

Ionic liquids as Green Solvents for Cellulose Chemistry

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DECLARATION

I hereby declare that the dissertation entitled “Ionic liquids as a green solvents for cellulose chemistry” submitted to the Department of Chemistry, North-West University, Mafikeng Campus for the fulfilment of the requirements of the degree of Master of Science in Chemistry is a faithful record and original research work carried out by me under the guidance and supervision of Prof I Bahadur. No part of this work has been submitted by any other researcher or students in any tertiary institution. Sources of my information have been properly acknowledged in the reference pages.

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ABSTRACT

Cellulose is a polymer that lacks solubility in many conventional solvents and this limits its applications. Recently ionic liquids (ILs) have been reported to be good and green solvents for the cellulose processing. Therefore, the aim of this project was to provide the experimental perspective of the influence of the dimethyl formamide (DMF) on microcrystalline cellulose (MCC) dissolution process using ionic liquids (ILs) namely: 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]), 1-allyl-3-methylimidazolium chloride ([AMIM][Cl]), 1-Butyl-3-methylpyridinium chloride ([BMPy][Cl]).

The MCC dissolution process was carried out in three ionic liquids solvents namely: [BMIM][Cl], [AMIM][Cl] and [BMPy][Cl] as well as their co-solvents with (DMF). The dissolution process of ILs, and their co-solvent systems was carried out at temperature of $65\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ at ambient pressure. After cellulose had been dissolved, it was then regenerated using deionized water. The regenerated cellulose fibers were characterized by various techniques: Fourier Transform Infrared Spectrometry (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

Characterization results revealed that the regenerated cellulose previously dissolved in ILs [BMIM][Cl], [AMIM][Cl] and [BMPy][Cl] was similar to the regenerated cellulose previously dissolved in ILs with DMF: [BMIM][Cl]/DMF, [AMIM][Cl]/DMF and [BMPy][Cl]/DMF, respectively. Furthermore, these results were compared with the results of the pure cellulose (MCC). Properties of the regenerated cellulose were slightly different from those of the pure cellulose. The regenerated cellulose was mainly cellulose II and amorphous whereas pure cellulose was cellulose I, which showed that during regeneration process, the pure cellulose was unable to reconstruct back to its native state hence it precipitated as cellulose II having high amorphous region. Moreover, FTIR results for the regenerated cellulose showed that no new chemical bonds

were formed which revealed that during the dissolution process there was no chemical reaction taking place.

Using the obtained results of the regenerated cellulose fibres previously dissolved in ILs and their co-solvents, it was concluded that during the dissolution process DMF does not interact with cellulose however, it increases the ionic mobility of anion which lead to faster dissolution rate and it also increases ILs ability to dissolve more cellulose as shown in the theoretical studies [108-119]. Thermophysical properties (density, ρ , sound velocity, u , and refractive index, n_D ,) measurements of cellulose mixtures at various molalities were made to confirm the dissolution process took place in the solvent system of [BMIM][Cl]/DMF or [AMIM][Cl]/DMF or [BMPy][Cl]/DMF. Thermophysical properties of cellulose with ILs was not conducted since those mixtures were not liquid at room temperature As molality increased density, ρ , sound velocity, u , and refractive index, n_D , also increased which showed that cellulose were dissolved due to solvent-solute interaction.

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List of Symbols

1°	Primary
2°	Secondary
K	Kelvin
m	Mass
m	Molality
mg	Miligram
n_D	Refractive index
u	Sound velocity
T	Temperature
v	Volume
ρ	Density
ϵ_0	Permittivity of vacuum

List of Abbreviations

$\cdot\text{OH}$	Hydroxyl
CH_3COOH	Acetic acid
CH_3OH	Methanol
CS_2	Carbon disulfide
DMAc	Dimethyl acetamide
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
DP	Degree of polymerization
DSC	Differential scanning calorimetry
FTIR	Fourier transform infrared spectroscopy
H_2O	Water
HCOOH	Formic acid
ILs	Ionic liquids
N_2O_2	Dioxidodiazene
NaOH	Sodium hydroxide
NH_3	Ammonia
NH_4SCN	Ammonium thiocyanate
NMMO	N-Methylmorpholine N-oxide
LiCl	Lithium chloride
mmol	Milimole
SEM	Scanning electron microscope
SLS	Static light scattering
TBAF	Tetra-n-butylammonium fluoride
TEM	Transmission Electron Microscopy
TGA	Thermal gravimetric analysis

THF	Tetrahydrofuran
XRD	X-ray diffraction
[AEIM][HCOO]	1-Allyl-3-ethylimidazolium formate
[AMIM][Cl]	1-Allyl-3-methylimidazolium chloride
[AMIM][HCOO]	1-Allyl-3-methylimidazolium formate
[AMMorp][OAc]	N-allyl-N-methylmorpholinium acetate
[AMMorp] ₃ [PO ₄]	N-allyl-N-methylmorpholinium phosphate
[AMMorp] ₂ [CO ₃]	N-allyl-N-methylmorpholinium carbonate
[AMPy][Cl]	1-Allyl-3-pyridinium chloride
[ATBA][OAc]	N-allyltributylammonium acetate
[ATEA][OAc]	N-allyltriethylammonium acetate
[ATMA][OAc]	N-allyltrimethylammonium acetate
[A ₄ N][OAc]	Tetraallylammonium acetate
[ADMAP][OAc]	N-allyl-N',N'-dimethylaminopyridinium acetate
[BMIM][Cl]/ [C ₄ MIM][Cl]	1-Butyl-3-methylimidazolium chloride.
[BMIM][CF ₃ SO ₃]	1-Butyl-3-methylimidazolium triflate
[BzMIM]Cl	1-Benzyl-3-methylimidazolium chloride
[BMIM][BF ₄]	1-Butyl-3-methylimidazolium tetrafluoroborate
[BMIM][PF ₆]	1-Butyl-3-methylimidazolium phosphorus hexafluoride
BDTAC	Benzyltrimethyl(tetradecyl)ammonium chloride
[BMMorp][OAc]	N-butyl-N-methylmorpholinium acetate
[BnMMorp][Cl]	N-benzyl-N-methylmorpholinium chloride
[BMPy][Cl]	1-Butyl-3-methylpyridinium chloride
[C ₂ MIM][(MeO) ₂ PO ₂]	1-Ethyl-3-methylimidazolium dimethylphosphate
[C ₂ MPy][Br]	1-Ethyl-3-pyridinium bromide
[C ₄ C ₁ IM][OAc]	1-Butyl-3-methylimidazolium acetate

[C ₄ MPy][Br]	1-Butyl-3-methylpyridinium bromide
[C ₄ MPy][OAc]	1-Butyl-3-methylpyridinium acetate
[ECOENG]	1,3-Dimethylimidazolium-dimethylphosphate
[EMIM][CH ₃ COO]/[Ac]	1-Ethyl-3-methylimidazolium acetate
[EMMIM][Ac]	1-Ethyl-3-methylimidazoliumacetate
[EMIM][BF ₄]	1-Ethyl-3-methylimidazolium tetrafluoroborate
[EMIM][DEP]	1-Ethyl-3-methylimidazolium diethyl phthalate
[HBIM][CH ₂ (OH)COO]	1-Butylimidazolium glycolate
[HBIM][CH ₃ CH(OH)COO]	1-Butylimidazolium lactate
[HEIM][CH ₂ (OH)COO]	1-Ethylimidazolium glycolate
[HEIM][CH ₃ CH(OH)COO]	1-Ethylimidazolium lactate
[HMIM][CH ₃ CH(OH)COO]	2-Methylimidazolium lactate
[HMIM][Cl]/[BF ₄]	1-Hexyl-3-methylimidazolium chloride/tetrafluoroborate
[HMIM][CH ₂ (OH)COO]	2-Methylimidazolium glycolate
[MMIM][MeSO ₄]	1-Methyl-3-methylimidazolium methylsulfate
[P14888][OAc]	Trioctyl(tetradecyl)phosphonium acetate
[P8888][OAc]	Tetraoctylphosphonium acetate

CHAPTER 1: INTRODUCTION

1.1 Introduction

Cellulose is a natural bio-polymer which is obtained from biomass. This type of polymer has been viewed as an environmental friendly and economically changing material. Cellulose possess massive industrial processes challenges because it lacks solubility with most conventional solvents as it has very strong inter and intra-molecular hydrogen bonding which leads to high degree of structural regularities and crystallinity [1-12].

The traditional organic solvents (DMAc/LiCl, N₂O₄/DMF, NMMO, DMSO/TBAF, etc.) which are used to dissolve the cellulose are highly reactive which compromise solvent recyclability, toxicity and therefore produces greater amount of waste [1, 11]. Recently, new green solvents known as ionic liquids (ILs) have been identified to be a good solvents for cellulose dissolution due to their high polarity [8, 10, 13].

Graenacher in 1934 published a patent suggesting that molten *N*-ethylpyridinium chloride could dissolve cellulose, [13] nonetheless, his study was treated just as an idea due to the little practical value of the molten salts back then [9]. Recently, those molten salts have been further investigated by various researchers and found not only to be good as greener solvents also as: electrolytes in batteries, lubricants, catalysts in synthesis etc. [14, 15].

The use of cellulose is becoming increasingly attractive since cellulose is readily available, non-toxic, cheap etc. and various materials can be produced from it as it is capable of chemical modifications [16, 17]. Modified cellulose can be applied in various fields such as in industrial chemicals as stabilizers, pharmaceuticals for drug delivery systems and biomedical technology for medical implant devices, water treatment for dyes adsorption, oil and gas for enhanced oil and gas recovery etc. [18].

1.2 Cellulose

1.2.1 Background of cellulose

Cellulose is a homo-linear polysaccharide which is formed from repetitive D-glucose units, that are linked through $\beta(1\rightarrow4)$ -glycosidic bond [19]. Cellulose has a molecular formula of $C_6H_{10}O_5$ and its degree of polymerization (DP) can be up to 10,000 or higher depending upon the raw materials [20]. Its linearity arises from the fact that it does not have side chains/branches (as illustrated in Figure 1.1), as a result, it exists in an ordered structure. Cellulose is semi-crystalline containing both crystalline and amorphous phases [21].

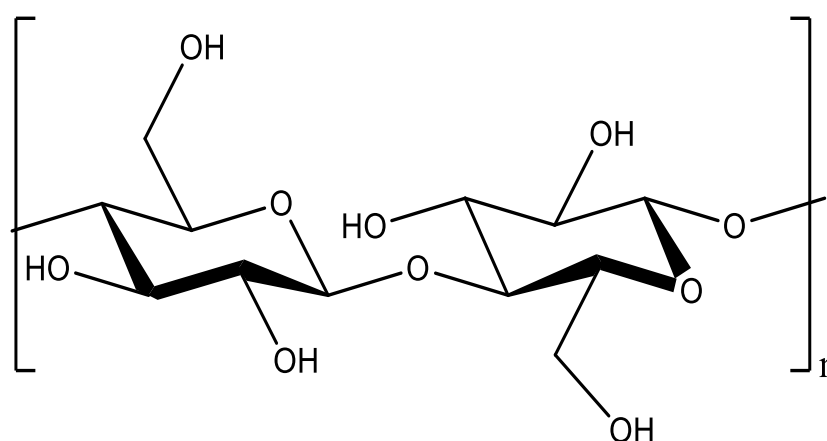


Figure 1.1 Structure of cellulose.

Cellulose has two types of OH^- groups (see Figure 1.1) one which is 1° at C-6 making it to be hydrophilic and two which are 2° at C-2 and C-3 which are hydrophobic making cellulose to be highly insoluble in water. Furthermore, the presence of very strong inter- and intra-molecular hydrogen bonding between cellulose linkages (as shown in Figure 1.2) limits cellulose solubility in most common solvents [21]. Lack of solubility of cellulose hinders its applications, so far cellulose has only been applied in fibers, paper membranes, tissues, polymers, paints, cosmetics and pharmaceuticals [22].

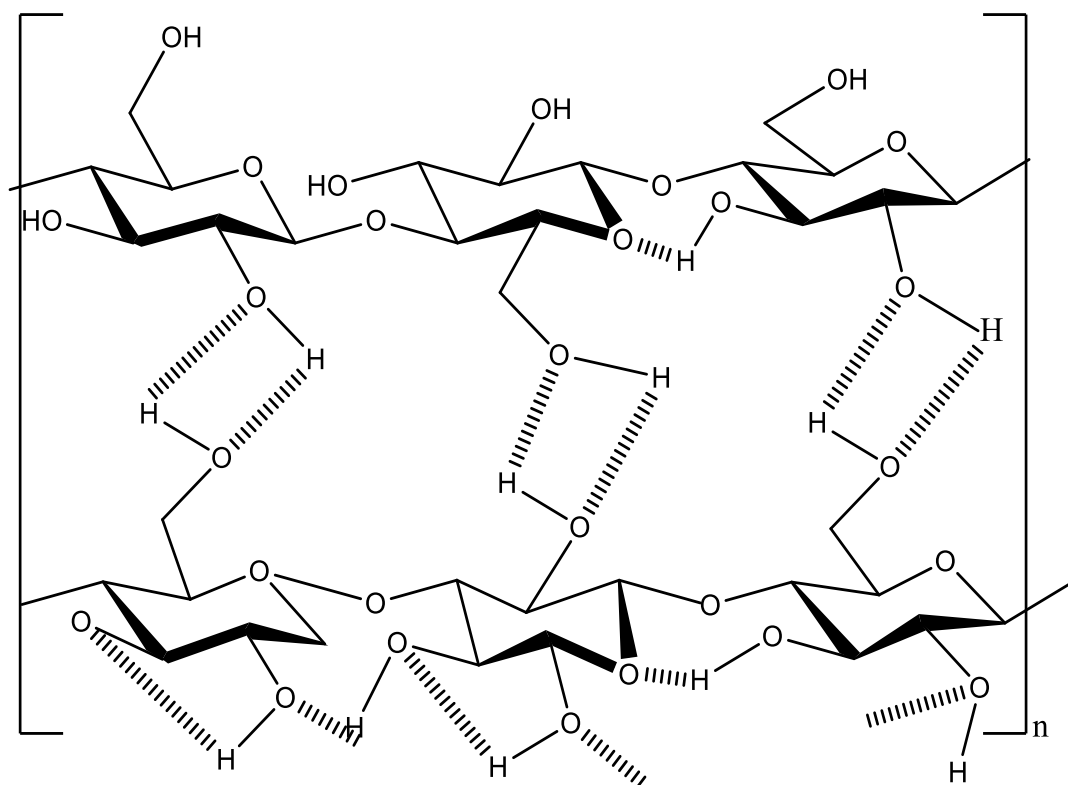


Figure 1.2 Multiple cellulose inter and intra molecular hydrogen bonding.

1.2.2 Types of cellulose

(a) Pulp

Pulp cellulose is a type of cellulose that is obtained from plants (wood chips) primarily gum trees (Eucalyptus) and they have high amount of cellulose [23]. These wood chips are then treated with acidic solution such as: sulphite (sulphurous acid + sulphur dioxide and water) or pre-hydrolysis kraft [24-26], to remove lignin, thus producing the wood pulp which contains more than 90% of cellulose [23]. Pulp cellulose is widely used in paper, tissue and clothing fiber [27].

(b) Microcrystalline / Avicel

Microcrystalline cellulose (MCC) is a type of cellulose which is highly purified and partially depolymerised, prepared by treating α -cellulose obtained from pulp with mineral acids [28, 29]. This type of cellulose is a fine, white and odourless crystalline powder, whose commercial products include Avicel®, Heweten®, Microcel®, Nilyn®, and Novagel® [30]. MCC is primarily used in pharmaceuticals; and applied in cosmetics, food industries and plastic processing industries [31].

1.2.3 Physical properties of cellulose

Cellulose is hygroscopic due to its primary hydroxyl group which is at C-6. However, this occurs under atmospheric conditions of 20 °C with at least 60% relative humidity, where it absorbs ca. 8-14% water [32]. However, cellulose is insoluble in water as well as in dilute acids due to its strong inter- and intra-molecular hydrogen bonding [8].

The multiple hydrogen bonding interactions between cellulose linkages causes it to be a semi-crystalline polymer having highly structured crystalline regions. The complex bonding makes cellulose to form materials with great tensile strength having no melting point and its degradation begins at 180 °C [3, 8, 23]. Microcrystalline-cellulose has been reported to have a density of 0.6 g/mL at 25°C and pH of 5-7 (11 wt. %) [SIGMA-ALDRICH®].

1.2.4 Cellulose dissolution

Methods which are currently in place for the cellulose treatment suffer from various drawbacks like: high volatility and very high dissolution temperature [2, 3], which also, destroy the cellulose structure and also generate great amount of waste [33, 34], e.g. in viscose processes 2 kg of waste is produced for every 1 kg of cellulose generated [35]. The second famous industrial cellulose solvent is *N*-methylmorpholine-*N*-oxide (NMMO), which is thermally unstable and requires major investments in industrial safety [36]. NaOH/water which can be

used with and also without urea as well as thiourea is also a non-green solvent for cellulose [37], NaOH allows dissolution of cellulose only with low molecular weight and due to this fact, it has never been applied commercially [38, 39]. Other non-green solvents which are used for cellulose processing include: lithium chloride/N,N-dimethylacetamide, (LiCl/DMAc) [40, 41], ammonium fluorides/dimethyl sulfoxide [42], and mixtures of ammonia or ethylenediamine and thiocyanate salts [37]. There are newly synthesized solvents which are known as ‘Ionic Liquids (ILs)’. ILs were introduced to cellulose processing by Swatloski *et.al.* [9] and were found to have enormous ability to dissolve cellulose directly without causing major structural deformation, in addition, to being environmental friendly solvents.

1.3. Ionic liquids

1.3.1 Background of ionic liquids

ILs are defined as the molten organic salts with low melting point below 100 °C, which consist of inorganic or organic anions and organic cations [43-46]. Although they were identified from late 1970’s [47], their usage and impact started to be studied around 1990’s [48]. ILs are incredibly tunable since the ionic structure would allow more than 10¹⁴ anion and cation combinations [49, 50] thus giving ILs better properties than common molecular solvents some of which are listed below [51, 52]:

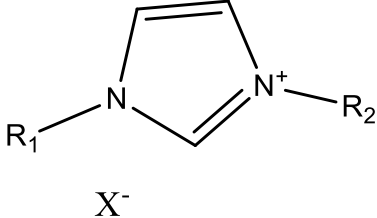
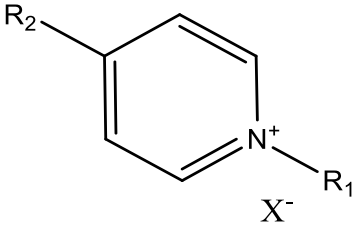
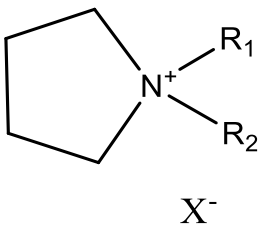
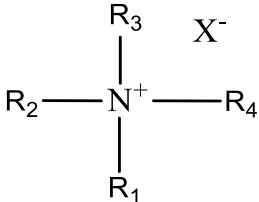
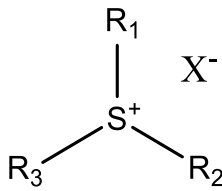
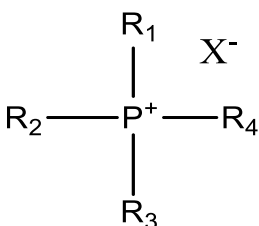
- Highly polar.
- Made up of loosely coordinating bulky ions.
- Very low vapor pressures.
- High thermal stability.
- Great electrochemical properties which is: thermal conductivity and huge electrochemical window.
- Immiscible with many organic solvents.

- The physical and chemical properties of ILs can be controlled by changing the anion and cation combinations.

These properties make ILs to be ideal solvents in all fields of chemistry, including organic, electro, physical, analytical and green chemistry and also in green technology [51, 53].

ILs are available in various categories; those which are liquid at room temperature are said to be ‘room temperature ionic liquids’ (RTILs). RTILs are liquid because they are composed of polyatomic, bulk, asymmetric organic cations and charge-diffuse ions [33, 53]. Furthermore, their ions are not packed well at room temperature; hence they remain liquids [48, 54]. RTILs are made up of: imidazolium, pyridinium, pyrrolidinium, ammonium, sulfonium and phosphonium organic derivatives cations (See Table 1.1 for graphics) with various anions such as: bromide, chloride, acetate, tetrafluoroborate, nitrate, triflate and etc. [55-59].

Table 1.1 Structures of various types of RTILs cations.

Cation	Structure
Imidazolium	
Pyridinium	
Pyrrolidinium,	
Ammonium	
Sulfonium	
Phosponium	

R represent Alkyl chain, X⁻ represent anion, N represent nitrogen, P represent Phosphorus and S represent Sulfur

RTILs are considered to be ‘designers solvents’ since ILs physicochemical properties are easily altered simply by just varying the structure of component ions, [55, 60]. This allows a researcher to tailor ILs both physical and chemical properties by changing different types and sizes of the anion or cation, i.e., one can use same cation by varying the alkyl chain length or use relatively small anion and the resulting IL can be used for almost any application in the field of chemical sciences [48, 61].

1.3.2. Physical properties of ILs

ILs physical properties have several advantages over those of molecular liquids [51, 60, 62] such as:

- low melting point $<100\text{ }^{\circ}\text{C}$.
- high viscosity ranging from 10Cp to over 500 Cp.
- low density generally $1.0\text{ to }1.69\text{ g.cm}^{-3}$.
- high refractive index.
- high surface tension which is less than that of H_2O but higher than that of n-alkane (72.7 N m^{-1} at $20\text{ }^{\circ}\text{C}$).
- low vapor pressure which is usually negligible.
- high conductivity.
- high electrochemical window usually (2 to 4.5)V.

1.3.3 Applications of ILs

Properties listed above are highly influenced by the nature and structure of the cation and anion properties [51, 60]. In the meantime, ILs ions influence the ion-ion interactions, such as Van der Waals interactions and hydrogen bonding [63] thus giving ILs high polarity and high electrical conductivity allowing ILs to be able to be used in various areas of sciences and technology [45, 50, 64] such as:

- Solvents for separation technology, manufacturing of nano-materials etc.
- Electrolytes in batteries.
- Lubricants.
- Plasticizers.
- Catalysts.
- Extraction.

ILs are fundamentally researched using thermophysical and thermodynamic properties. Those properties give strong information on ILs pure and their mixtures which is important to the industrial application in separation processes such as extraction, petroleum refining; oil recovery and etc. [65].

1.4 Thermophysical properties of mixtures

Thermophysical properties are temperature dependent physical properties which include: density, viscosity, refractive index and sound velocity, heat capacity, thermal expansion surface and interfacial tension in fluids etc. Thermophysical properties provide valuable information used to understand the fundamental knowledge of the solution chemistry [66]. In most cases, scientific research have needs of the thermophysical properties. Recently thermophysical properties have been utilized to investigate the physicochemical properties of pure and mixed liquids both in academia and in industrial research [67]. In addition, thermophysical properties information have abundant industrial applications such as: surface facilities, pipeline systems, heat transfer, mass transfer, and fluid flow. [46, 55, 68-73], and in various industries [74] such as:

- Chemical; for the design of separation processes,
- Pharmaceutical and polymer; for solvent selection and emission,
- Petroleum refining; for flow assurance and oil recovery,

- Biotechnology; for the origin of many diseases is traced to aggregation of proteins and several protein separations.

Furthermore, thermophysical data can be used to derive thermodynamic properties data such as: apparent molar volume, apparent molar adiabatic compressibility limiting apparent molar volume, limiting apparent molar expansibility, deviation in refractive index, deviation in viscosity, deviation in isentropic compressibility, excess molar volume, excess Gibbs free energy, isentropic compressibility etc. Thermodynamic properties are useful in relation to providing information concerning intermolecular interactions at microscopic level which occurs between or amongst unlike/like molecules [75-77].

In addition, thermophysical and thermodynamic properties also provide information concerning solvent-solvent, solute-solute and solute-solvent interactions between the ions of ILs solvent, solute molecules or solvent of the binary or ternary liquid mixtures which are required for the scientific community [78-85].

1.5 Aim and objectives

1.5.1 Aim

The aim of this project was to investigate the influence of DMF on cellulose dissolution using ionic liquids.

1.5.2 Objectives

The objectives of this project were to:

- carry out dissolution process of cellulose using [BMIM][Cl], [AMIM][Cl] and [BMPy][Cl] and also a co-solvents of ILs-DMF mixtures: [BMIM][Cl]/DMF, [AMIM][Cl]/DMF and [BMPy][Cl]/DMF.

- investigate the properties and morphology of the regenerated cellulose using FTIR, XRD, SEM, TGA and DSC techniques and compare the results with those of the pure cellulose.
- compare the results of the regenerated cellulose previously dissolved in [BMIM][Cl], [AMIM][Cl] and [BMPy][Cl] with the ones previously dissolved in [BMIM][Cl]/DMF, [AMIM][Cl]/DMF and [BMPy][Cl]/DMF.
- study the interactions occurring between cellulose and ILs.
- confirm the dissolution process using thermophysical properties; density, ρ , sound velocity, u , and refractive index, n_D .

1.6 Outline of the chapters in the dissertation

Chapter 1 gives the contextual information behind this research, the background of cellulose, ionic liquids and thermophysical properties as well as aims and objectives.

Chapter 2 gives a summary of the literature information related to this research. The literature information covered is: solvents which are used in cellulose processing, new promising solvents for cellulose (ILs and ILs/co-solvents) and also some of the functionalized cellulose applications.

Chapter 3 is devoted to the description of the experimental methods used.

Chapter 4 presents all of the experimental results obtained. The results covered are from FTIR, XRD, SEM, TGA, DSC and thermophysical properties (density, ρ , sound velocity, u , and refractive index, n_D). These results are illustrated in the form of tables, graphs and image. Chapter 4 also gives the discussions of the results obtained.

Chapter 5 gives a summary statement of the work which was done, the results obtained and recommendations for the future studies.

CHAPTER 2: LITERATURE REVIEW

2.1 Cellulose solvents

From 1838 when cellulose was discovered by Paven [86] there has been tremendous amount of research on cellulose chemistry using various solvents and analytical techniques. After the first industrial solvent (viscose) was found, the research advanced in search of new cellulose industrial solvent with very low or non-environmental problems [86]. These solvents have been characterized as: derivatising and non-derivatising solvents. Both of these solvents break down the prevailing strong hydrogen network of cellulose resulting in formation of a homogeneous cellulose solution [13, 16], (see Figure 2.1 which illustrates the classification of the cellulose solvents) [87, 88].

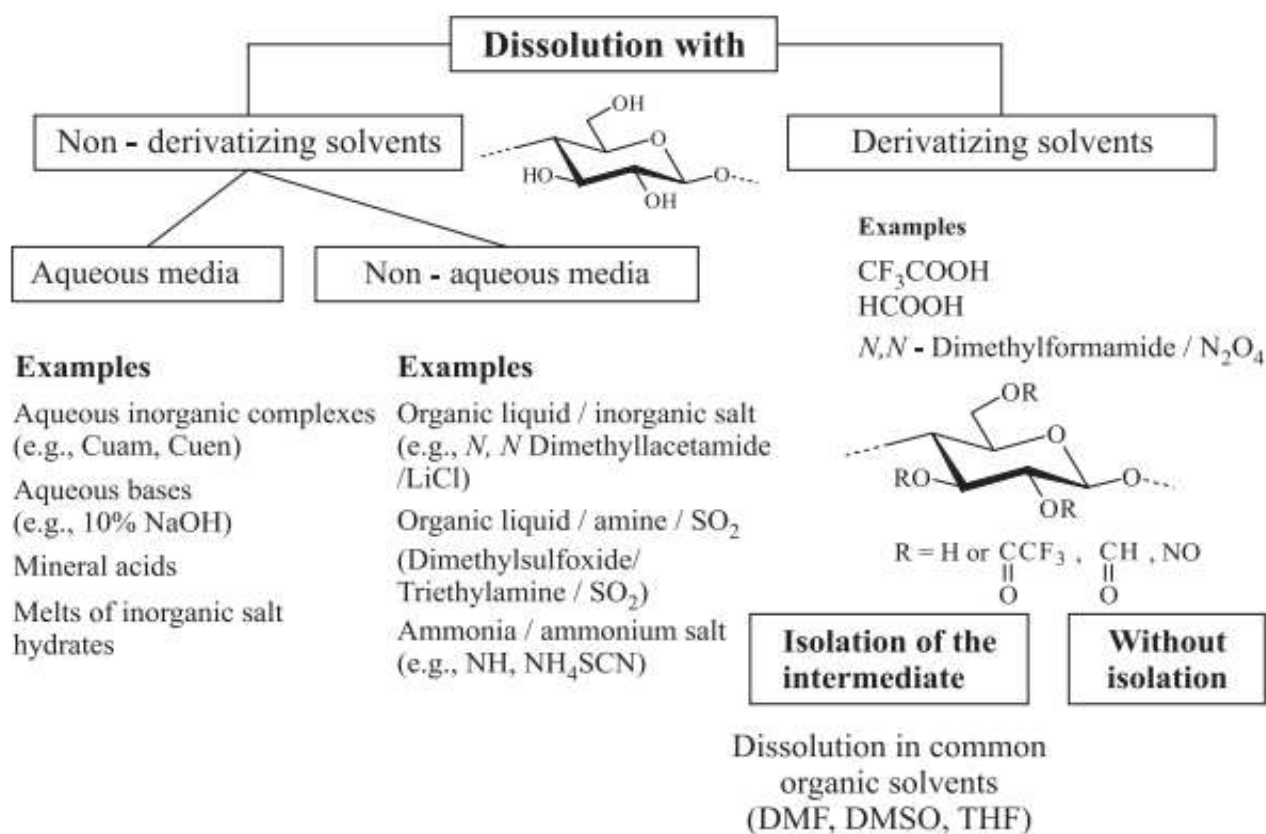


Figure. 2.1 Classification of cellulose solvents. Reproduced from Heinze and Koschella [89].

2.1.1 Derivatising solvents

These are solvents which dissolve cellulose by the process of covalent modification and in the process there is formation of unstable ether, ester and acetal derivatives [89, 90]. Klemm *et.al.* [90] indicated that “cellulose interactions with the solvent on molecular level is fairly defined and understood”.

The regeneration of the cellulose (the removal of the functional groups produced during dissolution process) is carried out by simply changing the pH of the solution or changing medium (from non-aqueous to aqueous) [89].

The drawbacks of these types of solvents include lack of reproducibility caused by side reactions which leads to unidentified side structures, however some of these solvents have been found to be very efficient [88].

2.1.2 Non-derivatising solvents

Non-derivatising solvents dissolve cellulose directly without any chemical reactions simply by disrupting the strong inter- and intra-molecular hydrogen-bonding network [9, 34, 88, 89, 91, 92] and the regeneration process involves the re-formation of the cellulose hydrogen bonding. These types of solvents are aqueous inorganic compounds such as: transition-metal complexes, salt hydrates, mineral acids and mixtures of organic solvents with inorganic salts e.g., organic liquids with amines and sulphur dioxide, also mixtures of ammonia and ammonium salts [93], organic/non-aqueous solvent systems and also ionic liquids.

These solvents are considered to be worthy solvents for cellulose processing; however they have their own drawbacks such as: high reactivity which causes side reactions and the solvent recyclability which causes toxicity to become flimsy [38, 87].

Non-derivatising solvents can be grouped into two classes: conventional solvents and ionic liquids.

2.1.2.1 Conventional solvents

These are types of cellulose solvents that include aqueous and organic solvent systems

2.1.2.1.1 Aqueous solvent systems

Aqueous solvents consist of inorganic salts and complex compounds, which can be used to dissolve cellulose. The widely reported [36] complexes are cuprammonium hydroxide (Cuam) and cupriethylenediamine hydroxide (Cuen) [40]. Aqueous solvents systems used some aqueous solvents include: 1,2- ethylenediamine cadmium hydroxide (Cadoxen), nickel ammonium hydroxide (Nioxam), tri-aminoethyl- amine nickel hydroxide (Nitren), ethylenediamine palladium hydroxide (Pd-en), guanidinium hydroxide (GuOH), Tetraethylammonium hydroxide (TEOH) etc. Metal complexes solvents have very strong interactions however, they are considered as non-derivatising solvents because they do not form covalent interactions with the polymer [36]. Aqueous solvents also include molten salt hydrates as well as alkali hydroxides such as: magnesium chloridehexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), lithium chloridepentahydrate ($\text{LiCl} \cdot 5\text{H}_2\text{O}$), lithium perchlorotrihydrate ($\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$), zincchloridetetrahydrate ($\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$) [40, 41] NaOH and LiOH [89].

2.1.2.1.2 Organic/non-aqueous solvent systems

Organic/non-aqueous solvent systems are water free solvents that consist of more than one component such include 1,3-dimethyl-2-imidazolidinone/lithium chloride (DMI/LiCl), N,N-dimethylacetamide/lithium chloride (DMA/LiCl) [94, 95], dimethyl sulfoxide/calcium chloride (DMSO/CaCl), N-methylpyrrolidone/lithium chloride (NPM/LiCl) [89] etc.

The extreme used organic solvent in cellulose fiber processing is monohydrated N-methylmorpholine-N-oxide (NMMO) in the lyocell process [44, 45]. NMMO is a direct solvent for cellulose that in the process it does not cause any derivatization. NMMO dissolves cellulose due to its strong N-O dipole [96]. The major drawback is poor thermal stability of NMMO which requires huge investment in the industrial safety measures [97, 98].

2.1.2.2 Ionic liquids in cellulose chemistry

The documentary of ILs in cellulose chemistry dates back to 1934, when Graenacher [13] theorized that “molten N-ethylpyridinium chloride could be used to dissolve cellulose”. Thereafter, in 2002, Swatloski *et.al* [9] became the first researcher to put Graenacher theory into practice [9] and studied cellulose dissolution process using various ILs. He obtained positive results with [BMIM][Cl] able to dissolve 25 wt% of cellulose when the solution is heated by microwave oven, in addition, his results also show that not all ILs anion types are suitable for the dissolution process.

There is an enormous amount of ILs having different properties. However in order for an ionic liquid to be suitable solvent for cellulose, it should have the following properties [97]:

- low melting point with a high decomposition point.
- should not cause cellulose decomposition.
- the cellulose solution should be stable and storable.
- the cellulose regeneration process should be easy.
- ILs recovery should be cost-effective and uncomplicated.
- be non-toxic and have a very low vapor pressure.

2.2 Cellulose dissolution

2.2.1 Cellulose dissolution using ionic liquids

The first article indicating the dissolution process of cellulose in ILs was published in 2002 by Swatloski *et al.* [9] in which ILs containing $[C_4MIM]^+$ cation were examined with wide range of anions including: Cl^- , Br^- and SCN^- . ILs having anions with $[BF_4]^-$ and $[PF_6]^-$ could not dissolve cellulose while those which could dissolve it, their dissolution rates could significantly be increased by heating using a microwave oven. The morphology of the regenerated cellulose depended on the type of IL as well as the precipitating agent used.

Dissolution of cellulose and cellulose oligomers in IL solutions were studied by Moulthrop *et. al* [99]. These celluloses were dissolved in $[BMIM][Cl]$ and the dissolution process was studied using ^{13}C NMR. The results revealed that cellulose oligomers are disordered in IL solutions like in aqueous solution, in addition this behavior was conserved for cellulose results.

The dissolution of cellulose with different degrees of polymerization (DP) was investigated by Kosan *et al.* [6] using $[BMIM]Cl$ at 358.15 K. The results revealed that the DP of cellulose also influenced both the dissolution process and the rate since cellulose with a DP of 569 had a solubility of 13.6 (wt%) dissolved at 358.15 K and the one with cellulose DP of 454 its solubility was 13.4 (wt%) and its dissolution temperature was much lower than that one of 569.

The dissolution and regeneration of microcrystalline obtained from cotton linters was examined by Zhang *et. al.* [12] using $[AMIM][Cl]$. It was found to dissolve cellulose rapidly at temperature of 60 °C and with addition of stirring, more cellulose dissolved. Cellulose having a DP of 650 was found to dissolve in $[AMIM][Cl]$ within 30 minutes. In addition, they also reported that $[AMIM][Cl]$ was easily recycled due to its thermo-stability and non-volatility.

Moreover, [AMIM][Cl] could not dissolve cellulose at room temperature, instead it caused only swelling.

The dissolution of cellulose in [AMIM]⁺ carboxylates anions at room temperature was investigated by Zhang *et al.* [100]. The anions investigated were: [HCOO]⁻, [CH₃COO]⁻, [CH₃CH₂COO]⁻, [CH₃CH₂CH₂COO]⁻, [HOCH₂COO]⁻, [CH₃CHOHCOO]⁻ and [C₆H₅COO]⁻. Solvatochromic UV/vis probe and ¹³C NMR that were used to study the dissolution process revealed that, cellulose dissolution process depend on the type of the ILs anion since, cellulose was highly soluble in [AMIM]⁺ with [CH₃CH₂COO]⁻ and not soluble in [AMIM]⁺ having [HOCH₂COO]⁻, [CH₃CHOHCOO]⁻ and [C₆H₅COO]⁻ anions. Furthermore IL cations were found to have a substantial contribution to the dissolution process, although, hydrogen bonding between the IL anions and cellulose were found to be predominant.

[C₄MIM][Cl], [C₄MPY][Cl] and BDTAC were investigated for cellulose dissolution ability having DP the range of 290-1200 by Heinze *et.al* [4]. It was found that the wt% of cellulose solubility decreased as the DP increased, moreover, the degree of solubility also depended on type of the cellulose and the solubility range in the manner: [C₄MPY][Cl] > [C₄MIM][Cl] > BDTAC. Furthermore, the carbomethylation process was also investigated and the results obtained showed that [C₄MIM]Cl could be used without any addition of the base and the cellulose acetate obtained could not be dissolved in acetone. In addition, 100% of [C₄MIM]Cl was able to be recycled since there were no by-products. However, [C₄MPY][Cl] could not be used as a reaction medium of cellulose carbomethylation since, [C₄MPY][Cl] and reagents were destroyed during the reaction. BDTAC was not studied further since it could dissolve small amount of cellulose and cellulose acetate was synthesized without addition of any base.

The solubility of cellulose in various types of ILs was investigated by Lee *et.al* [7] under the same atmospheric conditions. The results were: [MMIM][MeSO₄] with >50, [BMIM][CF₃SO₃] >50, [EMIM][CH₃COO] >30, [AMIM]Cl >30, [BMIM]Cl = 10, [BzMIM]Cl = 10, [BMIM][BF₄] = 4, [BMIM][PF₆] < 1 and [EMIM]Ac >30. All solution were measured using wt% at 363.15 K in 24h incubation.

Kilpeläinen *et. al* [5] studied the dissolution process of lignocellulosic materials obtained from wood using various imidazolium-based ionic liquids at temperatures around 367.15 K. The solubility of between 2-10 wt % was obtained.

The effect of the alkyl chain length varying from ethyl to decyl on the solubility of cellulose using 1-alkyl-3-methylimidazolium based ILs having Cl⁻ counter ion was studied by Erdmenger *et.al* [1] and found that methylimidazoliums with even number of carbons have high solubilizing power than the ones with odd number of carbons. Furthermore, the solubility of cellulose was found to decrease as the alkyl chain length increased. The recycling of the ionic liquids were accomplished in two ways, (1) use of acetonitrile, where trityl chloride is not soluble, (2) by filtrations since when trityl chloride is treated with water it is converted to triphenyl methanol which is hydrophobic and hence can easily be filtered.

Zavrel *et.al* [11] screened a wide range of ILs to determine which one was the most effective in dissolution of (Ligno-)cellulose. ILs tested were: [HEMIM][BF₄], [ECOENG], [AMIM][Cl], [BMIM][Cl], [Br], [PF₆], [I], CH₃SO₃/ [BF₄], [BMPY][Cl], [BMPL][Cl]/ [BTI], [EMIM][Ac]/[Cl]/[C₂H₅OSO₃]/[BF₄], [HMIM][Cl]/[BF₄], [OMIM][Cl] and [TBPM][Cl]. Amongst those ILs [EMIM][Ac] was found to be the most effective in dissolving cellulose, besides, [AMIM][Cl] was effective for hard wood as well as soft wood. Furthermore, the morphology of the regenerated cellulose using water was found to be altered.

The dissolution of cellulose which was extracted from red oak tree and southern yellow pine using [EMIM]Ac was investigated by Sun *et.al* [8] at same temperature of 383.15 K under same duration of heating 16h. Southern yellow pine cellulose had low solubility compared to red oak.

Dadi *et.al.* [101] investigated the hydrolysis kinetics of the regenerated cellulose previously dissolved in [BMIM][Cl]. The dissolution process was carried under nitrogen atmosphere to avoid the up taking of moisture since water is an anti-solvent for cellulose, while the regeneration of the cellulose fibers was carried out using deionized water, methanol and ethanol. The hydrolysis kinetics as well as the structure of untreated and regenerated cellulose were examined using XRD.

Imidazolium based ionic liquids were investigated for extended dissolution of cellulose by Vits *et al.* [10]. The results obtained were remarkable as they showed the existence of an odd–even effect on different alkyl side-chain lengths of the imidazolium chlorides whereas bromides did not show any resemblance. Furthermore, the best IL found, was [EMIM][DEP] for cellulose dissolution amongst the studied imidazolium based ILs. In addition, no color change was observed using microwave irradiation for the dissolution process.

Fukaya *et.al* [3] studied the dissolution of microcrystalline cellulose in 3 similar alkyl-imidazolium based ILs having anion: [MeOSO₃], [EtOSO₃] and [(MeO)₂PO₂], and cation [C₂MIM]. The MCC used had a DP of 200-250. [C₂MIM][(MeO)₂PO₂] was found to dissolve cellulose without derivatization. In addition, those polar RTILs were found to be able to dissolve cellulose only by stirring at room temperature.

Fukaya *et.al* [2] examined the dissolution of various polysaccharides in ionic liquids that are low viscous, polar and halogen-free which were [AMIM][HCO₂] and [AEIM][HCO₂]. The solubility of those polysaccharides were: pectin<xylan<cellulose<amylose<inulin< dextrin.

The effects of six different types of imidazolium protic ionic liquids having glycolate and lactate anions; ([HMIM][CH₃CH(OH)COO], [HEIM][CH₃CH(OH)COO], [HBIM][CH₃CH(OH)COO], [HMIM][CH₂(OH)COO], [HEIM][H₂(OH)COO], [HBIM][CH₂(OH)COO]) were investigated by Meenatchi *et. al* [102] on cellulose dissolution. The results obtained revealed that the type of cation also plays a role in the solvation process. The acidic protons increased the solubility rate by forming hydrogen bonds with the oxygen of the hydroxyl as well as the ether oxygen of the cellulose. Furthermore, the regenerated cellulose was found to have lower thermal stability than the original cellulose since it was transformed to cellulose II from the original cellulose (cellulose I).

Pyridinium-based ionic liquids ([C_nMPy][Cl], where n= 2–10, [AMPy]Cl, [C₂MPy]Br, [C₄MPy]Br and [C₄MPy][OAc]) were investigated for cellulose dissolution by Sashina *et.al* [43]. The obtained results revealed that increase in alkyl chain length at the pyridinium cation decreased the interaction energy as well as the change of the anion Cl[−] to Br[−], leading to decrease in dipole moment values of the ion pairs.

Xu *et.al* [103] investigated effects of anionic structure on cellulose dissolution using 1-N-butyl-3-methylimidazolium cation, with the following anions: [CH₃COO][−], [HSCH₂COO][−], [HCOO][−], [(C₆H₅)COO][−], [H₂NCH₂COO][−], [HOCH₂COO][−], [CH₃CHOHCOO][−] and [N(CN)₂][−], as well as the effects of the lithium salts addition. The results showed that the cellulose solubility increased almost linearly with increasing hydrogen bond accepting ability of anions in the ionic liquids and the addition of the lithium salts also increased the solubility of the cellulose. Furthermore, the regenerated cellulose had decent thermal stability.

Sescousse *et.al* [37] studied the viscosity of the microcrystalline cellulose solution prepared from [EMMIM][Ac] or [BMIM][Cl], in which the intrinsic viscosity was also calculated using Flory Huggins equation. The results revealed that the cellulose intrinsic viscosity was not the

same for both solvents and it decreased as temperature increased, hence both solvents had similar thermodynamic quality that decreased as temperature increased.

Theoretical studies on cellulose dissolution mechanism was done by Zhen *et.al* [104] as well as experimental investigation using [EMIM][Ac]. The theoretical simulation was performed using density functional theory (DTF) and atoms in molecules (AIM) theory calculations, moreover, (1,4)-dimethoxy- β -D-glucose (Glc) was used as the model for cellulose. The theoretical studies showed that [EMIM][Ac] had a stronger bond than Glc-Glc bond which suggested that it was a possible cellulose solvent and this theory was confirmed by experimental studies. In addition, the regenerated cellulose was converted to cellulose II since the original/starting cellulose was cellulose I.

Allyl ammonium acetates and series of substituted morpholinium ionic salts were synthesized and studied for cellulose dissolution ability by Raut *et.al* [22]. These ILs were: [AMMorp][OAc], [AMMorp]₃[PO₄], [AMMorp]₂[CO₃], [BMMorp][OAc], [BnMMorp][Cl], [ATBA][OAc], [ATEA][OAc], [ATMA][OAc], [A₄N][OAc] and [ADMAP][OAc]. Amongst those ILs only [AMMorp][OAc] could dissolve cellulose, furthermore [AMMorp][OAc] was studied to see how it would dissolve cellulose of various degree of polymerization. The results showed that as DP increased the solubility wt% decreased as this was observed by DP of 789 dissolved 30 wt%, DP of 1644 dissolved 28 wt% and DP of 2082 dissolved 25 wt%. The regenerated cellulose was characterized using SEM, TGA, XRD, FTIR and CP/MAS ¹³C NMR.

Thermophysical properties (density, viscosity, refractive index, isobaric thermal expansivity and heat capacities) of cellulose were determined by Freire *et.al* [105] using [C₂MIM]⁺ cation with 8 different types of anions:[SCN]⁻, [(OCH₃)₂PO₂]⁻, [CH₃CO₂]⁻, [CH₃SO₃]⁻, [Tos]⁻, [CH₃OHPO₂]⁻, [N(CN)₂]⁻ and [CF₃SO₃]⁻. Density, viscosity, and refractive index were

investigated as a function of temperature and isobaric thermal expansivity and heat capacities were investigated at a constant temperature. Amongst the studied anions, $[\text{CH}_3\text{CO}_2]^-$ was found to have the best cellulose dissolution properties having low viscosity as well as low density-favorable properties.

A theoretical study of cellulose crystal dissolution in imidazolium-based ILs was conducted by Uto *et.al* [106]. They studied a wide range of ILs which were: $[\text{AMIM}]^+$, $[\text{BMIM}]^+$ and $[\text{EMIM}]^+$ with anions $[\text{Cl}]^-$, $[\text{Br}]^-$ and $[\text{OAc}]^-$. To gain deep mechanistic insights, a molecular dynamic (MD) approach was utilized. The results showed that amongst the studied ILs $[\text{AMIM}][\text{Cl}]$ was the most powerful solvent for cellulose dissolution followed by $[\text{BMIM}][\text{Cl}]$ then $[\text{BMIM}][\text{Br}]$. Furthermore, the obtained results also showed that both anion and cation of great dissolving power play a role in stepwise breakage of hydrogen bonds between cellulose chains while for poor solubilizing ILs the effect was the reverse.

2.2.2 Cellulose dissolution using both ionic liquids and their co-solvents

Rinaldi [107] studied the dissolution of cellulose in the organic electrolytes solutions. The organic electrolyte solution was composed of: $[\text{BMIM}][\text{Cl}]$ and ,3-dimethyl-2-imidazolidinone (DMI). The solvents system $[\text{BMIM}][\text{Cl}]/\text{DMI}$ was found to have better dissolution properties than LiCl/DMI and $\text{LiCl}/\text{N,N-dimethylacetamide}$ since LiCl solvents were capable of dissolving only 2 wt% of cellulose under harsh conditions, whereas $[\text{BMIM}][\text{Cl}]/\text{DMI}$ could dissolve 10 wt% easily in few minutes. Furthermore, when $[\text{BMIM}][\text{Cl}]$ was replaced with $[\text{EMIM}][\text{Ac}]$ the dissolution was instantaneous and dissolved a large amount of cellulose.

Molecular dissolution process of cellulose using $[\text{EMIM}][\text{OAc}]$ and DMF was studied by Rein and colleagues [108], using cryo-TEM, SLS, XRD, electrical conductivity and small angle neutron scattering (SANS) for characterization. From the results, it was found that using a co-solvent to dissolve cellulose at 90 °C the process took no more than five (5) minutes. The

electrical conductivity results were high since more anions were available for interaction in the solution, in addition, SLS and SANS measurements showed no evidence of molecular aggregation.

Theoretical studies were performed by Zhao *et.al* [109] to understand the interaction of the cellulose dissolution using Imidazolium-based Ionic Liquids with the various co-solvents (DMSO, DMF, H₂O and CH₃OH). When the portion of the co-solvent was included in the system, the energy alteration in the electrostatic portion was greater than van der Waals portion which suggested that the co-solvent had an impact on hydrogen bonding between anions and cellulose hydroxyl oxygen. Furthermore, the interaction of cellulose, increased when DMSO or DMF was added to the ionic liquid and decreased when CH₃OH and H₂O were added, therefore protic solvents are non-solvents and aprotic solvents increase cellulose solubility in the ILs system.

The impact of the organic solvent (DMSO) in cellulose dissolution behavior using ILs was researched by Xu *et.al* [110]. In that study, the insights into the alkyl chain length of the imidazolium cation were revealed. ILs used were: [C₂MIM][CH₃COO], [C₄MIM][CH₃COO], [C₆MIM][CH₃COO] and [C₈MIM][CH₃COO] together with DMSO as a co-solvent. It was observed that, after DMSO was added into cellulose ILs solution, cellulose became readily soluble and as the alkyl chain length of the imidazolium cation increased cellulose solubility also increased, moreover when the cation is [C₆MIM]⁺, cellulose solubility starts to decrease. This was due to the steric hindrance of the hydrogen bond formation between cellulose hydroxyl and ionic liquid anion, which lead to hydrophilicity of the imidazolium cation decreasing, hence cellulose solubility decreased.

[C₄MIM][CH₃COO]/DMF solvent system was developed and investigated for possible cellulose dissolution by Xu [111] and his group. It was found that cellulose gradually dissolved without heating in [C₄MIM][CH₃COO]. The dissolution mechanism was explained in terms of DMF partially dissociating [C₄MIM][CH₃COO] into free ion and anion [CH₃COO]⁻ which readily interact with cellulose hydroxyl's. Further, as amount of DMF increased the solubility of cellulose also increases. Moreover, FTIR indicated that there was no formation of a new chemical bond between cellulose and [C₄MIM][CH₃COO]/DMF. XRD showed that the original cellulose (cellulose I) were transformed into cellulose II after regeneration. Furthermore, DP examinations were almost the same as the original cellulose hence the cellulose chain structure was hardly affected during the dissolution and regeneration process.

Xu and Zhang [112] studied the insights of the dissolution mechanism of [C₄MIM][CH₃COO]/DMSO solvent system with cellulose using ¹³C NMR and found that during cellulose dissolution process [C₄MIM][CH₃COO] dominates cellulose dissolution whereas in DMSO, its function is to dissociate the ion pairs of [C₄MIM][CH₃COO] into free ions (solvated cations and free anions). Furthermore, the hydrogen bonding interaction of [C₄MIM][CH₃COO] with cellulose hydroxyl oxygen was weaker than in [C₄MIM][CH₃COO]/DMSO.

Bengtsson, [113] conducted a study to evaluate the recyclability and suitability of tetrabutylammonium acetate:dimethyl sulfoxide ([TBA][Ac]:DMSO) as a solvent for cellulose with her group. That study was done by evaluating the efficiency of [TBA][Ac]:DMSO solvent system in the dissolution of cellulose. It was found that TBAAc was an efficient solvent for cellulose. Further, if more of TBAAc was added to the solution more cellulose dissolved. In addition, this solvent system could also tolerate small amounts of non-solvents such as water.

Theoretical and experimental studies about the effects of the co-solvent: DMSO on the dissolution rate of cellulose with [C₄C₁IM][OAc] were performed by Andanson and colleagues [114]. The results showed that, by adding more DMSO in the ILs + cellulose solution the viscosity of [C₄C₁IM][OAc] did not increase and the viscosity of the solution decreased. Furthermore, the slight decrease in conductivity was observed when more DMSO was added to the system and that was because when more DMSO was added, the number of charges was not increased, instead it accelerated significantly.

Holding *et.al* [115] conducted a study to investigate phosphonium-based ionic liquids and cellulose with DMSO. Using [P14888][OAc] and [P8888][OAc]. The feasibility of these ILs was studied as well as dissolution and regeneration. The recyclability of these ILs was studied using liquid-liquid equilibria of the ternary systems. After regeneration of cellulose, the yield was 99%. Only 60% of the IL was recovered from ionic liquid-rich organic phase using the liquid-liquid separation and the other 37% of the IL recovered was from cellulose purification, making the total to be 97% of the recovered IL.

Lv *et.al.* [116] investigated the rheological properties of cellulose in [AMIM][Cl] and [BMIM][Cl] with DMSO as a co-solvent. The concentration range of the cellulose was from 0.07 to 6.0 wt. %. The results of viscosity decreased exponentially when DMSO was added in the concentration of range 0-100 wt. %. Furthermore, cellulose morphology was not altered by the addition of the DMSO at all concentrations.

The effect of DMSO on dissolution process of ground eucalyptus wood with [EMIM][OAc] was investigated by Wu *et.al* [117]. The study was conducted using wood since cellulose is the primary material of the plant cell walls. XRD was used to characterize the regenerated cellulose. DMSO was found to have increased the solubility rate and also help to reduce the

degradability of both cellulose and ionic liquid. In addition, Wu [118] illustrated that the proper use of DMSO could overall improve the cost effectiveness of the bio-refining process.

Tetra(n-butyl)ammonium Hydroxide/Dimethyl Sulfoxide (TBAH/DMSO) was studied by Chen *et al.* [118] in the dissolution of cellulose with and without water. TBAH/DMSO was found to have dissolved cellulose within 5 minutes at room temperature and the regenerated cellulose was converted into amorphous phase. This was confirmed by XRD, FTIR, TGA and DP analyses.

Huo *et.al* [119] investigated the impact of co/antisolvent in dissolution process of cellulose using [BMIM][Cl], [EMIM][Cl] and [OMIM][Cl]. This was a theoretical study which was conducted by molecular dynamics simulations (MDS). The density and pair energy distribution (PEDs) results showed that anion interacts with cellulose more than the cation therefore, anion play a major role in the dissolution process. Cellulose-chlorides PEDs were found to be sensitive when DMSO/water was included in the system. Furthermore, Chlorides ions became sensitive and the multiple hydrogen bond pattern formed between chlorides ions and cellulose hydroxyls where somewhat changed in the presence of any co-solvent.

2.2.3 Cellulose dissolution mechanism

Cellulose consist of D-glucose units, which are linked through $\beta(1\rightarrow4)$ -glycosidic bond as show in Figure 1.1 in chapter 1, and ILs consist of cations and anions, therefore the dissolution process involve the disruption of the strong inter- and intra- molecular hydrogen bonding of cellulose by the formation of the electron donor-electron acceptor with the anion from the ionic liquid as shown in Figure 2.2. Upon cellulose OH^- and the IL interaction, eventually the OH^- atoms are separated resulting in initiation of cellulose hydrogen bonds to open between molecular chains of cellulose, consequently cellulose dissolve [120-122].

During dissolution process ionic liquid cation also takes part, by interacting with the top and bottom of the cellulose surface sheets, which are probably held together by Van der Waals interactions. The IL cation replace the stacking interactions between sheets and the anions which separate the sheets from each other [123, 124].

The addition of the co-solvent such as DMF, DMSO, and DMI does not change the dissolution mechanism, rather, it promotes ionic mobility from the ILs which favors the interactions of cellulose and the IL, dissolution rate increases [107, 109, 112, 114].

The dissolved cellulose can be precipitated by addition of polar protic solvents such as water, methanol, ethanol, acetone or by any precipitating agent. However during the precipitation process cellulose changes crystal symmetry and precipitate often as cellulose II which is highly amorphous [125].

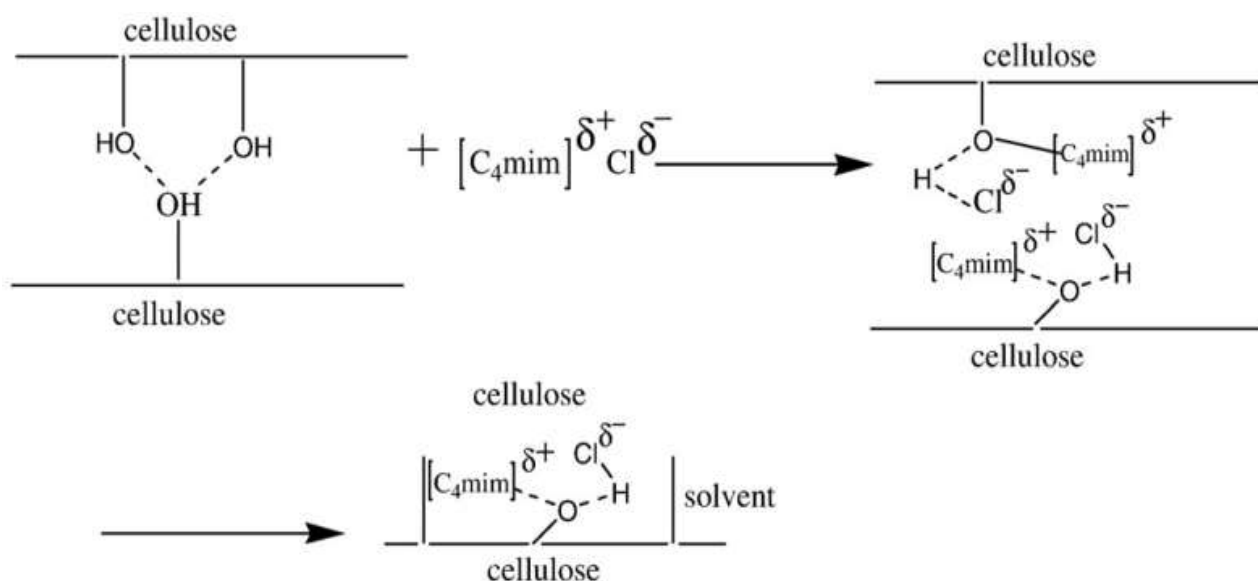


Figure 2.2 Cellulose dissolution mechanism in ionic liquids. reproduced from [122].

2.2.4 Summary of cellulose dissolution

Cellulose dissolution process can be carried out using different methods (microwave heating, oil bath heating with stirring or sonication) [126, 127]. During the dissolution process there are many factors which play a role. These factors are presence of water, anions type, alkyl chain length, degree of polymerization, dissolution time, ILs viscosity, co-solvent property (the explanations of these factors is given by Table 2.1)

Table 2.1 Factors affecting cellulose solubility.

Factor	Explanation	Reference
Presence of water	Water content should be very low in IL typically <1%	[128].
Anions type	ILs containing anions that have strong electronegativity such as halides e.g Cl ⁻ have better dissolution properties unlike non coordinating anions such as [BF ₄] and [PF ₆]	[9], [100], [101] and [100].
Alkyl chain length	Methylimidazolium cations with even number of carbons was found to have high solubilizing power than the ones with odd number and Pyridinium-based ionic liquids showed that as alkyl chain length of the cation increases the solubility decreases.	[1], [43] and [130].
Degree of polymerization	Solubility rate of cellulose decrease as degree of polymerization increases.	[6] and [12].
Dissolution time	Dissolution time should be short typically around 12 hours at low heating temperature	[5].
ILs viscosity	Low viscosity promotes higher dissolution since it supports greater ions mobility.	[5] and [131].
Co-solvent	Polar aprotic co-solvents promotes higher and quicker dissolution at room temperature. Polar protic is non-solvent which causes precipitation of the cellulose from the IL solution.	[107], [109], [110], [112-116].

2.3 Application of dissolved cellulose

Cellulose was first applied commercially in 1870 to produce cellulose-based thermoplastic by treating cellulose with nitric acid from Hyatt Manufacturing Co. [132, 133] As time progressed a new process of treating cellulose was found which was “Viscose”, to generate cellulose fibers. Viscose process allowed utilization of cellulose in textile industries, paints, ceramics, construction, cosmetics and food industry. In 1980s a better process than viscose was developed which was “Lyocess”, this process expanded the textile industry, however its drawback were numerous [86]. Lately, ionic liquids have been found to be the best greener solvents for cellulose dissolution process [9, 30].

Ionic liquids can open up a new horizon in the field of cellulose chemistry as ILs dissolve cellulose without destroying cellulose intrinsic properties such as: biocompatibility, good strength and thermal stability, low density etc. [134, 135]. After cellulose has been dissolved it can be modified and the new cellulose derivatives can be applied in: pharmaceuticals, agriculture, water treatment, different industries such as textile etc. [136]. (See Figure 2.3. which shows some of the possible cellulose modification after dissolved in ILs).

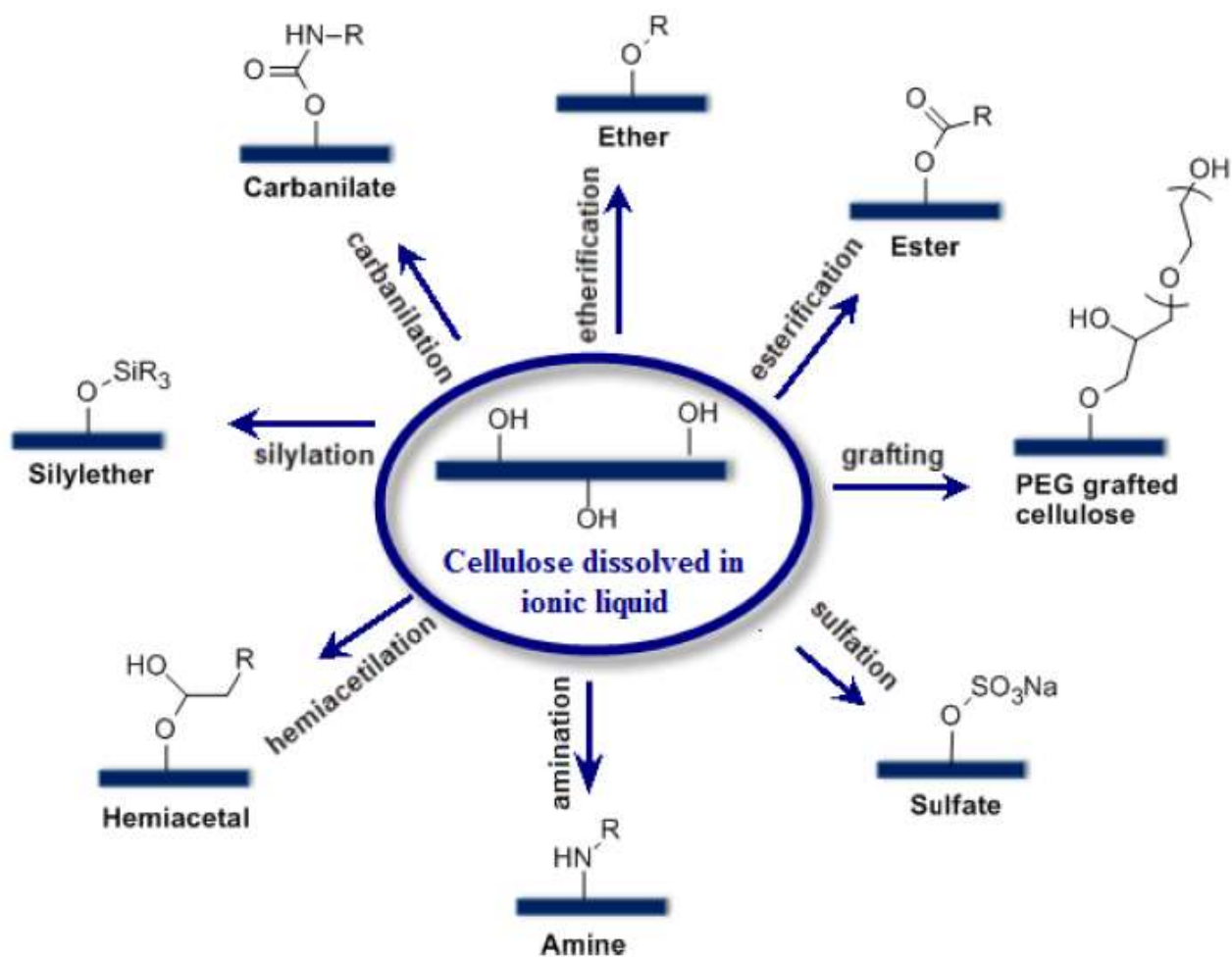


Figure 2.3 Some of the possible cellulose derivatives, obtained when cellulose is dissolved in ionic liquids. Reproduced from Isik *et.al.* [86].

CHAPTER 3: EXPERIMENTAL METHODS

3.1 Density and sound velocity measurement

3.1.1 Density

Density, ρ , is a mass, m , of a sample divided by the volume, v .

$$\rho = \frac{m}{v} \quad (3.1)$$

Density is a thermophysical property hence it depends on temperature. Density of the sample can be determined using pycnometry, mechanical oscillating densitometer and magnetic float densitometer. In this work magnetic float densitometer was used, it is type of densitometer which is linked to a digital output display. Magnetic oscillating densitometers are used in different laboratories such as chemical industry and research to measure the density of all types of liquids either pure or mixed. Densitometers with a precision of $\pm 0.001\%$ are commercially available nowadays [137] See 3.1.3

3.1.2 Sound velocity

Sound velocity is a thermophysical property which is very useful in studying the physicochemical properties of liquids at small concentration changes or to detect changes in gas composition when sample is exposed to various environments. Since the discovery of sound velocity this technique have rapidly increased and attained a high level of precision. Sound velocity measurements provides some equilibrium thermodynamic data that are impossible to obtain by other experiments [138]. Results of speed of sound can be used to calculate isentropic compressibility (k_s) given by equation (3.2). k_s gives thermodynamic related information about the mixture

$$k_s = u^{-2} \rho^{-1} \quad (3.2)$$

where u and ρ is the measured sound velocity density respectively.

In this work density and sound velocity was measured using Anton Paar DSA 5000 M.

3.1.3 Density and sound velocity apparatus used in this work

3.1.3.1 Instrument used

Density and sound velocity of all liquid mixtures were measured using Anton Paar (DSA 5000M). DSA 5000M has a temperature accuracy of ± 0.02 K at atmospheric pressure (101,325 pascals). It gives error in density and speed velocity measurements of $\pm 9 \times 10^{-4} \text{ g}\cdot\text{cm}^{-3}$ and $\pm 0.8 \text{ m}\cdot\text{s}^{-1}$ respectively. A diagram of the Anton Paar (DSA 5000M) apparatus used in this work is shown in Figure 3.1.



Figure 3.1 Anton Paar (DSA 5000M) density and speed of sound analyser.

3.1.3.2 Mode of operation

For the density measurements, the vibrating U-shaped tube was kept inside a cavity of a metallic block with peltier devices which allowed temperature and stability. The sound velocity cell was connected to one end of the U-shaped tube so that the same liquid can pass into it without loss and the same metallic block can control temperature.

3.1.3.3 Oscillating U-tube method

The sample is injected into a U-shaped borosilicate glass tube that is excited to vibrate at its characteristic frequency electronically. The characteristic frequency changes depending on the density of the sample. Through a precise determination of the characteristic frequency and a mathematical conversion, the density of the sample can be measured. The density, ρ , is calculated from the quotient of the period of oscillation of the U-tube and the reference oscillator:

$$\rho = KA \times Q^2 \times f_1 - KB \times f_2 \quad (3.4)$$

KA, KB Apparatus constant

Q Quotient for the period of oscillation of the U-tube divided by the period of oscillation for the reference oscillator

f_1, f_2 Correction terms for temperature, viscosity and non-linearity

The value of the density is displayed on the LCD screen. The DSA 5000 M is coupled with a computer which is loaded with a software that stores all the measured density values.

3.1.3.4 Sound velocity analyser

The sample is introduced into the sound velocity measuring cell that is bordered by an ultrasonic transmitter on the one side, and a receiver on the other side. The transmitter sends sound waves of a known period through the sample. The velocity of sound, u , can be calculated by using the period of the sound waves and the distance between the transmitter and receiver shows by equation (3.5).

$$u = \frac{l \times (1 + 1.6 \times 10^{-5} \times \Delta T)}{\frac{P_s}{512} - A \times f_3} \quad (3.5)$$

where l is the original path length of the sound waves, ΔT is the temperature deviation to 5 °C, P_s is the oscillation period of the received sound waves, A is apparatus constant for sound velocity, and f_3 is the correction term for temperature.

The measuring cell is thermostated precisely, using the Peltier elements as density and sound velocity strongly depend on temperature.

3.1.4 Features of DSA 5000 M

3.1.4.1 Accuracy

DSA 5000 M instrument provides the most advanced digital density and sound velocity measurement technology in the world where:

- The period of oscillation of the U-tube is measured by optical pickups.
- Two integrated Pt 100 platinum thermometers together with the Peltier elements provide an extremely precise thermostating of the sample.
- There is a thermo-balance which is an additional reference oscillator that provides long-term stability and enables precise measurements over the whole temperature range of the instrument with only one adjustment at 20 °C.

3.1.4.2 Error detection

A major source of measuring errors when using a density and sound velocity meter is gas bubbles in the measuring cells. To reduce the formation of gas bubbles Anton Paar introduced two new features:

Filling Check: The instrument automatically detects gas bubbles in the density measuring cell by an advanced analysis of its oscillation pattern and generates a warning message.

U-View: Using a real-time camera with zoom function the U-tube can be visually inspected for gas bubbles in the density measuring cell. The Specifications for the DSA 5000 M are given in Table 3.1.

Table 3.1 Specifications of the DSA 5000 M.

Measuring range density	0 to 3 g/cm ³
Measuring range sound velocity	1000 to 2000 m/s
Measuring range temperature	0 to 70 °C (32 to 158 °F)
Pressure range	0 to 3 bar (0 to 44 psi)
Repeatability density	0.000001 g/cm ³
Repeatability sound velocity	0.1 m/s
Repeatability temperatures	0.001 °C (0.002 °F)
Measuring time per sample	1 to 4 minutes
Sample volume	approx. 3 ml
Ambient air pressure sensor	yes
Reference oscillator	yes
Automatic bubble detection	yes
Visual check of the density measuring cell	camera

3.2 Refractive index

3.2.1 Refractive index background

Refractive index is the ratio between the phase velocity of wave propagation in a reference medium and the phase velocity in the medium itself [139] which is mathematically shown by the equation (3.6) :

$$n = \frac{\text{speed of light in material 1}}{\text{speed of light in material 2}}, \quad (3.6)$$

where 1 represent incident light in and 2 represent refracted light

When light passes through materials it changes direction, therefore light won't pass in the same manner in different materials as a results refractive index tend to provide physicochemical properties of materials. Refractive index in a vacuum 1 is termed absolute refractive index of material 2. Hence practically, air makes absolute refractive index of 1.0008. Consequently, absolute refractive index is taken assuming that the incident light is in the air.

Refractive index of non-magnetic and transparent materials can also be determined by the interaction of an electrical field of the wave and the permittivity ϵ of the medium.

$$n = \sqrt{\epsilon_r} = \sqrt{\frac{\epsilon}{\epsilon_0}}, \quad (3.7)$$

where ϵ_0 is the permittivity of vacuum which is equal to $10^7 / (4\pi c^2) \text{ Fm}^{-1}$ [139]

Refractive index of material is bigger than 1 and normally less than 1.7, for most common material e.g. petroleum. Refractive index is also a thermophysical property therefore, it strongly depends on the temperature.

Refractive index can also be defined using Snell's law or by Law of refraction given in mathematical expression below:

$$n = \frac{\sin \theta_1}{\sin \theta_2}, \quad (3.8)$$

The equation above relates the ratio of the sine of the angle of incidence (material 1) θ_1 and with the angle of refraction (material 2) θ_2 [140].

3.2.2 Refractive index measurements

ATAGO RX 5000 Refractometer (Figure 3.2), Abbemat Digital Refractometer (figure 3.3), Anton Paar refractive index analyser RXA 156 (Figure 3.4) etc. are one of the instruments which are used to measure refractive index. In this work Anton Paar refractive index analyser RXA 156.



Figure 3.2 Illustration of an ATAGO RX 5000 refractometer.



Figure 3.3 Illustration of an Abbemat digital refractometer 350/550.



Figure 3.4 Illustration of Anton Paar refractive index analyser RXA 156.

Table 3.2 lists the conditions of the refractometer RXA 156.

Table 3.2 Conditions of the refractometer RXA 156.

	Refractive index
Measuring range	1.32 – 1.56 nD
Resolution	0.000001
Accuracy	0.00002
	Temperature
Measuring temperature	283.15 - 343.15 K
Resolution	273.16 K
Accuracy	273.18 K
Stability	273.152 K
Speed of temperature change from ambient temperature to 293.15 K	20s

3.3 Fourier transform infrared spectroscopy

FTIR is analytical technique which is used to measure the intensity of the infrared radiation as a function of a wavelength when the matter interacts with infrared radiation (IR). This technique gives fingerprint information about the chemical composition of the sample. Not all molecules are proficient to absorb IR therefore, in order for a molecule to absorb IR it must have a permanent dipole moment, homonuclear diatomic molecules such as: N₂, H₂, O₂ etc. can't absorb IR since they do not have a dipole moment whereas heteronuclear diatomic molecules such as: CO, NO, HCl etc. have a permanent dipole moment making them to be strong IR absorbers. FTIR uses electro-magnetic radiation of wavelength range from 700nm to 1mm [141-143].

The mathematical expression of FTIR is given below (equation 3.9)

$$F(\omega) = \int_{-\infty}^{+\infty} f(x)e^{i\omega x} dx \quad (3.9)$$

The equation of the interferogram, $f(x)$, can be written as (equation 3.10)

$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} F(\omega)e^{-i\omega x} d\omega \quad (3.10)$$

where ω is angular frequency and x is the optical path difference.

$f(x)$ is determined experimentally whereas $F(\omega)$ can be obtained by using Fourier transform.

FTIR uses Michelson interferometer which consists of a detector, light source, beam splitter, fixed and moving mirror, see Figure 3.5 below showing Michelson interferometer

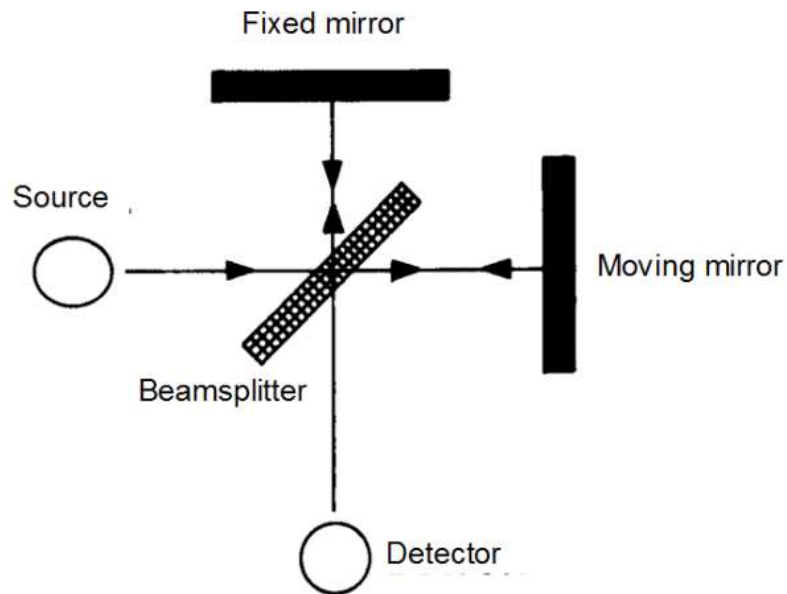


Figure 3.5: Schematic diagram of Michelson interferometer.

Working principles of Michelson interferometer

Light is generated by the light source and directed to the beam splitter, then it is reflected and also transmitted between the fixed mirror, beam splitter and the moving mirror until it is detected by the detector. The spectrum is then generated automatically. In this work Bruker Alpha FTIR ATR was used which is given by Figure 3.6.



Figure 3.6 Bruker Alpha FTIR ATR.

3.4 Thermal analysis

3.4.1 Thermo-gravimetric analysis

TGA is an analytical technique which the mass changes of the substance are monitored as a function of controlled temperature (Figure 3.7). The change of mass versus temperature results gives information about thermal stability of the sample. It is often used in research and development of various substances and engineering of materials [144-146] [NETZSCH Thermal Analysis Methods hand-book].

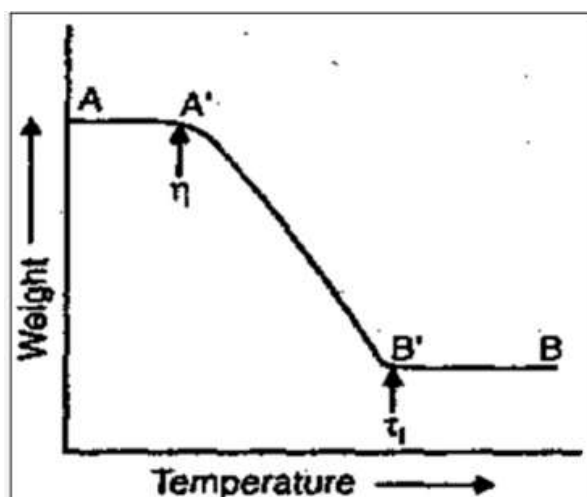


Figure: 3.7 TGA curve.

where A shows initial (stable) compound, A'B' shows decomposition (weight loss) and B is the final mass of the initial compound

Figure 3.7 shows changes of weight of the specimen, this gives information about the rupture or formation of various chemical bonds. The information obtained is used in evaluating volatile products or the formation of heavier reaction products. TGA results also give information about the thermodynamics and kinetics of various chemical reactions. The mass conversion in TGA is typically calculated using equation (3.11)

$$Y = \frac{m_0 - m}{m_0 - m_f} \quad (3.11)$$

where m current mass and m_0 is the initial mass and m_f denotes final mass, y is fraction of initial molecules not yet decomposed.

3.4.2 Differential scanning calorimetry

DSC is a thermal analytical technique which is used to investigate how material's heat capacity is changed by temperature. A sample of known mass is heated or cooled and the changes in its heat capacity is tracked as changes in the heat flow. DSC can be used to track transitions such as melts, glass transitions, crystallinity, phase changes, and curing. DSC is applied in various fields such as in industries, pharmaceuticals, polymers, food, paper, printing, manufacturing, agriculture, semiconductors, and electronics. Furthermore, DSC is the most widely used thermal method because of its speed, simplicity, and availability. Additionally, it is mostly used for quantitative analysis.[145-147] [NETZSCH Thermal Analysis Methods hand-book]. Figure 3.8 below shows the illustrations of DSC

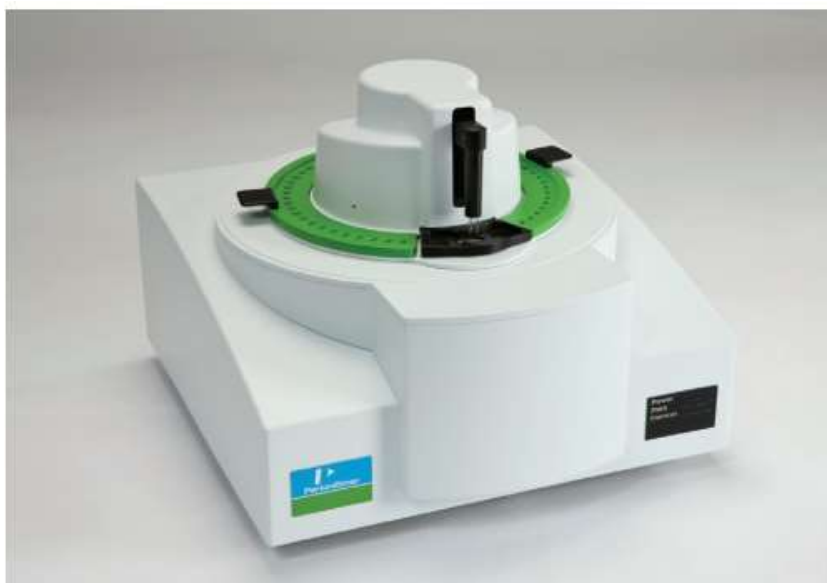


Figure 3.8 DSC instrument. Reproduced from PerkinElmer DSC handbook.

3.5 Scanning electron microscopy

SEM is a technique which is used to observe surface area of different specimen by focusing the beam of high-energy electrons to produce a variation of signals at the surface of solid specimens. SEM can also be used to determine the chemical composition of materials due to its fluorescent properties, the formation of magnetic domains etc. [148, 149]. Figure 3.9 shows the working principle of SEM.

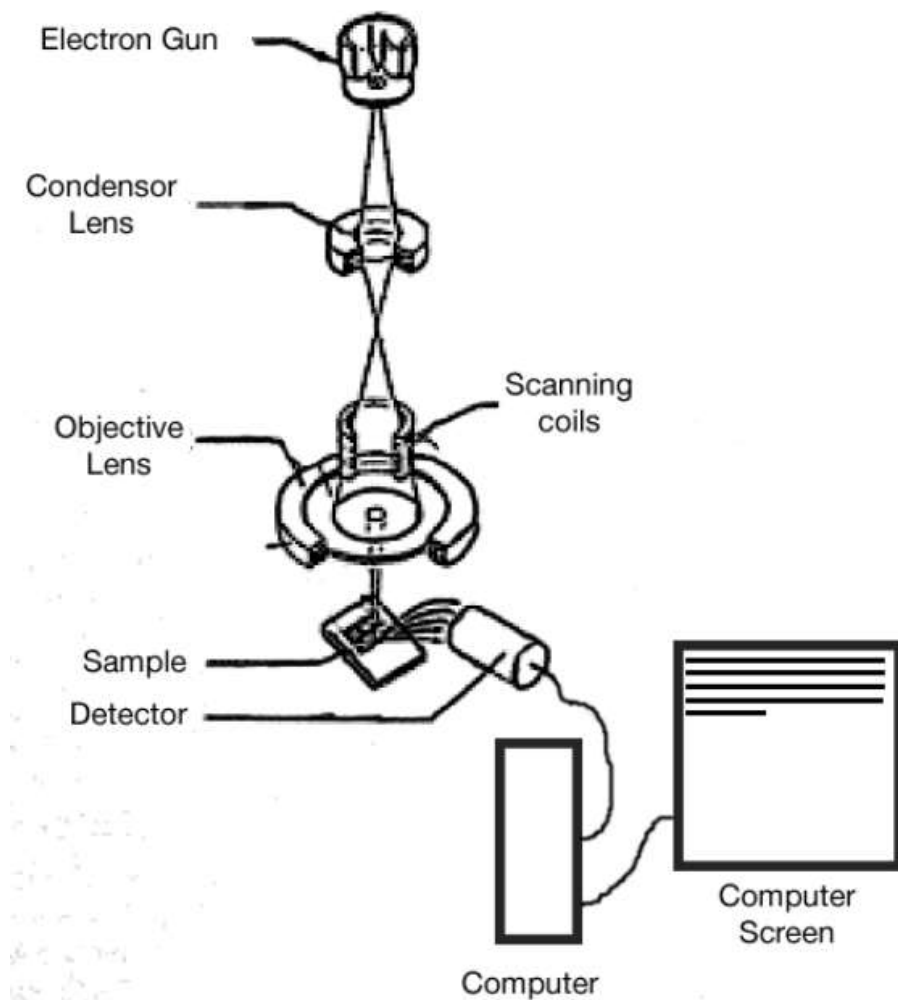


Figure 3.9 Schematic diagram of SEM.

3.5.1 SEM operating principle

The sample is bombarded by beam of electron which is scanned across the surface, after the bombardment then the electron beam generates different signal types which are then emitted from the area of the sample. The induced signals are detected and amplified, this gives rise to the intensity of the pixel. After the first position is completed. the electron beam moves on to the next one, then second pixel is generated and so on [149] until the whole image is formed and displaced on computer screen Figure 3.9 shows how the SEM operates.

3.6 X-ray crystallography

XRD is an analytical technique which is used to characterize molecular structures of unknown materials. XRD uses X-ray rays which are produced by the cathode and filtered to produce monochromatic radiation, which is collimated to concentrate and directed towards the sample. After the interaction of the rays with the sample it get diffracted in a pattern characteristic to its structure then the rays are detected, processed and counted. If the specimen is in powder phase, the diffraction is carried out in powder X-ray diffraction rather than individual crystal, in addition, powder sample is often easier as it does not require single crystal. The use of 2θ angle allows all diffraction direction to be attained then the results is plotted as plot intensity versus angle of the detector (2θ). Diffraction pattern can be obtained using both transmission and reflection configuration, however reflection is most common in most diffractometers. Interactions between the incident X-ray and the sample produce powerful reflected X-rays by constructive interference when conditions satisfy Bragg's Law ($n\lambda = 2d \sin \theta$). Bragg's law describes the relationship between the incident X-rays wavelength and the incident angle of the beam and the spacing between the crystal lattice planes of atoms [150, 151]. Figure 3.10: Shows the schematic diagram of XRD diffractometer.

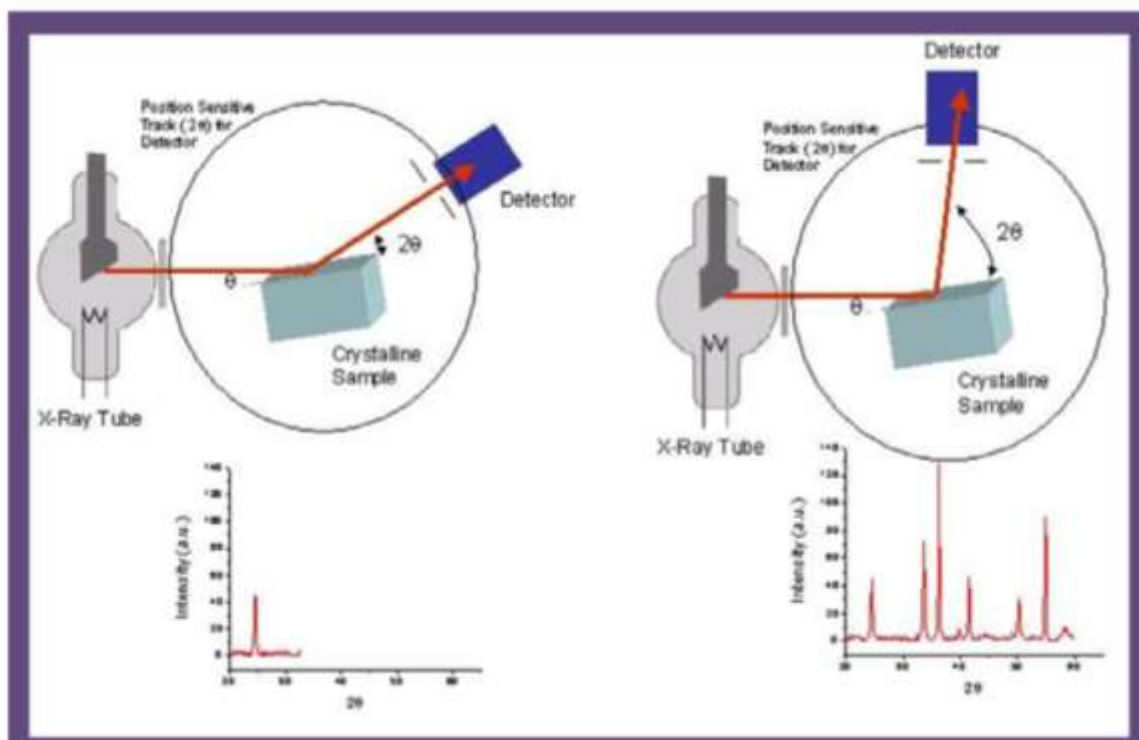


Figure 3.10 Schematic diagram of XRD diffractometer

3.7 Experimental techniques

3.7.1 Materials

Chemicals used in this work is listed in Table 3.3 as well as their suppliers and purities, molar mass and CAS no. This chemicals were used without further purification.

Table 3.3 Chemicals, their suppliers, mass fraction purity, molar mass and CAS No.

Chemicals	Supplier	Mass fraction Purity (%)	Molar mass (g.mol^{-1})	CAS No.
MCC	Aldrich	99.0	37098	435244
[BMIM] ⁺ [Cl] ⁻	Aldrich	99.0	236.29	94128
[AMIM] ⁺ [Cl] ⁻	Aldrich	99.0	197.3	43961
[BMPy] ⁺ [Cl] ⁻	Aldrich	99.0	60.05	07326
Dimethyl formamide	Aldrich	99.5	74.08	227056
Ethanol	Aldrich	99.0	41.05	24104

Molecular mass of cellulose was obtained by using equation (3.12-3.14) below:

$$[\eta] = \frac{(\eta_{\text{rel}} - 1)/c}{1 + K_n \bullet (\eta_{\text{rel}} - 1)} \quad (3.12)$$

$$M_w = ([\eta]/0.0116)^{1/0.83} (g/mol) \quad (3.13)$$

$$M_w = DP \times 162 \quad (3.14)$$

where DP used was 229 obtained from Zhang *et.al* [100] since the used MCC is the same,

$[\eta]$ = intrinsic viscosity (ml.g⁻¹), $[\eta_{\text{rel}}] = t/t_0$ relative viscosity and t = flow rate of the solutions.

3.7.2 Thermophysical properties measurements

3.7.2.1 Preparation of the cellulose mixtures

The cellulose mixtures were prepared using OHAUS analytical mass balance with a precision of ± 0.0001 g. Various mixtures (Table 3.4) were prepared by mixing weighed IL (3.5g for [BMPy][Cl] and [BMIM][Cl] and 0.35g of [AMIM][Cl]) then added approximately 2ml of DMF in the vial to dissolve the solid IL. After the IL + DMF solution was prepared it was then subjected to heat until the temperature of the solution reached 65 ± 5 °C, then the weighed microcrystalline cellulose (ranging from 0.002 to 0.1g) was added to the solution with continuous magnetic bar stirring, after 5 minutes, the remaining DMF (8 ml) was added to the solution. The total amount of DMF used for [BMPy][Cl] and [BMIM][Cl] was 10ml and for [AMIM][Cl] was 5ml. Immediately after the dissolution has completed (total dissolution process took ≈ 30 minutes) the sample was removed from the heat and allowed to cool off. In addition, 3 systems were prepared: [BMIM][Cl] +DMF+ MCC, [AMIM][Cl] +DMF+ MCC and [BMPy][Cl] +DMF+ MCC at various fractions as illustrated by Table 3.4.

Table 3.4 Masses used to prepare cellulose solutions.

Type of IL	Amount of IL used (g)	DMF used (mL)	MCC used (g)
[BMIM][Cl]/[BMPy][Cl]	3.5	10	1 st vial = 0.00
			2 nd vial = 0.02
			3 rd vial = 0.04
			4 th vial = 0.06
			5 th vial = 0.08
			6 th vial = 0.1
[AMIM][Cl]	0.35	5	1 st vial = 0.00
			2 nd vial = 0.002
			3 rd vial = 0.004
			4 th vial = 0.006
			5 th vial = 0.008
			6 th vial = 0.01

3.7.2.2 Measurement of the densities and sound velocities

Measurement of the density and sound velocity were conducted using Anton Paar DSA 5000M which is a digital vibrating-tube densitometer and sound velocity analyser. Anton Paar DSA 5000M measures density and also sound velocity of the samples simultaneously and it has a temperature accuracy of ± 0.02 K.

3.7.2.3 Measurement of the refractive indices

Refractive indices of the cellulose mixtures were measured using a digital automatic refractometer (Anton Paar RXA 156) with an accuracy of 0.03 K. Anton Paar RXA 156 has been estimated to have an error less than 0.005.

3.7.3 Preparation of the regenerated cellulose

3.7.3.1 Preparation of cellulose fibres using IL only

About 3 g of weighed [BMIM][Cl] or [BMPy][Cl] was melted using a hot plate then 0.3 g of microcrystalline cellulose was added. The dissolution process was carried out with a aid of magnetic stirring bar after the MCC has dissolved it was regenerated by addition of 10mL of

warm deionized water and the cellulose precipitate were washed by 20mL of absolute ethanol. To prepare cellulose fibers using [AMIM][Cl], 1.5g of it was used with 0.15g of MCC

3.7.3.2 Preparation of regenerated cellulose using IL and DMF

The dissolution process used in this method is the same as in section 4.3.1 except in this one 5mL of DMF was added for [BMIM][Cl] and [BMPy][Cl] whereas for [AMIM][Cl] 2.5mL was used. DMF was added before cellulose.

The regenerated fibers were vacuum dried at 60 °C for 4 hours before characterization.

3.7.3.3 Characterization of regenerated cellulose

3.7.3.3.1 Measurement of FTIR

Measurements of FTIR were made using Bruker ALPHA Platinum ATR which is robust and has high performance results. Prior to each experimental run the lens was washed by acetone. FTIR measurements were conducted at wavelength range of 400-4000 cm^{-1} and spectra were scanned 32 times using 4 resolution. FTIR technique was used investigate the chemical bonds of the pure MCC and regenerated one.

3.7.3.3.2 Measurement of SEM

SEM images were taken using Jeol 6310 Electron Probe analyser at 5kV accelerating voltage. Samples were first mounted onto the SEM aluminium stub with a carbon tape and then Au (gold) coated. They were cooked for ≈ 20 minutes to make them more electrical conducting [152].

3.7.3.3.3 Measurement of XRD

XRD measurements were taken using Bruker D2 Phaser Powder XRD instrument. The X-ray radiation were generated by Co at 30 kV, 10 mA at a range for angle of diffraction was $2\theta = 5-80^\circ$.

3.7.3.3.4 Thermal analysis measurement

Measurements of TGA and DSC were made using NETZSCH STA 449F3 at a heating rate of 10 °C /min in continuous nitrogen flow at a temperature range of 25 to 600 °C having an isotherm process at 75 °C for 30 min to remove any possible absorbed water [152].

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Dissolution process

The dissolution process of cellulose in ILs and their co-solvent was confirmed by thermophysical properties measurements such as density, sound velocity and refractive index, when cellulose dissolved. The values of density, sound velocity and refractive index were observed to increase as compared to (ILs + DMF) mixtures which confirm the dissolution of cellulose in mixtures (the results is elaborated in section 4.3 at page 71). The dissolution of cellulose were compared in pure ILs and their co-solvent with DMF and found that co-solvent is more effective pure ILs. Thermophysical properties of cellulose with pure ILs was not conducted since those mixtures were not liquid at room temperature. Cellulose and ILs mixtures containing a DMF was liquid mixtures at room temperature hence it made it possible to measure thermophysical properties. Concerning the dissolution of cellulose in pure [BMIM][Cl], [AMIM][Cl] and [BMPy][Cl] ILs are reported in the literatures [6, 7, 9, 11, 12, 27, 43, 100, 102, 107].

4.2 Characterization of regenerated fibers

Microcrystalline cellulose was dissolved in solutions of [BMIM][Cl], [AMIM][Cl], [BMPy][Cl], co-solvents [BMIM][Cl]/DMF, [AMIM][Cl]/DMF and [BMPy][Cl]/DMF and regenerated using deionised water. The recovered fibres were vacuum dried for 4 hours at 60 °C to remove any water residue then the fibres were analysed using different techniques: FTIR, XRD, SEM, TGA and DSC.

4.2.1 Fourier transform infrared spectroscopy

Six spectra of regenerated cellulose fibres (MCC + [BMIM][Cl] or [AMIM][Cl] or [BMPy][Cl], co-solvents [BMIM][Cl]/DMF or [AMIM][Cl]/DMF or [BMPy][Cl]/DMF) was conducted and the seventh one is for pure MCC, these spectra are illustrated as three groups, group of [BMIM][Cl] illustrated as Figure 4.1, [AMIM][Cl] illustrated as Figure 4.2 and

[BMPy][Cl] illustrated as Figure 4.3 and spectrum of MCC is present in all groups for comparison purposes. In addition Figure 4.4 is illustrating all spectra.

The spectra of the regenerated cellulose are similar to the spectrum of the MCC shown in (Figures 4.1-4.3) which suggest that the structures of the regenerated cellulose and MCC are similar to some extent and this indicate that during dissolution and regeneration process there was no chemical reaction [153]. Figure 4.1-4.3 shows that -CH_2 bond of the regenerated cellulose fibers at 2850cm^{-1} scissoring motion shifted from higher intensity to lower intensity and also from high to much higher intensity in Figure 4.1(C) which shows the damage of the intermolecular hydrogen bond linking O at C_6 [153]. Furthermore, Qiu *et.al* [154] showed that CH_2 stretching is not affected by changes in crystallinity.

O-H bond at 3427 cm^{-1} of the regenerated cellulose fibres had shifted either to higher or lower wavenumber to some extent which shows that the regenerated cellulose fibres had underwent minor structural changes such as decrystallization [12, 126, 127, 155] therefore, the molecular structure of the cellulose was not shattered [103] .

Figure 4.4 shows all spectra of the pure cellulose as well as regenerated cellulose previously dissolved in [BMIM][Cl] or [AMIM][Cl] or [BMPy][Cl], co-solvents [BMIM][Cl]/DMF or [AMIM][Cl]/DMF or [BMPy][Cl]/DMF. As it has been stated in the above paragraphs that the spectra of the regenerated cellulose is similar to the spectrum of the original cellulose, therefore, Figure 4.4 shows the best IL most suitable for the cellulose dissolution in this case, it is [BMIM][Cl] as its spectrum is almost the same as the one for pure MCC, hence, the regenerated cellulose previously dissolved in [BMIM][Cl] still has its bonding at the same axis with same bonding length as the original MCC, whereas the regenerated one from [BMIM][Cl]/DMF has a well define sp^3 hybridised carbon.

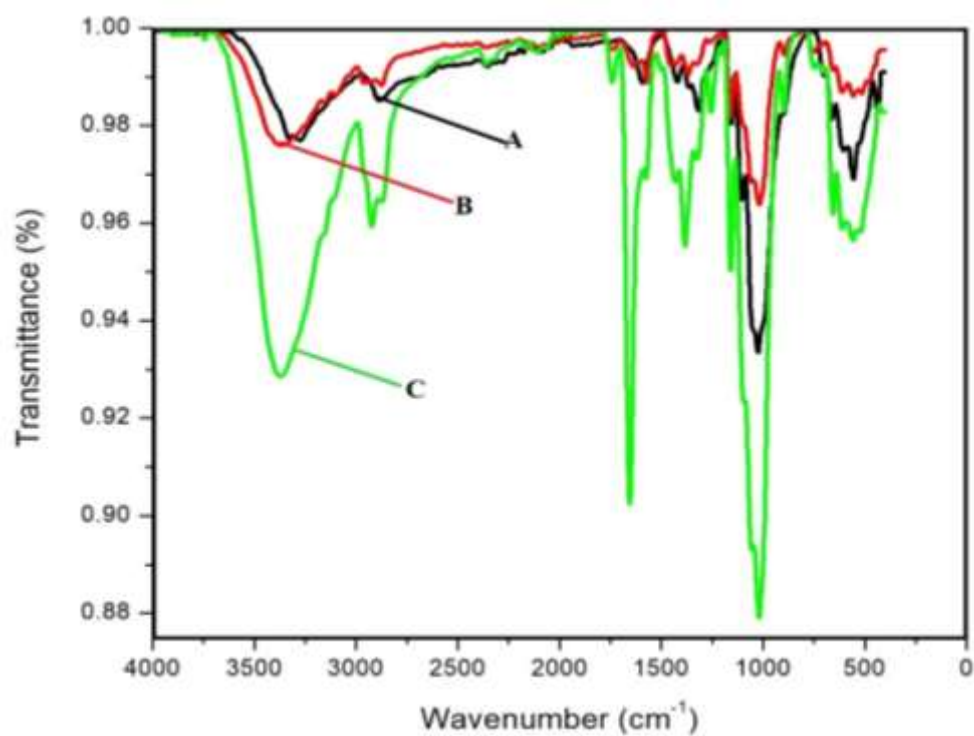


Figure 4.1 FTIR spectra of pure microcrystalline cellulose (A), regenerated cellulose after dissolved in [BMIM][Cl] (B) and in [BMIM][Cl]/DMF (C).

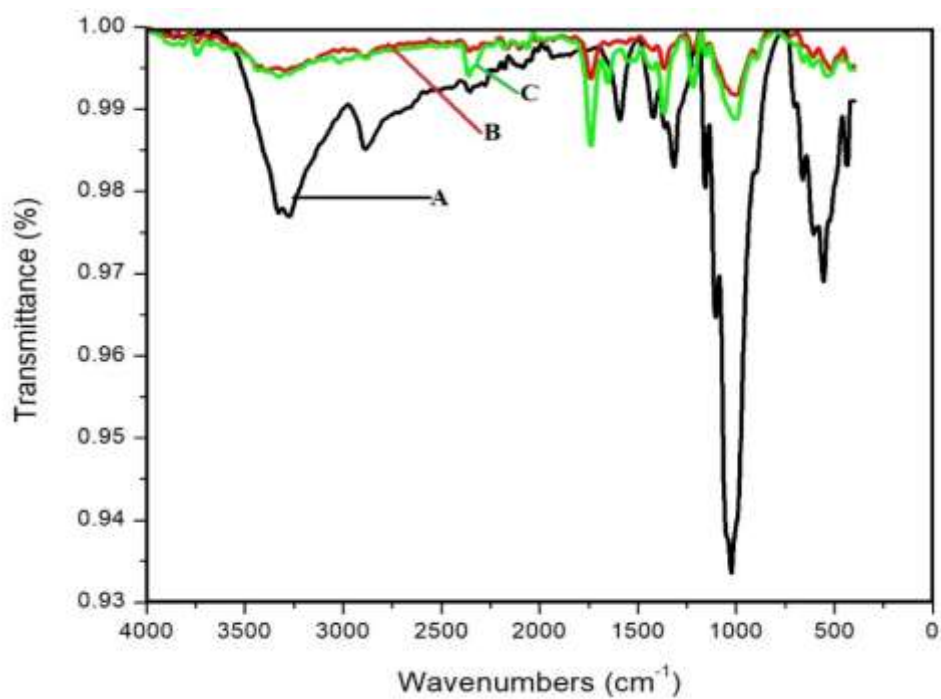


Figure 4.2 FTIR spectra of pure microcrystalline cellulose (A), regenerated cellulose after dissolved in [AMIM][Cl] (B) and in [AMIM][Cl]/DMF (C).

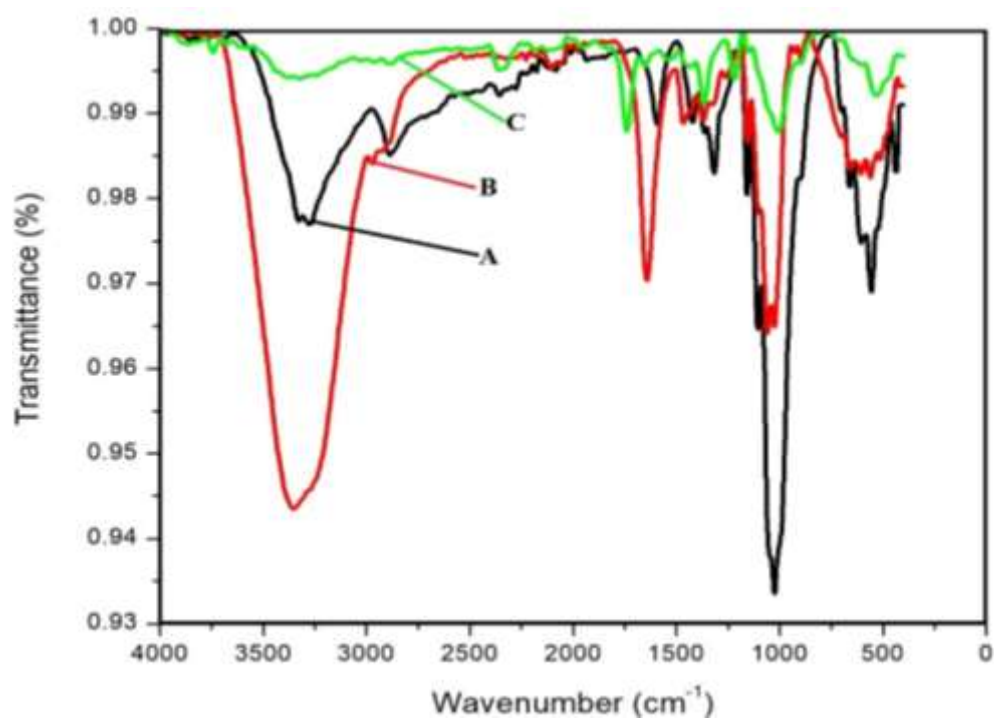


Figure 4.3 FTIR spectra of pure microcrystalline cellulose (A), regenerated cellulose after dissolved in [BMPy][Cl] (B) and in [BMPy][Cl]/DMF (C).

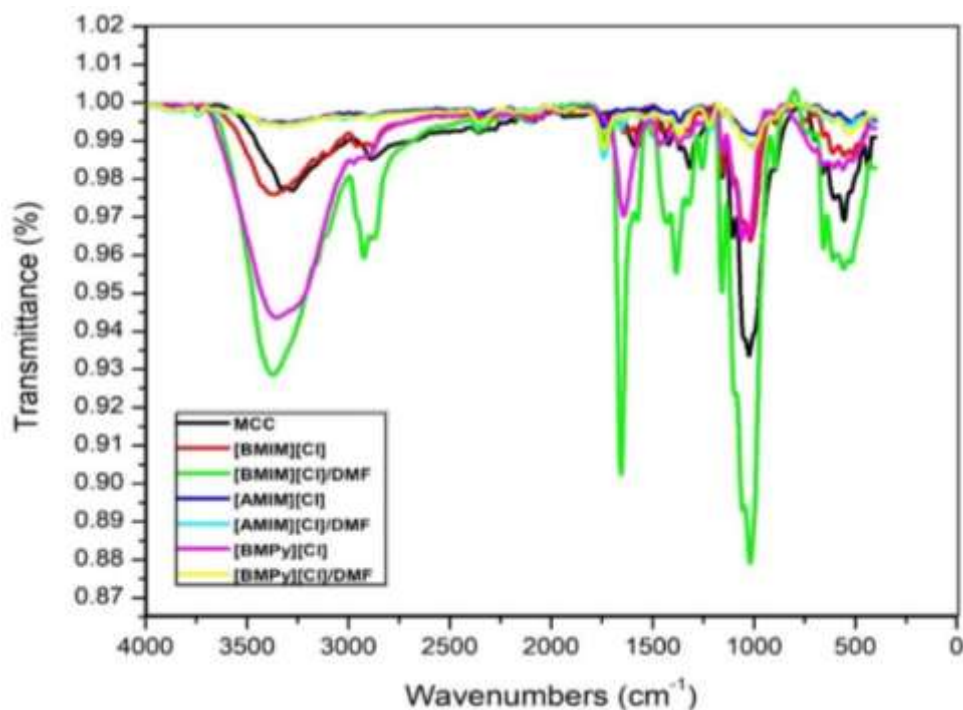


Figure 4.4 FTIR spectra of pure microcrystalline cellulose and regenerated cellulose after dissolved in various solvents.

4.2.2 X-ray diffraction

XRD results of regenerated cellulose together with MCC are given in Figure 4.5-4.8, with figure 5.8 showing all pattern in one plot. The diffraction patterns of the regenerated cellulose is different with the pure cellulose. MCC has been characterized as highly crystalline polymer having diffraction pattern at $2\theta = 17.2^\circ$, 19.6° and 26.3° which shows that it is cellulose I, for cellulose II exhibit diffraction pattern at $2\theta = 14.1^\circ$, 23.1° and 25.6° and for amorphous cellulose diffraction pattern at $2\theta = 25^\circ$ for Co K_α radiation.

The obtained diffraction pattern at 2θ of the regenerated cellulose as illustrated in Figure 4.5, 4.6 and 4.7 shows that it is rather amorphous and little traces of cellulose II were found. Therefore cellulose I (MCC) was converted into amorphous and also cellulose II state [156]. Rapid precipitation prevented the reconstruction of the dissolved cellulose into its native state (cellulose I) [101], in addition the same trend was reported by Zhang *et.al* [12], Dadi *et.al* [101] Chen *et.al* [157], Liu *et.al* [11].

The peaks of the regenerated cellulose in Figure 4.5 shows that cellulose previously dissolved in [BMIM][Cl] is more amorphous than the one previously dissolved in [BMIM][Cl]/DMF, similar trend was observed for [BMPy][Cl] and [BMPy][Cl]/DMF (Figure 4.6). This have been caused by the prolonged dissolution time of [BMIM][Cl] and [BMPy][Cl] as compared to [BMIM][Cl]/DMF and [BMPy][Cl]/DMF. Hence prolonged stirring destroy cellulose chains.

Regenerated cellulose previously dissolved in [AMIM][Cl] was more crystalline than the one previously dissolved in [AMIM][Cl]/DMF since the dissolution time for [AMIM][Cl] was much shorter than [AMIM][Cl]/DMF. Hence [AMIM][Cl] is the most powerful solvent amongst the studied ILs as it was able to dissolve cellulose directly without completely destroying cellulose fascinating crystallinity [106].

Figure 4.8 shows the comparison of the regenerated cellulose fibre previously dissolved in [BMIM][Cl] or [AMIM][Cl] or [BMPy][Cl], co-solvents [BMIM][Cl]/DMF or [AMIM][Cl]/DMF or [BMPy][Cl]/DMF. The crystallinity of the regenerated cellulose fibres is in the following order: [AMIM][Cl] > [BMPy][Cl]/DMF > [BMIM][Cl]/DMF > [BMIM][Cl] > [BMPy][Cl] > [AMIM][Cl]/DMF. Only the regenerated cellulose fibres previously dissolved in [AMIM][Cl] most of it was converted into cellulose II and whereas other regenerated fibres was amorphous.

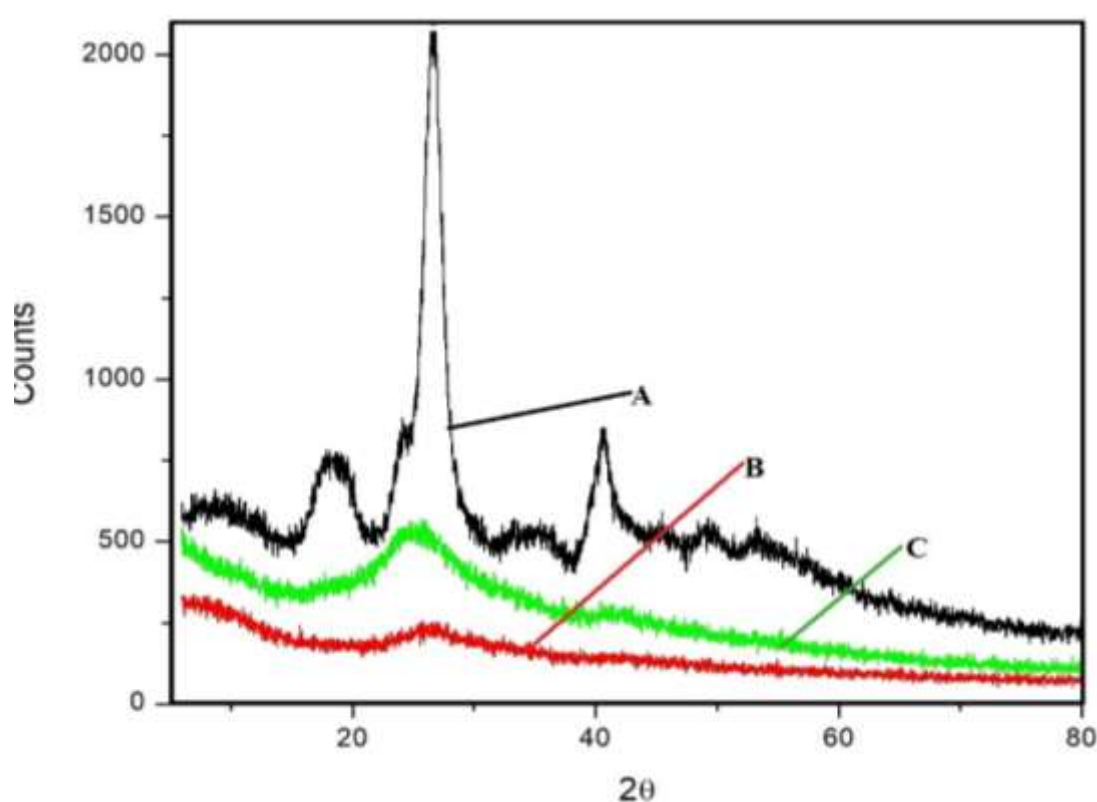


Figure 4.5 XRD patterns of pure microcrystalline cellulose (A), regenerated cellulose after dissolved in [BMIM][Cl] (B) and in [BMIM][Cl]/DMF (C).

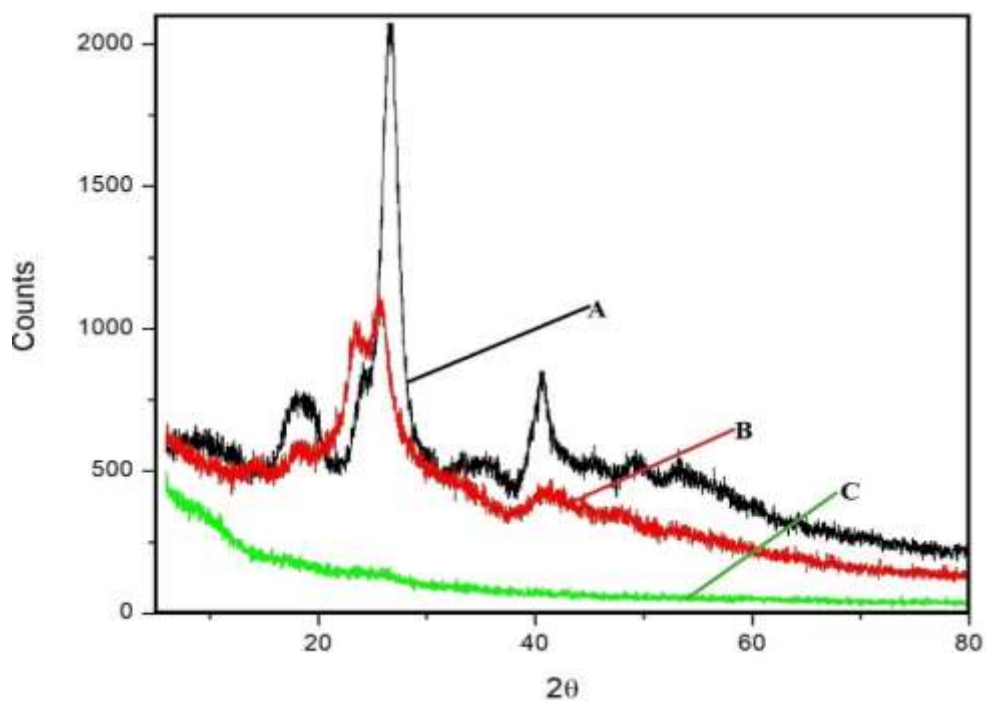


Figure 4.6 XRD patterns of pure microcrystalline cellulose (A), regenerated cellulose after dissolved in [AMIM][Cl] (B) and in [AMIM][Cl]/DMF (C).

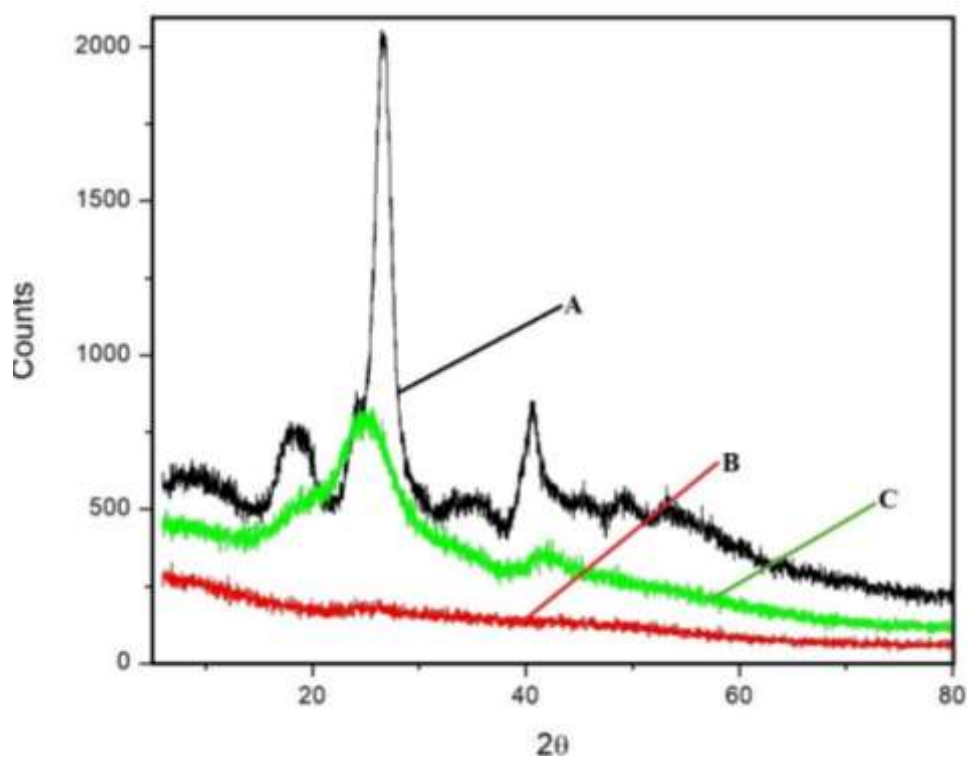


Figure 4.7 XRD patterns of pure microcrystalline cellulose (A), regenerated cellulose after dissolved in [BMPy][Cl] (B) and in [BMPy][Cl]/DMF (C).

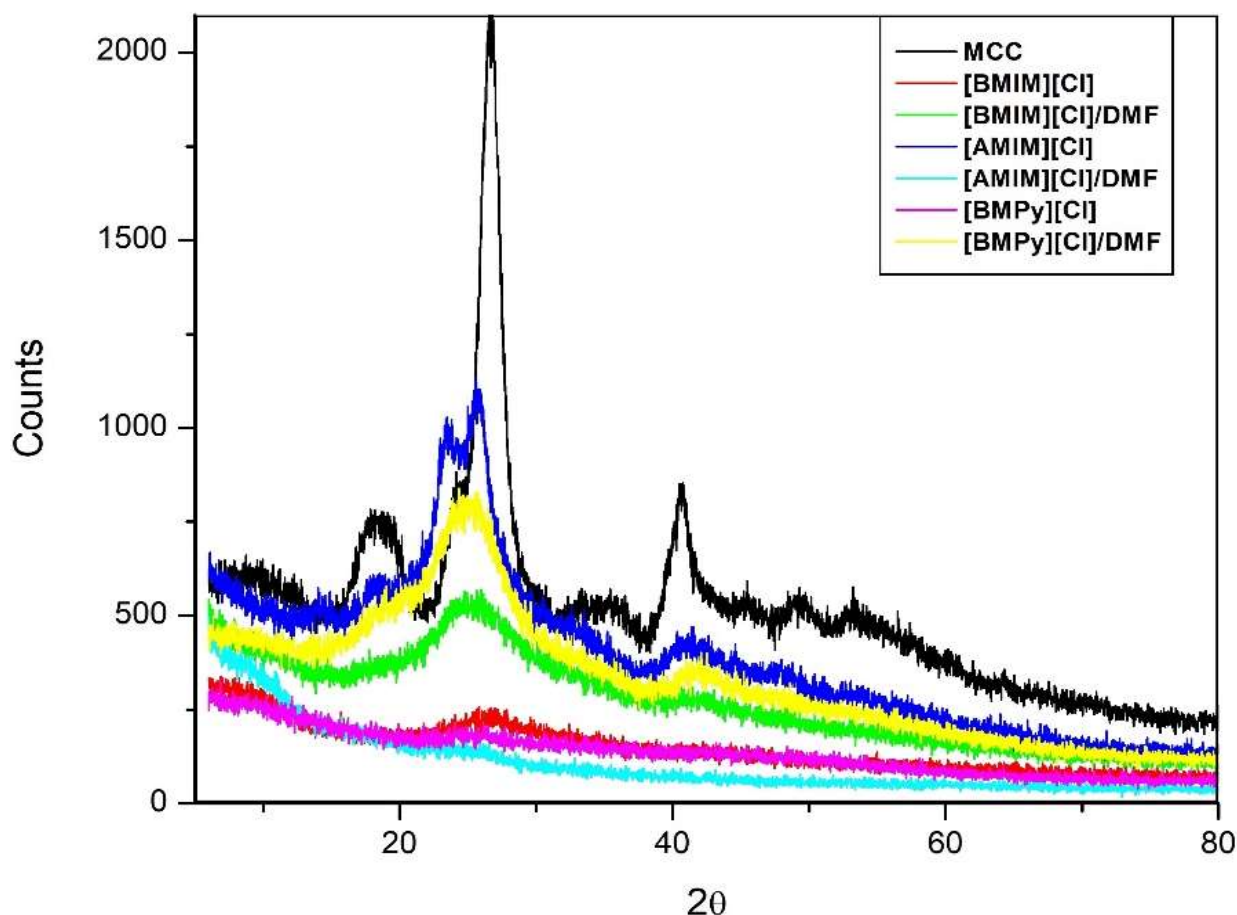


Figure 4.8 XRD patterns of pure microcrystalline cellulose (MCC) and regenerated cellulose after dissolved in different ILs with and without co-solvent (DMF).

4.2.3 Scanning electron microscope

SEM images of the regenerated cellulose previously dissolved in [BMIM][Cl], [AMIM][Cl], [BMPy][Cl], co-solvents [BMIM][Cl]/DMF, [AMIM][Cl]/DMF and [BMPy][Cl]/DMF as well as image of MCC are shown by Figure 4.9, SEM images shows that the texture of the regenerated cellulose (Figure 4.9 B-G) is rough and dense compering to the pure MCC (A). Furthermore, the fibers of the native MCC are now fused together into a relatively homogeneous macrostructure [9]. These results thus shows that the morphology of the regenerated cellulose was significantly transformed compering to the original MCC. In addition, the transformation of the regenerated cellulose have been explained that it is due to

its amorphocity, Hence it is of high dense compering to the original cellulose which is highly crystalline state structure by Swatloski *et.al* [9] and Zhu *et.al* [92]. Moreover, similar results were reported in literatures [8, 9, 12, 102, 158]

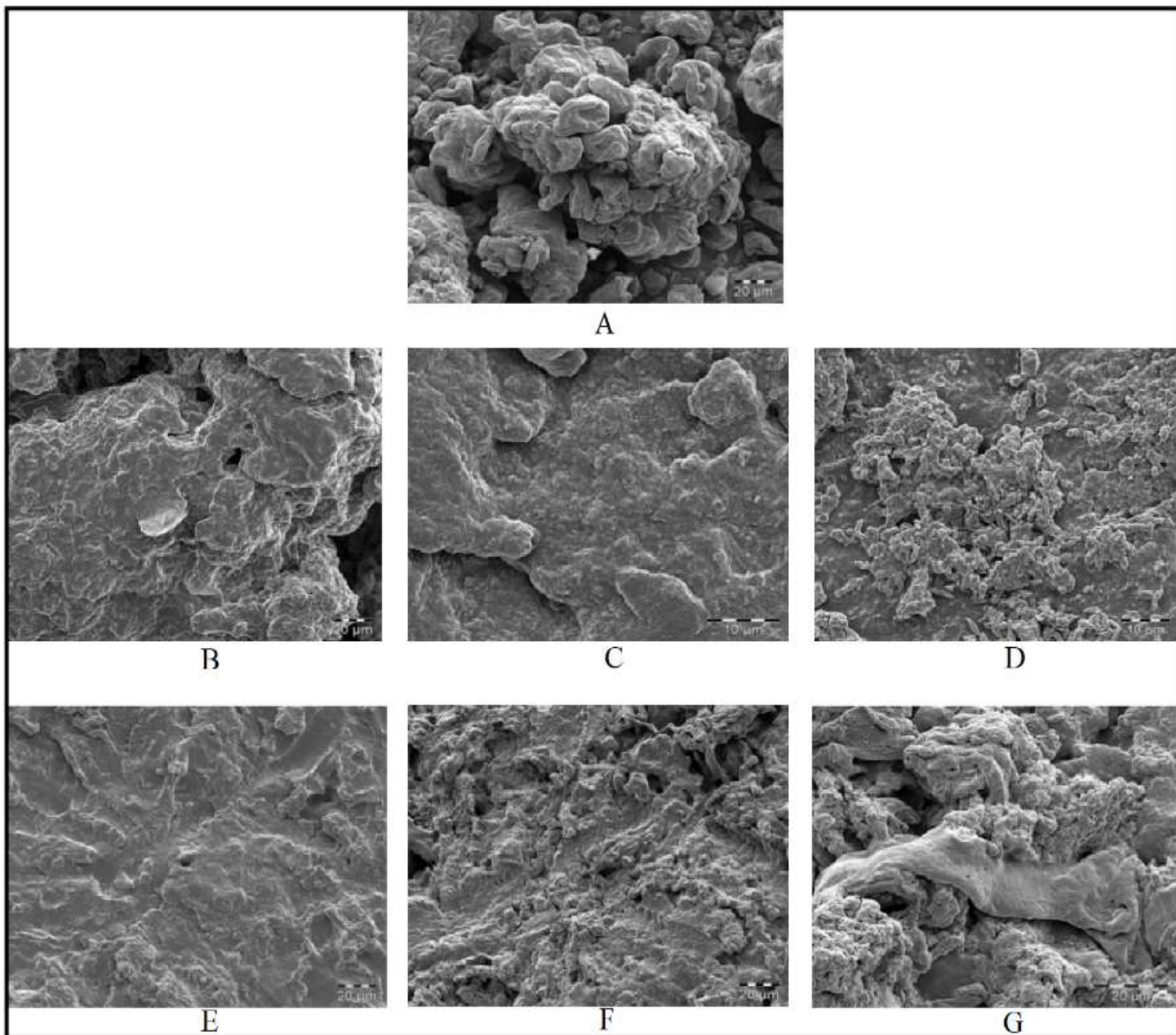


Figure 4.9 SEM micrograms of initial pure micro crystalline cellulose (A), and regenerated cellulose (B, C, D, E, F and G) after dissolved in B = [BMIM][Cl], C = [AMIM][Cl], D= [BMPy][Cl], E= [BMIM][Cl]/DMF, F = [AMIM][Cl]/DMF and G= [BMPy][Cl]/DMF.

4.2.4 Thermal analysis

4.2.4.1 Thermogravimetric analysis

The TGA graphs of the regenerated cellulose which were previously dissolved in [BMIM][Cl], [AMIM][Cl], [BMPy][Cl], co-solvents [BMIM][Cl]/DMF, [AMIM][Cl]/DMF and [BMPy][Cl]/DMF as well the TGA graph of the pure MCC are given in Figure 4.10-4.12 with Figure 4.13 showing all spectra in one plot.

Figure 4.10 illustrates the TGA results of regenerated cellulose previously dissolved in [BMIM][Cl] and [BMIM][Cl]/DMF together with MCC, from the graph it can be observed that the regenerated cellulose starts to decompose between 190-200 °C and released char yield of 32 mg for [BMIM][Cl] and 28 mg for [BMIM][Cl]/DMF whereas for MCC starts decomposing between 210-220 °C and released char yield of 20 mg.

Figure 4.11 illustrates the TGA results of regenerated cellulose previously dissolved in [AMIM][Cl] and [AMIM][Cl]/DMF together with MCC, from the graph it can be observed that the regenerated cellulose starts to decompose between 190-200 °C and released char yield of 29 mg for [AMIM][Cl] and 22 mg for [AMIM][Cl]/DMF whereas for MCC starts decomposing between 210-220 °C and released char yield of 20 mg. Furthermore, regenerated cellulose from [AMIM][Cl] had higher water content than regenerated cellulose fibres previously dissolved in [AMIM][Cl]/DMF and pure MCC which shows that regenerated cellulose fibres prepared from [AMIM][Cl] is hygroscopic.

Figure 4.12 illustrates the TGA results of regenerated cellulose previously dissolved in [BMPy][Cl] and [BMPy][Cl]/DMF together with MCC, from the graph it can be observed that the regenerated cellulose starts to decompose between 130-140 °C and released char yield of 22 mg for [BMPy][Cl] and 24 mg for [BMPy][Cl]/DMF whereas for MCC starts decomposing between 210-220 °C and released char yield of 20 mg.

Figure 4.13 illustrates the TGA results of all the regenerated cellulose fibres previously dissolved in [BMIM][Cl], [AMIM][Cl], [BMPy][Cl], co-solvents [BMIM][Cl]/DMF, [AMIM][Cl]/DMF and [BMPy][Cl]/DMF together with pure MCC. The graphs shows that all the regenerated cellulose fibres have similar thermal stability patterns. However, the original MCC released less char yield when compared to the regenerated celluloses. Furthermore, original MCC has highest decomposing temperature as compared to regenerated celluloses [103] which suggested that original cellulose is more thermally stable than the regenerated ones. In addition, the stability of cellulose is higher because it is highly crystalline than the regenerated ones which are amorphous.

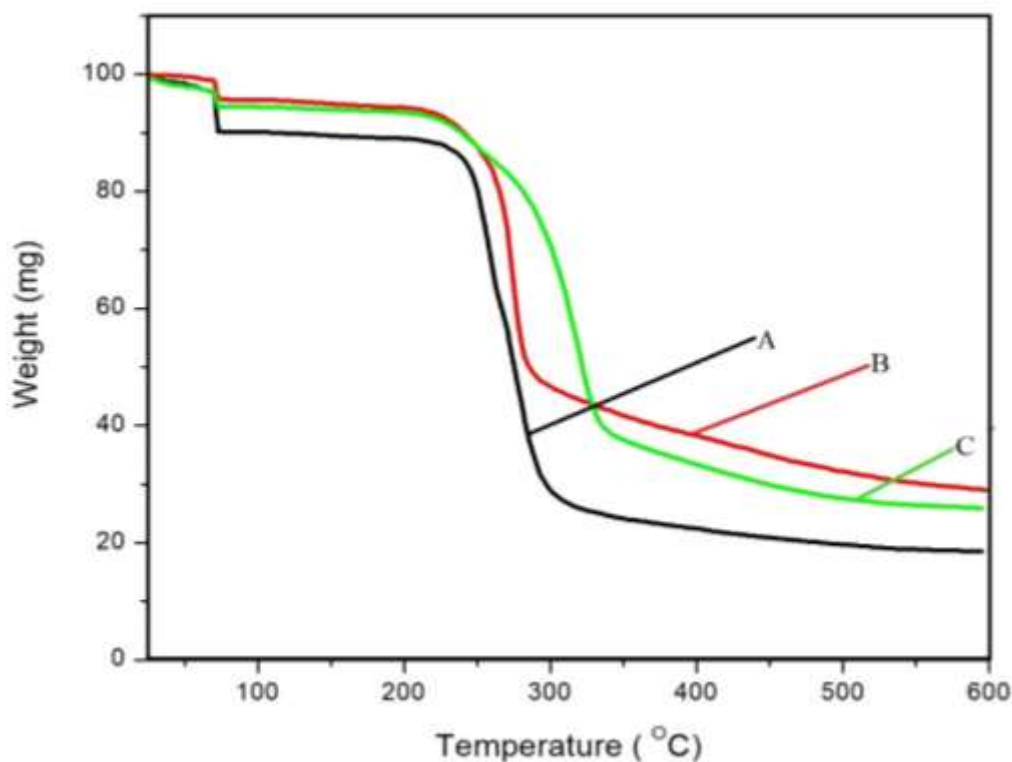


Figure 4.10 TGA analysis of pure microcrystalline cellulose (A), regenerated cellulose after dissolved in [BMIM][Cl] (B) and in [BMIM][Cl]/DMF (C).

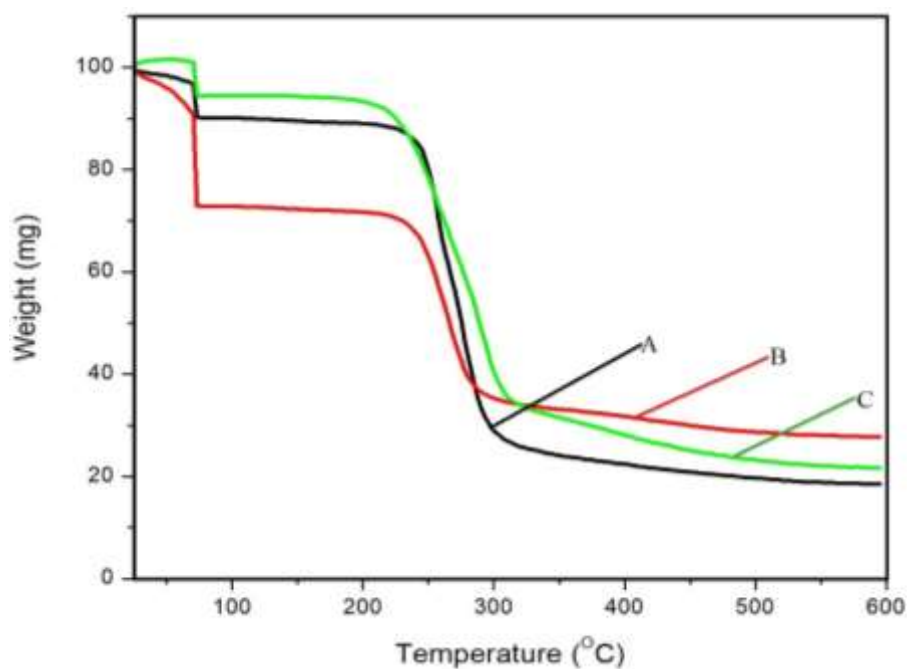


Figure 4.11 TGA analysis of pure microcrystalline cellulose (A), regenerated cellulose after dissolved in [AMIM][Cl] (B) and in [AMIM][Cl]/DMF (C).

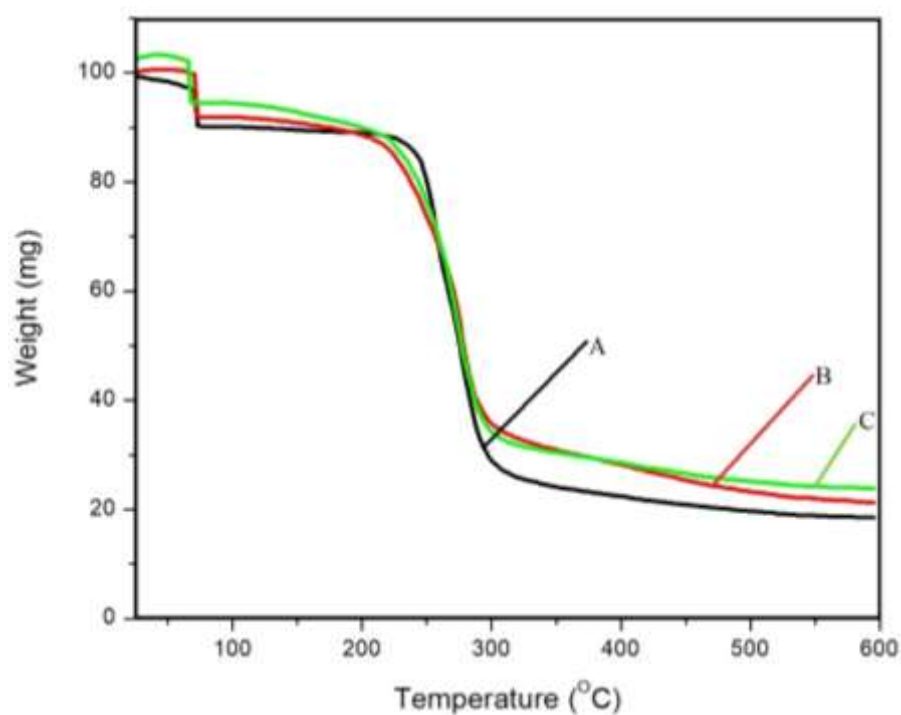


Figure 4.12 TGA analysis of pure microcrystalline cellulose (A), regenerated cellulose after dissolved in [BMPy][Cl] (B) and in [BMPy][Cl]/DMF (C).

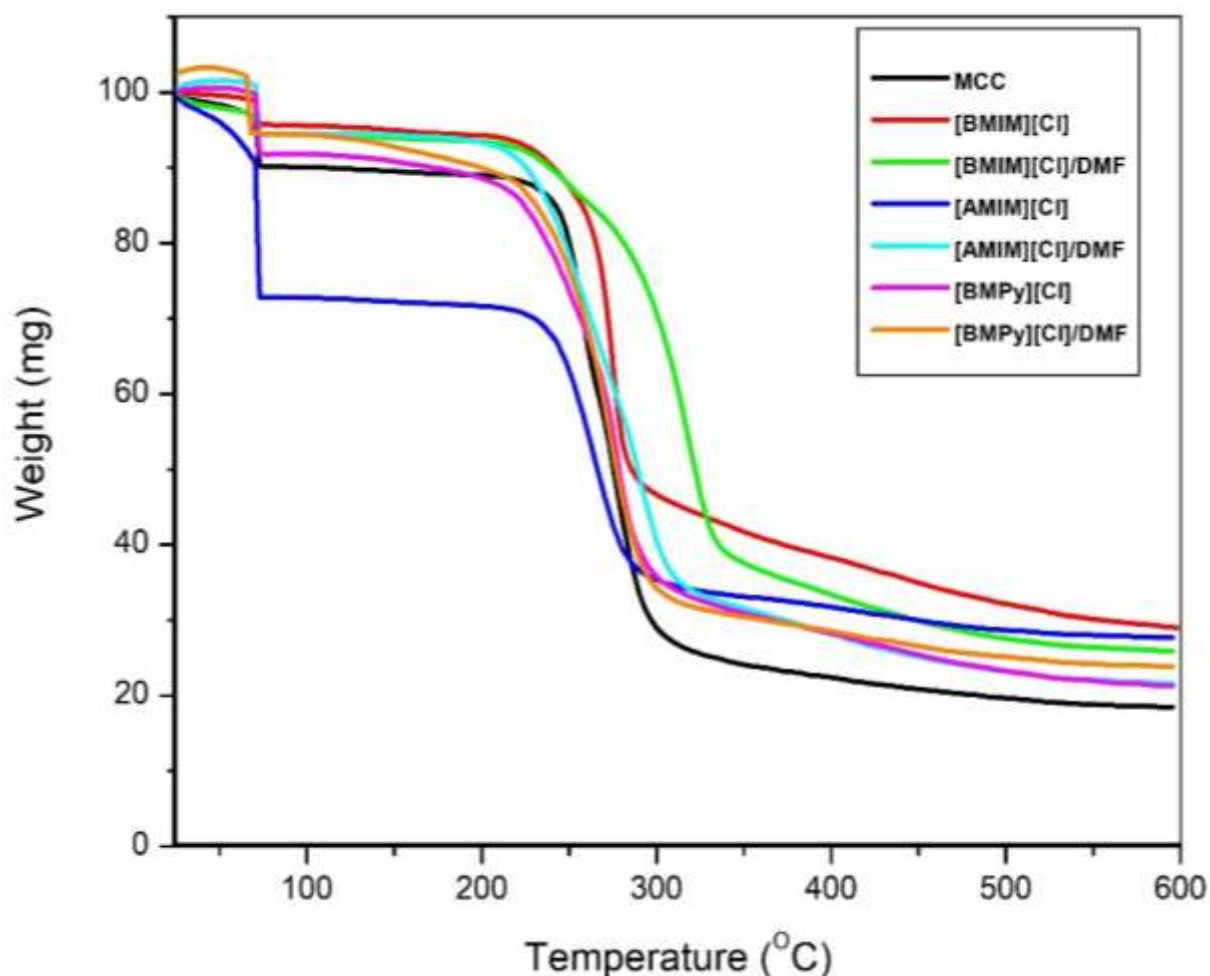


Figure 4.13 TGA analysis of pure microcrystalline cellulose (MCC) and regenerated cellulose after dissolved in different ILs with and without co-solvent (DMF).

4.2.4.2 Differential scanning calorimetry

DSC results of regenerated cellulose previously dissolved in [BMIM][Cl], [AMIM][Cl], [BMPy][Cl], co-solvents [BMIM][Cl]/DMF, [AMIM][Cl]/DMF and [BMPy][Cl]/DMF are given in Figures (4.14 to 4.16) and 4.17 illustrating all spectra in one plot for comparison purpose.

The DSC results of original MCC represented as “A” in all Figures (4.14, 4.15 and 4.16), is observed to have a glass transition from 75-240 °C, crystallization at 257 °C and melting point at 282 °C, the regenerated fibers in Figures (4.14, 4.15 and 4.16) are somewhat not the same to

the results of original MCC, rather, only the glass transition is similar. As it can be observed from the Figures 4.14 and 4.16 regenerated cellulose fibers previously dissolved in [BMIM][Cl] and [BMIM][Cl]/DMF in Figure 4.14 and [BMPy][Cl] in Figure 4.16 now have higher crystallization temperature than the original MCC and also no melting point was observed at the studied temperature range for those materials. Moreover, Figure 4.15 showing DSC results of regenerated material previously dissolved in [AMIM][Cl] and [AMIM][Cl]/DMF and Figure 4.16 showing DSC results of regenerated material previously dissolved in [BMPy][Cl]/DMF shows that those regenerated materials still have similar physical properties to the original MCC to some extent.

After comparison of all these DSC results using Figure 4.17 it can be concluded that, the changes in crystallization and melting point of the regenerated cellulose fibers is due to the disrupted intra- and intermolecular hydrogen bonding as the regenerated material are now more amorphous (as proven by XRD, SEM and TGA results) than the original MCC which is more crystalline.

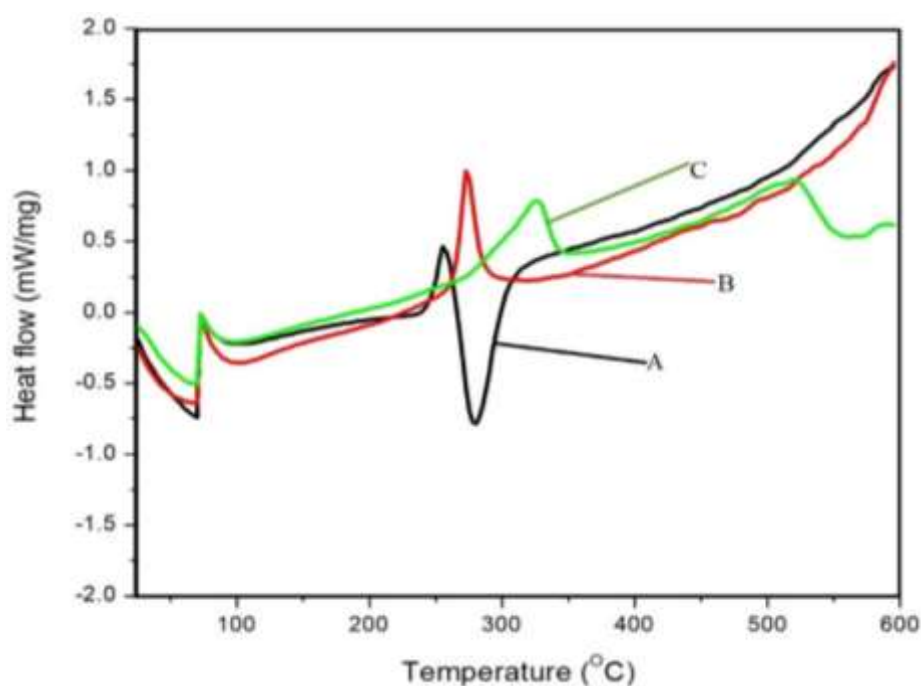


Figure 4.14 DSC analysis of pure microcrystalline cellulose (A), regenerated cellulose after dissolved in [BMIM][Cl] (B) and in [BMIM][Cl]/DMF (C).

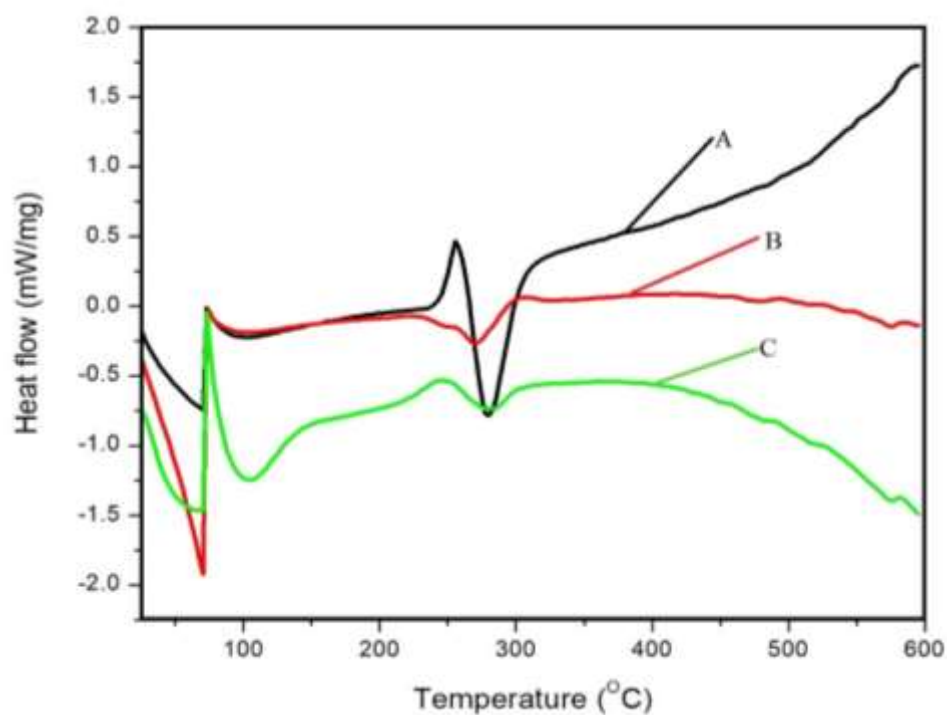


Figure 4.15 DSC analysis of pure microcrystalline cellulose (A), regenerated cellulose after dissolved in [AMIM][Cl] (B) and in [AMIM][Cl]/DMF (C).

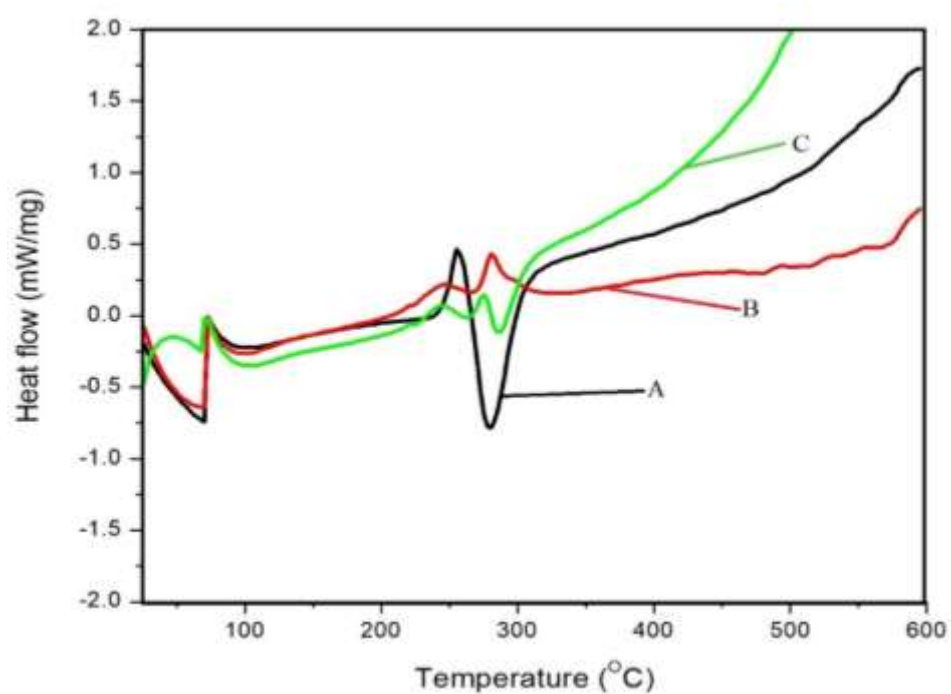


Figure 4.16 DSC analysis of pure microcrystalline cellulose (A), regenerated cellulose after dissolved in [BMPy][Cl] (B) and in [BMPy][Cl]/DMF (C).

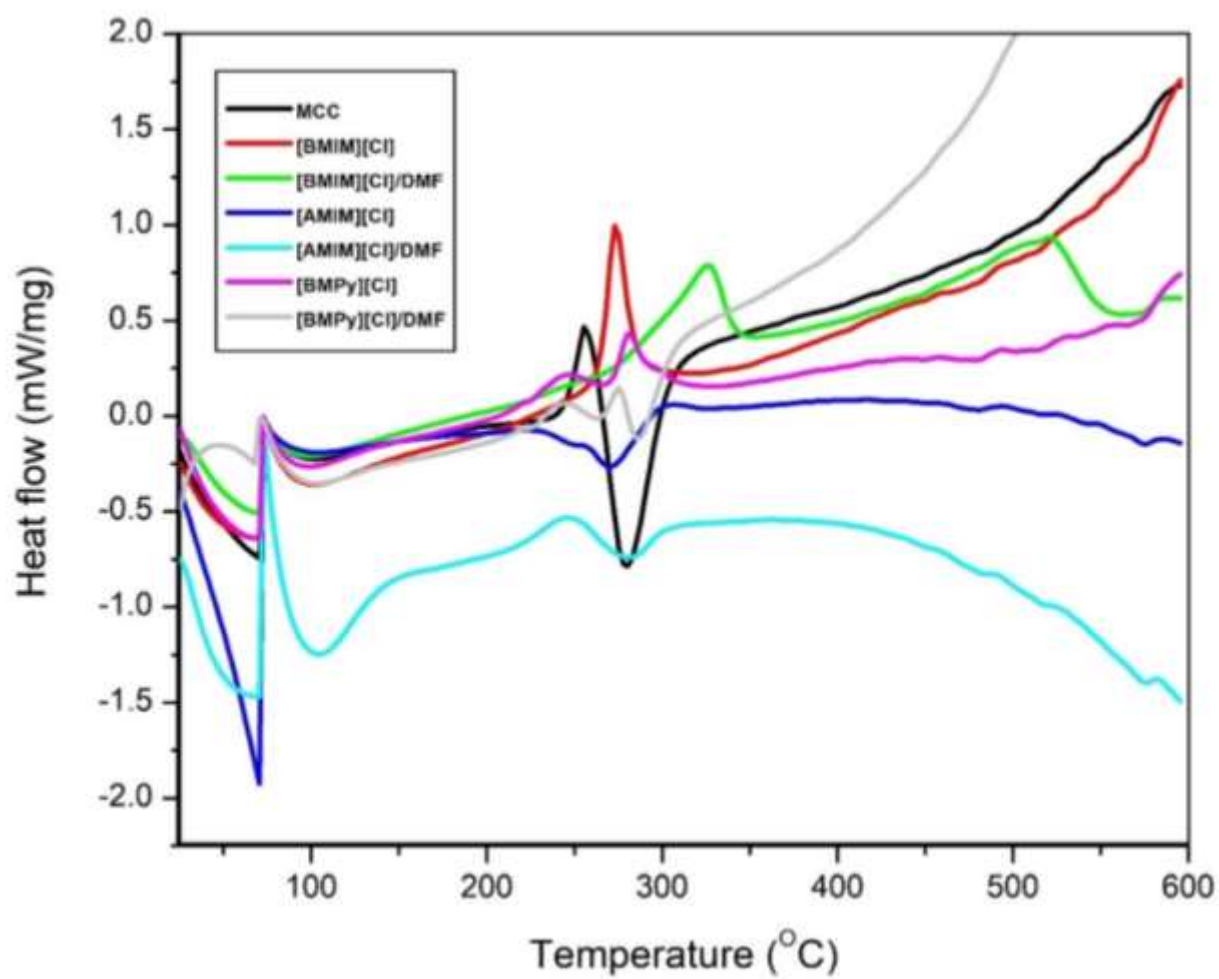


Figure 4.17 DSC analysis of pure microcrystalline cellulose (MCC) and regenerated cellulose after dissolved in different ILs with and without co-solvent (DMF).

4.3 Thermophysical properties

The density, ρ , sound velocity, u , and refractive index, n_D , of mixtures of MCC with [BMIM][Cl] + DMF or [AMIM][Cl] + DMF or [BMPy][Cl] + DMF at various molality were measured at $T = (298.15, 303.15, 308.15 \text{ and } 313.15) \text{ K}$ under ambient pressure and the values are presented in Table 4.1

Table 4.1 Densities, ρ , and sound velocities, u , and refractive indices, n_D , of MCC dissolved in [BMIM][Cl]/DMF or [AMIM][Cl]/DMF or [BMPy][Cl]/DMF at 298.15, 303.15, 308.15 and 313.15 K

$10^{-6} \times m \text{ (mol.kg}^{-1}\text{)}$	$\rho \text{ (kg.m}^{-3}\text{)}$	$u \text{ (m.s}^{-1}\text{)}$	n_D
DMF + [BMIM][Cl] + MCC			
T = 298.15 K			
0.0000	988.67	1537.35	1.4581
0.0424	988.80	1538.51	1.4582
0.0840	989.38	1539.65	1.4583
0.1258	990.20	1540.22	1.4587
0.1676	991.00	1540.88	1.4589
0.2118	991.50	1541.98	1.4592
T=303.15 K			
0.0000	984.56	1521.54	1.4561
0.0424	984.66	1522.35	1.4563
0.0840	985.21	1522.92	1.4564
0.1258	985.99	1523.01	1.4566
0.1676	986.72	1523.35	1.4568
0.2118	987.05	1524.02	1.4570
T=308.15 K			
0.0000	980.48	1503.12	1.4541
0.0424	980.51	1504.22	1.4543
0.0840	981.02	1504.88	1.4545
0.1258	981.80	1505.12	1.4546
0.1676	982.49	1505.66	1.4547
0.2118	982.62	1506.21	1.4549
T=313.15 K			
0.0000	976.10	1485.22	1.4518
0.0424	976.10	1486.33	1.4521
0.0840	976.55	1486.95	1.4523
0.1258	977.30	1487.45	1.4525
0.1676	977.90	1487.89	1.4527
0.2118	978.10	1488.52	1.4528
DMF + [AMIM][Cl]			
T=298.15 K			
0.0000	959.68	1476.97	1.4374

0.0166	960.09	1478.31	1.4377
0.0343	961.24	1479.65	1.4380
0.0499	961.65	1479.82	1.4382
0.0644	962.00	1480.05	1.4383
0.0901	961.88	1480.72	1.4384
T=303.15 K			
0.0000	955.08	1458.62	1.4351
0.0166	955.47	1459.34	1.4354
0.0343	956.13	1461.85	1.4357
0.0499	957.06	1461.82	1.4358
0.0644	957.22	1461.48	1.4358
0.0901	957.28	1461.21	1.4360
T=308.15 K			
0.0000	950.50	1439.85	1.4329
0.0166	950.81	1440.47	1.4330
0.0343	951.52	1443.06	1.4333
0.0499	952.45	1443.06	1.4332
0.0644	952.60	1442.57	1.4336
0.0901	952.66	1442.45	1.4336
T=313.15 K			
0.0000	945.89	1421.92	1.4307
0.0166	946.18	1421.72	1.4308
0.0343	946.89	1424.33	1.4310
0.0499	947.73	1424.35	1.4311
0.0644	947.97	1423.60	1.4311
0.0901	948.03	1423.72	1.4313
DMF + [BMPy][Cl]			
T=298.15 K			
0.0000	978.05	1556.67	1.4566
0.0468	978.15	1554.26	1.4543
0.0860	978.34	1554.96	1.4537
0.1311	978.78	1555.77	1.4545
0.1783	979.25	1557.08	1.4557
0.2108	979.73	1558.04	1.4565
T=303.15 K			
0.0000	974.13	1535.36	1.4545
0.0468	974.28	1534.44	1.4522
0.0860	974.39	1535.08	1.4517
0.1311	974.65	1536.55	1.4522
0.1783	975.00	1539.1	1.4535
0.2108	975.38	1540.04	1.4545
T=308.15 K			
0.0000	970.01	1516.91	1.4523
0.0468	970.00	1515.98	1.4501
0.0860	970.10	1517.25	1.4495
0.1311	970.34	1519.20	1.4504
0.1783	970.63	1520.55	1.4519
0.2108	970.97	1521.88	1.4524
T=313.15 K			
0.0000	965.90	1497.66	1.4500

0.0468	965.85	1497.43	1.4479
0.0860	965.89	1498.66	1.4474
0.1311	966.03	1501.30	1.4483
0.1783	966.32	1502.62	1.4500
0.2108	966.66	1503.88	1.4505

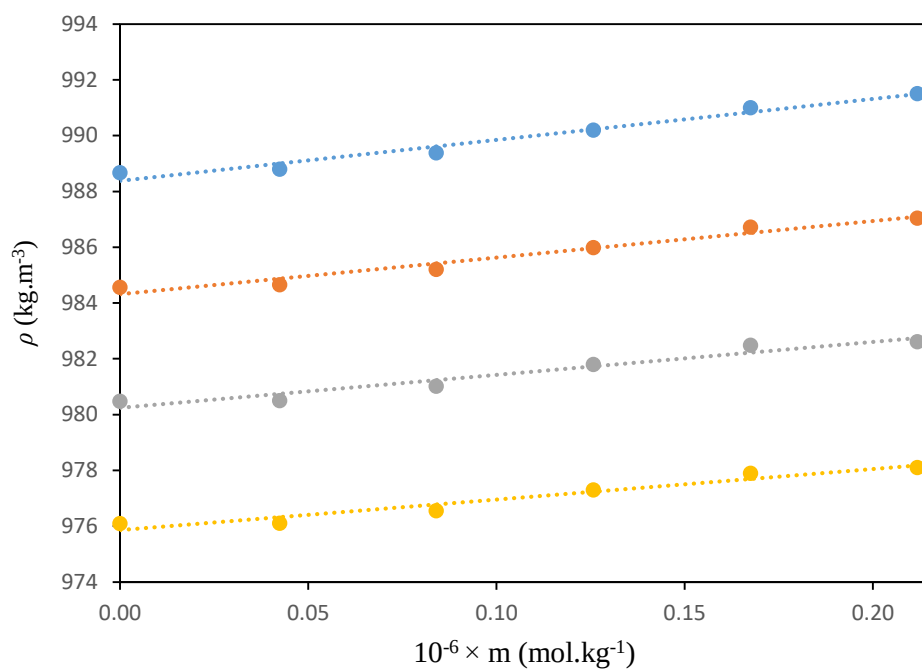


Figure 4.18 (a) Density, ρ , for the mixtures of {MCC + [BMIM][Cl]/DMF} at 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted line represents the smoothness of the data.

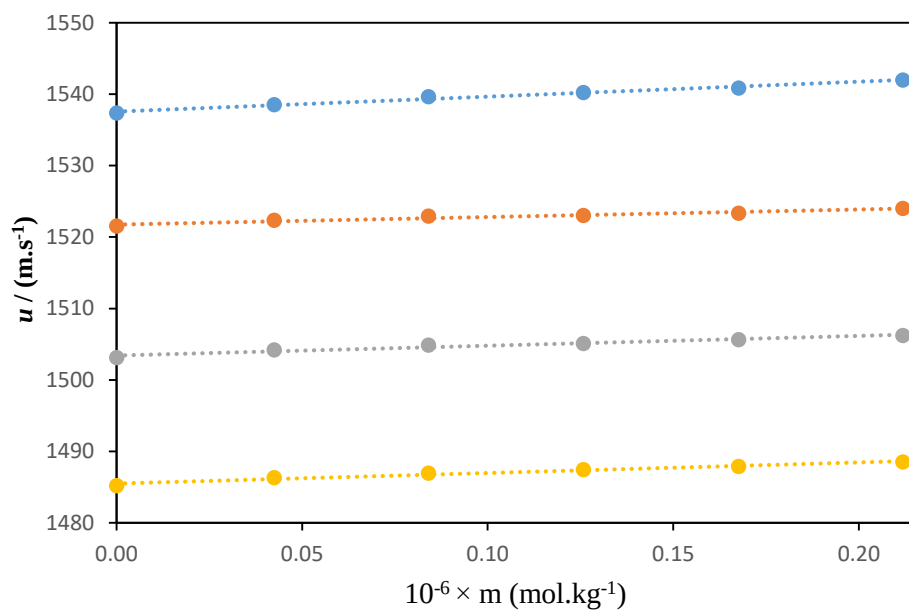


Figure 4.18 (b) Sound velocity, u , for the mixtures of {MCC + [BMIM][Cl]/DMF} at 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted line represents the smoothness of the data.

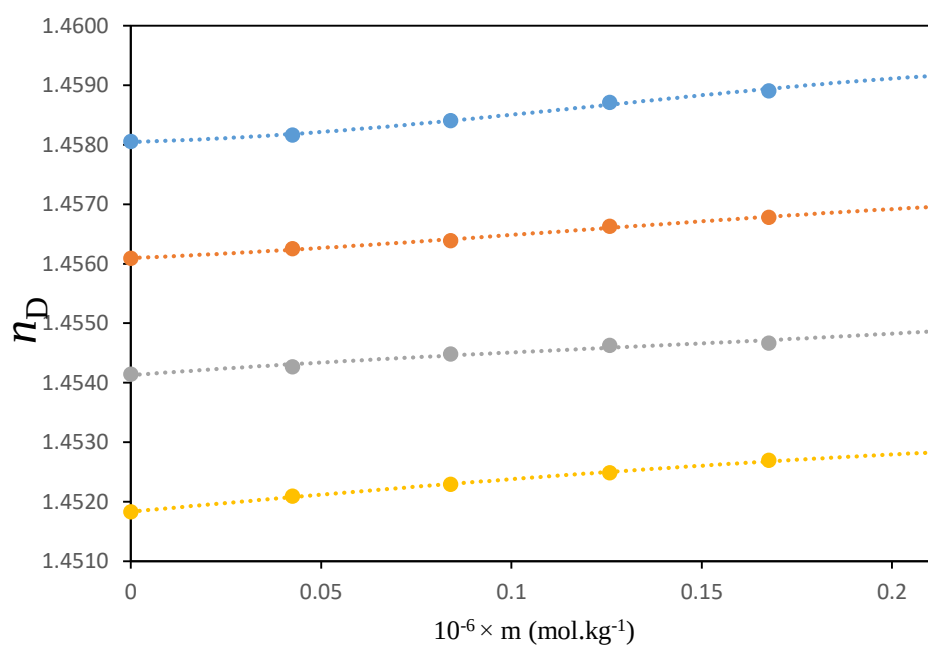


Figure 4.18 (c) Refractive index, n_D , for the mixtures of {MCC + [BMIM][Cl]/DMF} at 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted line represents the smoothness of the data.

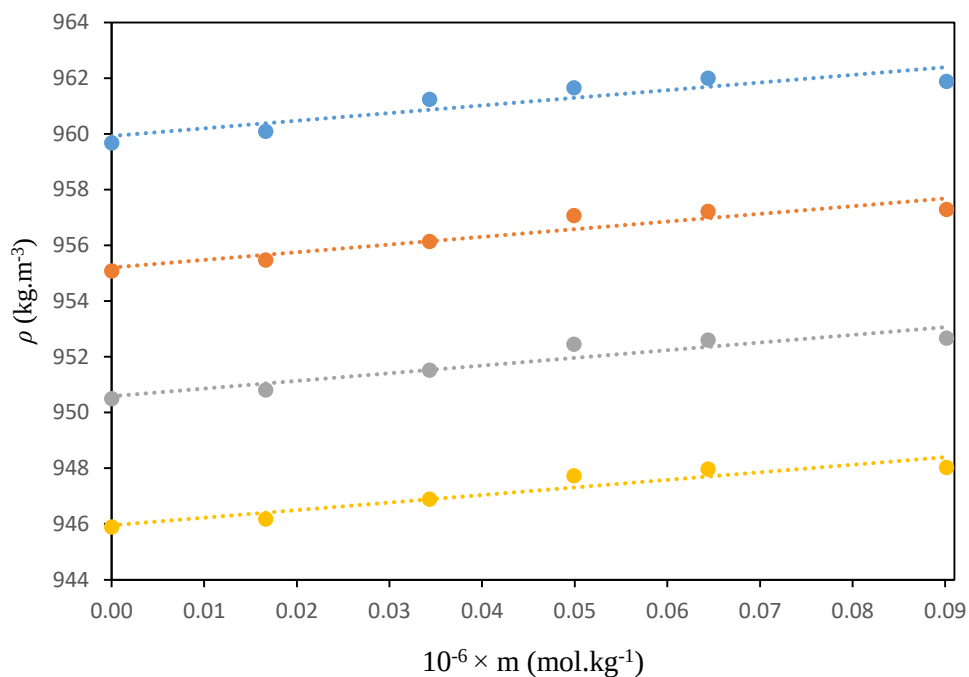


Figure 4.19 (a) Density, ρ , for the mixtures of {MCC + [AMIM][Cl]/DMF} at 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted line represents the smoothness of the data.

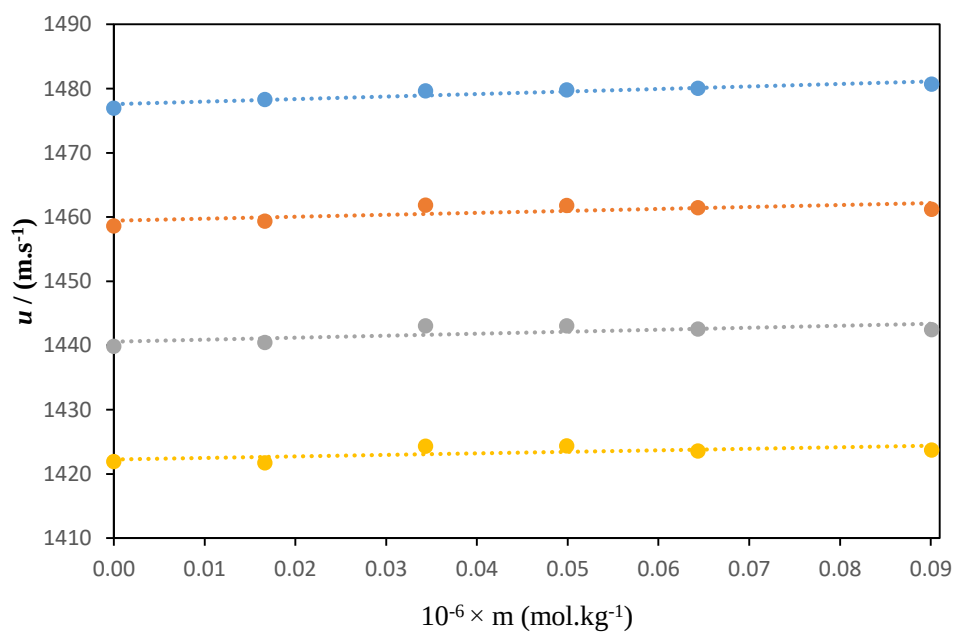


Figure 4.19 (b) Sound velocity, u , for the mixtures of {MCC + [AMIM][Cl]/DMF} at 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted line represents the smoothness of the data.

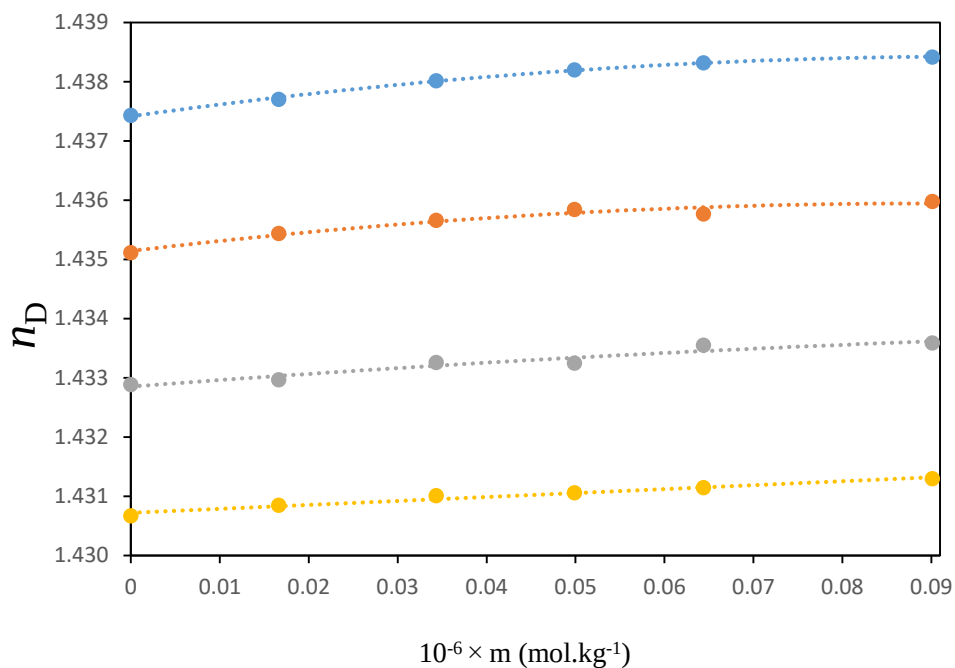


Figure 4.19 (c) Refractive index, n_D , for the mixtures of {MCC + [AMIM][Cl]/DMF} at 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted line represents the smoothness of the data.

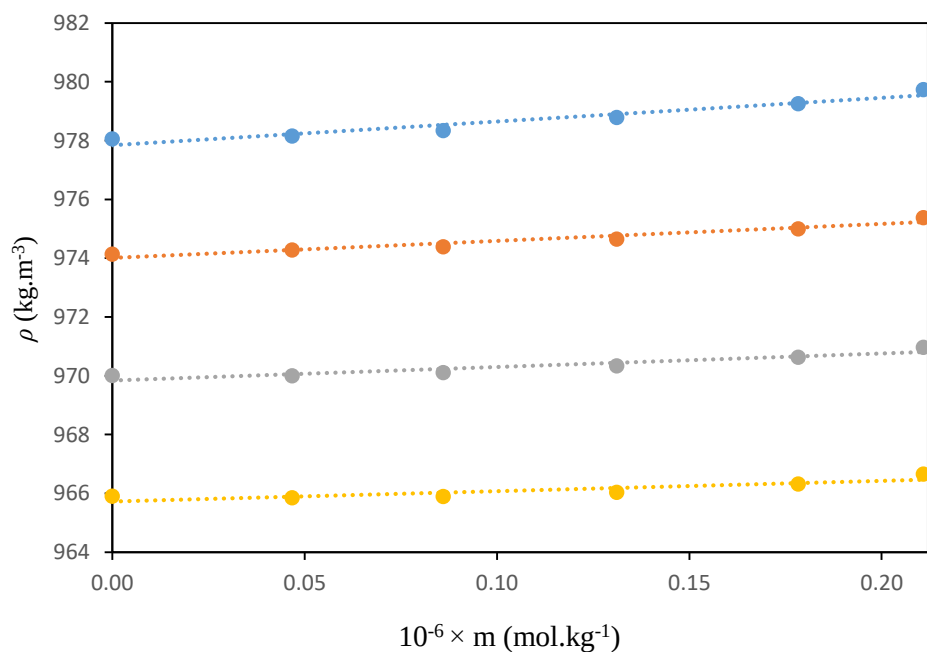


Figure 4.20 (a) Density, ρ , for the mixtures of {MCC + [BMPy][Cl]/DMF} at 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted line represents the smoothness of the data.

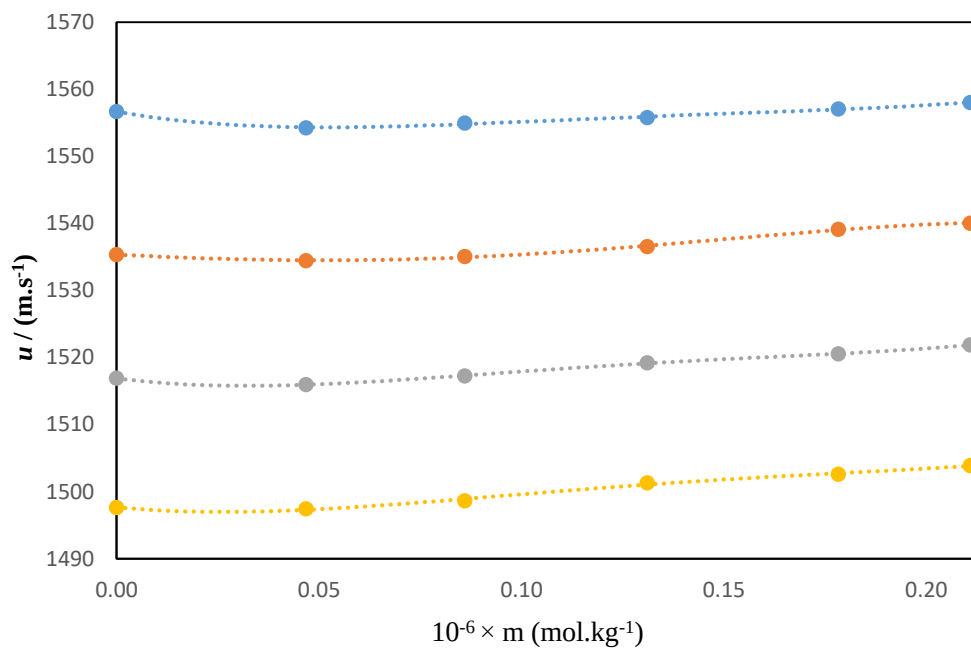


Figure 4.20 (b) Sound velocity, u , for the mixtures of {MCC + [BMPy][Cl]/DMF} at 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted line represents the smoothness of the data.

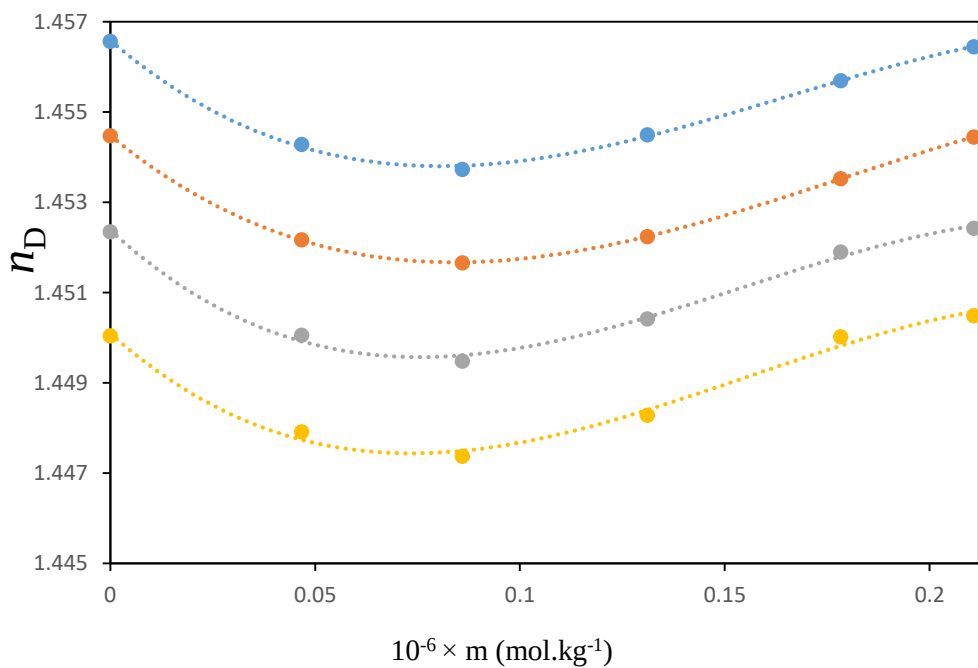


Figure 4.20 (c) Refractive index, n_D , for the mixtures of {MCC + [BMPy][Cl]/DMF} at 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●). The dotted line represents the smoothness of the data.

Thermophysical properties density, ρ , sound velocity, u , and refractive index, n_D , measurements were taken at temperature range of (298.15, 303.15, 308.15 and 313.15) K for various molality. Thermophysical properties measurements were taken to verify that the dissolution process is taking place/took place. The results of density, ρ , sound velocity, u , and refractive index, n_D , obtained which is given in Table 4.1 and illustrated in Figure 4.18 (a)-4.20 (c) were found to increase as molality increases the values of density, ρ , sound velocity, u , and refractive index, n_D , verified that the dissolution took place.

Density results shows the presence of a very strong/weak intermolecular attraction, therefore if density increases it shows that there is a very strong intermolecular interactions such as solute-solvent interaction, furthermore, the increase in density is attributed to the presence of strong dipole-dipole and hydrogen bonding [159]. The density results obtained of all studied system MCC with [BMIM][Cl] + DMF or [AMIM][Cl] + DMF or [BMPy][Cl] + DMF given in Figure 4.18(a), 4.19 (a) and 4.20 (a), respectively were found to increase as molality increases hence there was a presence of strong intermolecular interactions [159].

Sound velocity give the information about the structure and properties of the solute, if sound velocity increase it shows that the solutes are structure maker and if it decreases it shows that solutes are structure breaker [159]. The results of sound velocity obtained of all studied systems MCC with [BMIM][Cl]+ DMF or [AMIM][Cl] + DMF or [BMPy][Cl] + DMF given by figure 4.18(b), 4.19 (b) and 4.20 (b), respectively were found increased as molality increases.

Refractive index shows shed some light on both solute-solute and solute-solvent interactions [160]. Refractive index results of the systems MCC with [BMIM][Cl]/DMF or [AMIM][Cl]/DMF were found to increase as molality increases whereas for system of MCC with [BMPy][Cl]/ DMF were found to decrease then increase as molality increases.

CHAPTER 5: CONCLUSION

5.1 Conclusion

In this study three ionic liquids and their co-solvents with DMF, namely: 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]), 1-allyl-3-methylimidazolium chloride ([AMIM][Cl]), 1-Butyl-3-methylpyridinium chloride ([BMPy][Cl]), 1-butyl-3-methylimidazolium chloride/ dimethyl formamide ([BMIM][Cl]/DMF), 1-allyl-3-methylimidazolium chloride/ dimethyl formamide ([AMIM][Cl]/DMF), 1-Butyl-3-methylpyridinium chloride/ dimethyl formamide ([BMPy][Cl]/DMF) were used to carry out cellulose dissolution process at same experimental conditions. After cellulose has been dissolved it was regenerated and characterized using different techniques such as Fourier Transform Infrared spectrometry (FTIR), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Thermal gravimetric analysis (TGA) and Differential scanning calorimetry (DSC).

The regenerated cellulose was found to have similar characteristics to the original cellulose (microcrystalline cellulose), however the structural morphology of the regenerated cellulose were found to be high dense, this observation was made using SEM, XRD and DSC. The regenerated cellulose was rather amorphous unlike the original cellulose which was crystalline. DSC results also revealed that the melting point of the regenerated cellulose was altered, TGA results revealed that the regenerated cellulose is less thermally stable than the original cellulose, nonetheless, the regenerated cellulose previously dissolved from all the studied solvents was structurally similar to the original cellulose as FTIR results showed no formation of new bonds had been developed.

Furthermore, thermophysical properties (density, ρ , sound velocity, u , and refractive index, n_D), measurements were made using various prepared cellulose mixtures of various molalities using [BMIM][Cl]/DMF, [AMIM][Cl]/DMF and [BMPy][Cl]/DMF at temperature range of

(298.15, 303.15, 308.15 and 313.15) K. Thermophysical properties measurements were taken to confirm that cellulose indeed dissolved in solvent systems of [BMIM][Cl]/DMF, [AMIM][Cl]/DMF and [BMPy][Cl]/DMF as for pure ILs: [BMIM][Cl] [AMIM][Cl] and [BMPy][Cl] no thermophysical properties measurements were taken since there is plenty of literature proving that cellulose does indeed dissolve in those ILs. The solubility of cellulose in [BMIM][Cl]/DMF, [AMIM][Cl]/DMF and [BMPy][Cl]/DMF were observed as an increased in density, ρ , sound velocity, u , and refractive index, n_D , as molality increased.

Since the obtained results of the regenerated cellulose from co-solvents [BMIM][Cl]/DMF, [AMIM][Cl]/DMF and [BMPy][Cl]/DMF were similar with the results of the regenerated cellulose from pure [BMIM][Cl], [AMIM][Cl] and [BMPy][Cl] ILs, respectively, therefore, it can be concluded that DMF does not interact with cellulose during dissolution process as stated in the theoretical study, however, it increases the ionic mobility which further increase the dissolution rate.

5.2 Recommendations of the future studies

Ionic liquids are available in small quantities and also they are expensive, in order for them to be applied industrially some major problems still have to be addressed such as:

- Development of the efficient ways to synthesis ionic liquids so that ILs can be available in high quantity.
- The need to do further research in solvent recovery for both ILs and for ILs with a co-solvent.
- To do research on ILs chemical and toxicological data with cellulose.
- The dissolution mechanism of cellulose with ILs in details.

The outcomes on the ionic liquids research in cellulose chemistry will help to broaden up the application of cellulose in various industries as after cellulose has been dissolved it can be modified by inserting various functional groups, this however, does not destroy fascination intrinsic properties of cellulose [134-136] which makes cellulose to be magnificent candidate of nanocrystals [161-163]. Cellulose nanocrystals can be applied in pharmaceuticals for antibacterial and antiviral agents, tissue engineering scaffolds, biomarkers or sensors, gene vectors, drug delivery vehicles, and biocatalyst scaffolds using modified cellulose based nanoparticles [164]. Modified cellulose based nanoparticles can also be used in, in enhanced oil and gas recovery since cellulose nanocrystals have been found to stabilize the oil/water interface by Kalashnikova *et. al* [165-167].

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