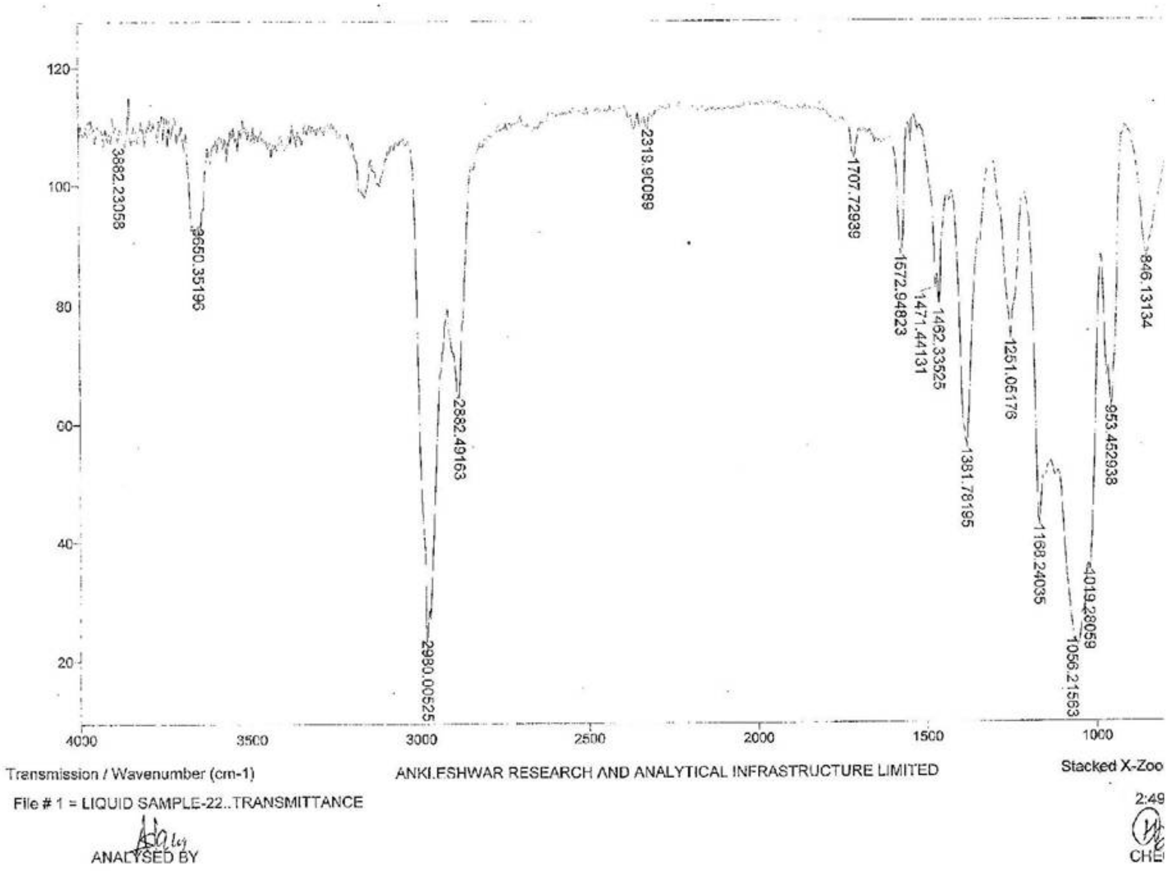


Figure 4.57: FTIR spectrum of [BMIm][BF_4] after distillation

Figure 4.58: Sodium hypochlorite formation

to the solution. This hypochlorite is formed by the chemistry:

$NaOH + Cl_2 \rightarrow NaOCl + HCl$

4.6 Cost of ionic liquids

The commercial price of ionic liquids is very high. This makes ionic liquids very expensive and their usage extremely limited.

4.6.1 Cost comparison of [BMIm][Br]

The commercial price of [BMIm][Br] as stated by Sigma-Aldrich is 92.5$ or Rs.6000 for 25 gm (i.e. Rs 240 per gm)
In our synthesis of [BMIm][Br], we utilised 1 mole of 1-methyl imidazole and 1.25 mole of 1-bromobutane.
For example, consider trial 6 of chlorination with [BMIm][Br];
We used 100 ml of 1-bromobutane and 80 ml of 1-methyl imidazole for synthesising 180 ml of the ionic liquid.
500 ml of 1-bromobutane costs Rs. 950
Therefore, cost of 100 ml = 950*100/500 = Rs. 190
500 ml 1-methyl imidazole costs Rs. 3400
Therefore, cost of 80 ml = 3400*80/500 = Rs. 544
Therefore we synthesised 180 ml (233.64 gm) of the ionic liquid at a cost of 190+544 = Rs. 734 (i.e. Rs. 3.15/gm)
This price is hardly 1.31% of the commercial price at which [BMIm][Br] is sold.

4.6.2 Cost comparison of [BMIm][BF_4]

The commercial price of [BMIm][BF_4] as stated by Sigma-Aldrich is 92.68$ or Rs.6000 for 25 gm (i.e. Rs 240 per gm)
In our synthesis of [BMIm][BF_4], we utilised 1 mole of [BMIm][Br] and 1 mole of Sodium Tetrafluoroborate ($NaBF_4$)
For example, consider trial 6 of chlorination with [BMIm][BF_4];
We used 100 gm of $NaBF_4$
500 gm of 1-bromobutane costs Rs. 515
Therefore, cost of 100 gm = 515*100/500 = Rs. 103
233.64 gm (1.066 mol, 180 ml) of [BMIm][Br] costs Rs. 734.
Therefore, 219.12 gm (1 mol, 168.8 ml) costs Rs. 689
We also used 170 ml of ethyl acetate 500 ml of Ethyl acetate costs Rs. 290
Therefore, cost of 170 ml = 170*290/500 = Rs. 99
Therefore we synthesised 175 ml (213.5 gm, 0.82 mol) of the ionic liquid at a cost of 689+103+99 = Rs. 891 (i.e. Rs. 4.18/gm)
This price is hardly 1.74% of the commercial price at which [BMIm][BF_4] is sold.

Chapter 5

Conclusion and Future Scope

5.1 Conclusion

In the above mentioned experiment, an attempt to chlorinate Copper Phthalocyanine Blue using ionic liquids was carried out. It was an attempt to provide an alternative reaction pathway to the existing industrial process. The ongoing process uses a melt of Sodium chloride and Aluminium chloride. This, when used as a solvent, has to be treated in the end as it is the effluent remaining after the process. This treatment involves costs which increases the overall cost of the process. Hence, the above mentioned attempt to provide an alternative using ionic liquids as a solvent. These liquids are particularly chosen owing to their recyclable nature. Ionic liquids have been recently used on a large scale mostly in research activities. The ionic liquids [BMIm][Br] and [BMIm][BF_4] were selected as these are the most exploited ionic liquids. [BMIm][Br] is an intermediate in the formation of [BMIm][BF_4].

The ionic liquids were synthesised and characterised in-situ. The procedure that was followed was taken from available literature. The ionic liquids were synthesised as stated therein. Characterisation methods adopted were Fourier Transform Infrared spectroscopy and Nuclear Magnetic Resonance spectroscopy. These methods confirmed that the desired product was formed.

The reactions were carried out at different temperatures and for different time intervals. Also, the stoichiometry of the reactants was changed to see any effects in the output. A rotameter ensured the appropriate chlorine gas supply. The reactions were typically between 3 hours to 10 hours, with the chlorine flow rate varying between 0.3 litres to 1 litre per hour. The reaction mixture, after reaction, was air purged to remove any residual chlorine. Distillation was then done to recycle and reuse the ionic liquids. The distilled ionic liquids showed the same FTIR spectrum thus ensuring that they did not lose their characteristic functional groups during the course of the reaction. Each freshly prepared batch of ionic liquid was recycled upto three times.

The conduct of the chlorinated experiment confirmed that CuPC blue is a highly stable compound as is already stated in previous literature. It does not get chlorinated using the ionic liquids [BMIm][Br] or [BMIm][BF_4]. The reaction mechanism could not be understood however. The samples obtained after the reaction remained almost as they were before the reaction. CuPC blue does not dissolve in ionic liquids which supports the previous literature that it is soluble only in strong acids like sulphuric acid. On stirring it in a solution of ionic liquid, it does not dissolve but forms a dispersion in the liquid. This phenomenon is observed in both the liquids.

CuPC blue undergoes chlorination only at higher temperatures of about 170°C and gives good yields when reacted in a melt of $AlCl_3$- NaCl along with the use of cupric chloride as a catalyst. $AlCl_3$ melts at 350°C while NaCl fuses at about 850°C. But their eutectic mixture melts at 160°C which forms an excellent reaction media for chlorination. This is currently being used in the industry. Moreover, the cost of $AlCl_3$ – NaCl eutectic mixture is Rs. 40/ kg which is very cheap as compared to the cost of ionic liquids. This has rendered its wide usage.

In the present study, the ionic liquids were synthesized in a highly cost effective manner as compared to the commercially available ionic liquids. We synthesised [BMIm][Br] at 1.31% while [BMIm][BF_4] at 1.74% of their commercial price respectively. This proved highly useful during new synthesis of every batch. Moreover, its recyclability added to its advantages, making it a desirable alternative. However, the non-compliance of the results with the expected results leads us to the opportunities of discovering new ionic liquids as alternative options to the existing process.

To conclude, the ionic liquid used in the experiment, despite being proven useful in many other cases, does not yield our desired product in this particular case.

5.2 Future Scope

Reactions can be carried out using other ionic liquids. Ionic liquids with Tetrachloroaluminate, $[AlCl]_4$ anion can be used for chlorination. This reaction might yield the expected results as the anion contains Aluminium chlorate similar to the traditional method which uses $AlCl_3$ in $AlCl_3$- NaCl melt. Chlorinating agents other than molecular chlorine gas can be tried out as handling chlorine gas is hazardous.

Bibliography

[1] Zhu, Q; Hussey, C.L.; " Galvanostatic Pulse Plating of Bulk Cu-Al alloys on Nickel electrodes from room temperature chloroaluminate molten salts containing benzene", Journal of Electrochemical Society , 2002, 149, C 268.

[2] Bockris, J.O.M.; Reddy, A. K. N.; "Ion Solvent Interactions", Modern Electrochemistry, 1970, pg 45-174.

[3] Plambeck, J.A., "Fused Salt Systems", Encyclopaedia of Electrochemistry of the Elements, 1976, Vol. X, Marcel Dekker, New York; Janz, G. J.; Molten Salts Handbook, 1967, Academic Press, New York.

[4] Trulove P.C.; Mantz, R. C.; "Ionic Liquids in Synthesis", Wasserscheid P. and Welton, T.; Editors, Wiley-VCH, Weinheim, 2003, pg 112.

[5] O'Donnell, T.; "Superacids and Acidic Melts", VCH, Weinheim, 1993, pg 8.

[6] Kolthoff, I.M.; Willman, A.; Journal of American Chemical Society, 1934, 56, 1007.

[7] Sandor, S; Prelipceanu, O; and Checiu, I; "Sulphonated Phthalocyanine induced Caudal Malformative Syndrome in the chick embryo." (Abstract), U.S. National Library of Medicine, 1985, National Institutes of Health.

[8] Gregory, Peter; "Industrial applications of Phthalocyanines", Journal of Porphyrins and Phthalocyanines (JPP), 2000, Volume 4, Issue 4.

[9] Ghani, Fatemeh; Kristen, Juliane; Riegler, Hans; "Solubility Properties of Unsubstituted Metal Phthalocyanines in Different Types of Solvents", Journal of Chemical Engineering Data, 2012, 57, 439–449.

[10] Tshibangu, Patrick Ngoy; Ndwandwe, Silindile Nomathemba; Dikio, Ezekiel Dixon; "Density, Viscosity and Conductivity Study of 1-Butyl-3-Methylimidazolium Bromide", International Journal for Electrochemical Science, 2011, Volume 6, pg 2201-2213.

[11] Dharaskar, Swapnil A.; Wasewar, Kailas L.; Varma, Mahesh N.; Shende, Diwakar Z.; Yoo, Chang Kyoo; "Synthesis, characterization and application of 1-butyl-3-methylimidazolium tetrafluoroborate for extractive desulfurization of liquid fuel", Arabian Journal of Chemistry, 2013.

[12] Holtzmann, Harris; Simon, Eric; “Process for Preparation of Chlorinated Copper Phthalocyanine”, US Patent 2662085.

[13] Pavlinac, J; Zupan, M; Laali, K; Stavber, S; “Halogenation of organic compounds in ionic liquids”, Tetrahedron, 2009, 65, pg 5625–5662.

[14] Ronald Barraclough, Johnstone; Langley, Robert; “Production of Phthalocyanine Green”, United States Patent 4091028, 1978

[15] Hermann Geeren, Ruchheim; Wolfgang Fabian, Wilhemsfeld; “Manufacture of Polychloro-copper Phthalocyanines”, United States Patent 4067881, 1978.

[16] Ryo Matsuura, Yamato; Segawa, Tomio; Nomiyama, Yukio; Yoichi Kumada, Zushi; Sawada, Hideo; “ Process for Producing Highly Chlorinated Copper Phthalocyanine”, United States Patent 4218376, 1980.

[17] Wessling, Diether; “ Process for the Halogenation of Copper Phthalocyanine”, United States Patent 4077974, 1978.

[18] Hamilton, Alexander; Stewart, John Dewar; “Process for the Halogenation of Phthalocyanines”, United States Patent 3320276, 1967.

[19] Pepoy, Louis J.; “ Preparation of Chlorinated Phthalocyanines”, United States Patent 4452740, 1984.

[20] Caliezi, Armin; Kern, Walter; Holbro, Theodor; “Process for Halogenating Compounds Having a Tetraza-Porphin Structure”, United States Patent 2862929, 1958.

[21] Randall, David I.; Taras, John; “Halogenation of Phthalocyanines”, United States Patent 2873279, 1959.

[22] Segawa, Tomio; Kuramoto, Sakae; “ Process for Producing Highly Chlorinated Copper Phthalocyanine”, United States Patent 4330470, 1982.

[23] Gonzales, Paula Barcelo; “Thermodynamics of Room Temperature Ionic Liquids: Modeling and Experiment”, 2011, University of Aberdeen.

[24] Robin, D.; Rogers and Kenneth, R. S, Editors, “Ionic Liquids: Industrial Applications to Green Chemistry”, ACS Symposium Series, 2002, 818.

[25] Ramli, Nur Aainaa Syahirah; Amin, Nor Aishah Saidina; “ Ionic Solid Nanomaterials: Synthesis, Characterization and Catalytic Properties Investigation”, Advanced Materials Research, 2013, Volume 699, pg 155-160.