Syntheses, Characterisation and Applications of Ionic Liquids to Recover Materials from WEEE

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By

Romain Faivre

Brunel University

Institute for the Environment

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Abstract

The recycling of materials from waste electrical and electronic equipment (WEEE) is of great concern today, as increasing public awareness and the implementation of recent legislations have created a situation where industries need to 1) comply with the environmental regulations and 2) fulfil producers' responsibility initiatives. In this context, the work described in this thesis investigates the applications of new leaching solvents, the ionic liquids (ILs), to recycle two materials, copper and decabromodiphenylether (DBDE), which are common in WEEE.

A total of 18 ILs, methylimidazolium (MIM) and methylpyridinium (MPy) based, were prepared using a microwave-assisted method. These ILs were selected to allow characterisation of performance with respect to three parameters: hydrophobicity of the cation, polarity of a terminal functional group in the cation side chain, and the type of aromatic ring, in order to identify their effects on the solubility and extraction processes. All ILs were successfully characterised by IR spectroscopy, mass spectrometry and NMR. Hydrophobicity was measured by HPLC, and the retention factors compared to logP values predicted from Molinspiration. High correlation (>88%) was observed, which indicated that the predicted logP values were representative of the real hydrophobicity of the cation.

Copper metal was not significantly dissolved in any of the ILs, and performance was therefore assessed with the dissolution of CuO. The dissolution tests were conducted at 70°C for ten minutes and the resultant solutions analysed for Cu by using atomic absorption spectroscopy. A short side chain and the presence of a strongly polarised functional group at the terminal position were required to achieve maximum dissolution. Furthermore, the short chain methylimidazolium system was better than methylpyridinium for dissolving CuO. Consequently, 1-(2-cyanoethyl)-1-methylimidazloium bromide was found to be the best solvent and dissolved 75.5 mg of Cu in one g of IL.

High impact polystyrene (HIPS), containing 4.4% of DBDE, was prepared in order to test the extraction abilities of various non-substituted ILs. The extraction of DBDE from the polymer was conducted at 90°C for 2 h 45 min. The results indicated that high hydrophobicity was required to achieve the maximum extraction of DBDE, however, the percentage extraction remained very low (<10%). The low extraction was attributed to the fact that only the DBDE present on the outer surface of the polymer was extracted during the process. In spite of being more hydrophobic, MPy-based systems did not dissolve as much as MIM-based systems because they were more viscous. The high viscosity value actually hindered the diffusion process and ultimately reduced the extraction of DBDE. The effects of different factors on the extraction process were evaluated and the maximum extraction was achieved by using 1-octyl-3-methylimidazolium bromide at 110 °C.

The results described in this thesis have identified and quantified the link between the structures of the ILs and extraction efficiencies in relation to their potential use for recovery of CuO and DBDE from WEEE. The recommendations for future work have also been identified. The results obtained in this work, however, have contributed to increase the knowledge about the properties of ILs and can be used in future research to design a large scale recycling process.

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Abbreviations

%RSD	Percentage of Relative Standard Deviation
ABS	copolymer Acrylonitrile-Butadiene-Styrene
BFR	Brominated Flame Retardant
DBDE	Decabromodiphenylether
EU	European Union
FAAS	Flame Atomic Absorption Spectroscopy
HIPS	High Impact PolyStyrene
HIPS / IL	Mass of HIPS / Mass of IL ratio
HPLC	High Performance Liquid Chromatography
IL	Ionic Liquid
logP	logarithm of the octanol/water partition coefficient
MIM	3-Methylimidazolium
MPy	3-Methylpyridium
MS	Mass Spectrometry
MW	MicroWave
PBDE	Polybrominated Diphenylether
PCB	Printed Circuit Board
PS	Polystyrene
Py	Pyridinium
RoHS	Restriction of Hazardous Substances
RTIL	Room Temperature ionic liquid
TSIL	Task Specific Ionic Liquid
WEEE	Waste Electric and Electronic Equipment
e-waste	Electronic Waste

1 Chapter 1: Introduction

The need to develop new waste recycling methods, especially when dealing with waste of heterogeneous composition, has become ever more important, since the newly implemented and impending legislations encouraged it by setting high recovery and recycling targets. In this respect, the electrical and electronic sector is of particular interest as the amount of electronic and electric waste (e-waste) generated increases by 16 to 20% per year in Europe (Dalrymple et al., 2007). Therefore, recycling represents a real challenge, as the collection, recovery and recycling targets are difficult to meet for domestic or industrial waste (European Commission, 2008; Bush, 2006). The present document aims at reporting the research work that I have done during the course of my PhD studies in the field of materials recovery from e- waste and particularly the development of task-specific ionic liquids (TSIL) to extract copper and decabromodiphenyl ether (DBDE) from waste electric and electronic equipment (WEEE). This introductory chapter presents the problems associated with the recycling of materials from WEEE and the reasons of why new recycling technologies should be developed to improve recycling in order to comply with EU regulations (European Commission, 2002a). Finally, the aims and objectives of this work along with the scope of this thesis are presented.

1.1. The existing recycling technologies and the end-of-life electrical and electronic waste

Waste management is a key feature in modern societies, as it involves financial, environmental and social issues. Many countries have adopted specific regulations to control and rationalise it, like the EU Waste Framework Directive (European Commission, 2006). This piece of legislation is an essential text for all European waste regulation, as it introduces the idea of waste hierarchy, where recycling is seen as the best solution when reducing the amount of waste produced and reusing the waste are not possible. In parallel, the Restriction of Hazardous Substance (RoHS) Directive (European Commission, 2002b) categorises and regulates the use of some hazardous materials use by industries producing manufactured goods, such as electronic and electric equipments. More specific directives are targeted at controlling a specific type of waste, such as the WEEE Directive (European Commission, 2002a) does for the highly challenging e-waste stream.

1.1.1. Recycling e-waste: a large-scale problem

Waste electrical and electronic equipment represents around 1 million tonnes of domestic e-waste a year out of the 300 millions tonnes of waste generated yearly in UK (Industry Council for Electronic Equipment Recycling, 2005). Although it represents only a small fraction of the total waste, it is a great cause of concern, as e-waste are toxic because they contain many heavy metals, brominated and chlorinated substances (Dalrympe et al., 2007). Another concern is the high rate at which it is produced. In Europe, 10 million tons of electronic and electric equipment are manufactured yearly, as opposed to the 9 million tons which reach end of life (Makela, 2009). Moreover, it is growing more rapidly than any other types of waste, but it also represents a challenge due to the multiplicity of its sources and its heterogeneous nature (Parliament Office of Science and Technology, 2007), which render recycling extremely difficult.

The WEEE Directive (EU, 2002b) provides guidance for the categorisation and the collection schemes of e-waste, as well as recovery targets for 2006 (70% to 80% by an average weight per appliance, depending on the appliance type). The WEEE terminology regroups many home electronics and appliances, and can be divided into several groups among which: white goods, such as small and large household appliances, brown goods, including toasters and irons, information and communication technology equipment, such as computers, consumer goods, such as TV and stereo players, or fluorescent lighting.

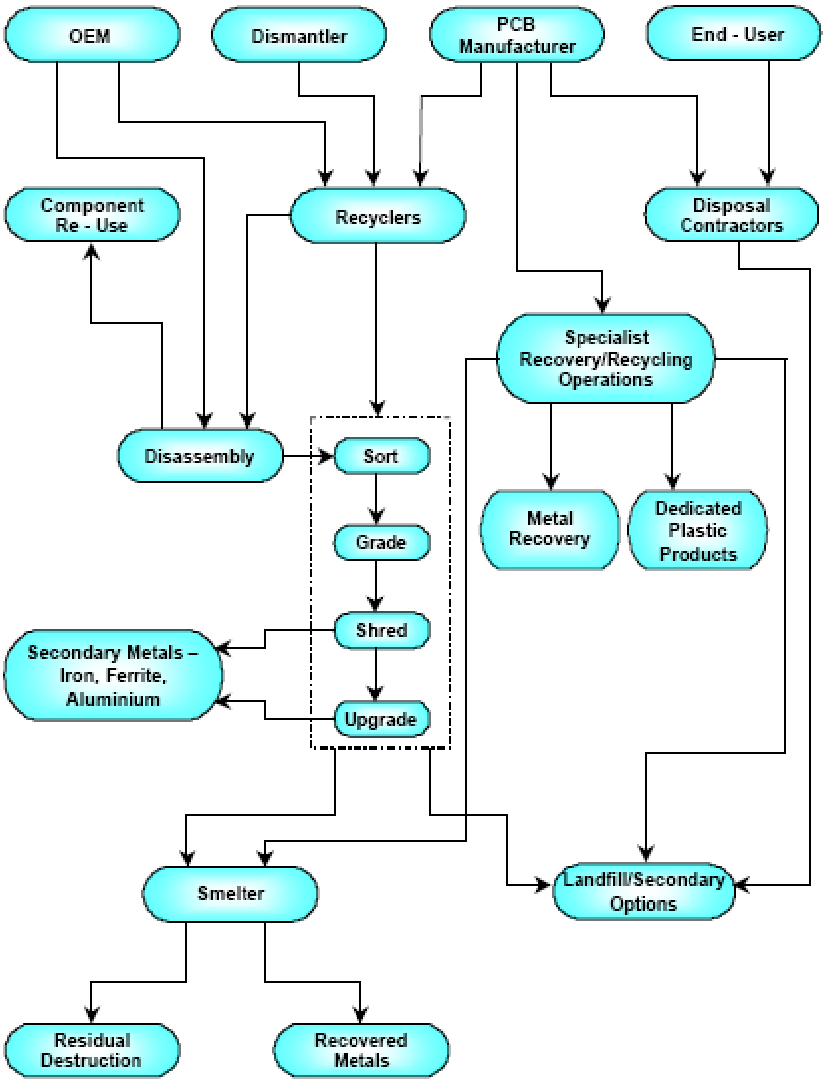
The diversity of sources and the mixed composition of these equipments render their recycling extremely difficult. Technologically advanced treatments might be available, but the market for recycled products from low-value e-waste is too underdeveloped to allow financial cost recovery. As a result, in Europe, an average of 1/3 of WEEE is collected and recycled, of which 54% is treated (European Commission, 2008). In addition, 70% of the world’s e-waste, including from European Union, is sent illegally or not, to poorer Asian countries, such as China or India (Bridgen et al., 2005), where cheap unqualified labour is employed to dismantle and crudely treat the scrap for metal recovery, leading to land contamination and health hazard (Leung et al., 2008). Because of the high recycling targets, and the producers’ responsibility to recycle their manufactured goods introduced by the WEEE directive, recovery systems must be more widely applied, and efforts must be made to either improve existing systems, or develop novel, more efficient, more environmentally friendly and ideally economically viable recovery systems.

1.1.2. Limitation of the existing e-waste recycling techniques

A way to tackle the diversity of e-waste is to separate the bulk waste into different fractions of similar composition, which can be specifically treated. For instance, printed circuit boards (PCB) can easily be separated from the main appliance and treated to recover precious metals and in some instances the polymer (Goosey and Kellner, 2003). In this context, the scope of this study will be focussed on the recovery of two materials contained in different WEEE: copper, a heavy metal present in PCBs (Goosey and Kellner, 2002), and DBDE, a brominated flame retardant (BFR), which is an organic compound contained in plastic housing, for instance in TV casing. Issues associated with the recycling of copper and DBDE from these types of wastes are summarised in the next sections.

1.1.2.1. Recovery and recycling of materials from printed circuit boards

Every year, 50,000 tons of PCBs are discarded worldwide, of which only 15% are recycled (Goosey and Kellner, 2003). According to a 2002 study, PCB are disposed of in three different ways (Goosey and Kellner, 2002), involving mechanical, pyrolytic and hydrometallurgical treatments (Figure 1.1). The first option involves the recovery of the metals, such as iron and aluminium, by mechanical treatments (Magnetic or Eddy current). The remaining material, which still contains copper, polymers and precious metals, is then sent for smelting. A recycling route involving hydrometallurgical treatments for specific recovery is also possible, in case of treating a specific waste.



OEM: Original Equipment Manufacturer

Figure 1.1: PCB disposal scheme (Goosey and Kellner, 2002)

Smelting is a pyrolitic treatment (Goosey and Kellner, 2002) that consists in igniting and melting the PCB feedstock at 1200 °C, while the organic content of PCB acts as fuels during the reaction. The resulting copper-rich black material is treated by electrorefining, followed by recovery of precious metals (gold, silver, palladium) using leaching, melting and precipitative route. Due to their high copper content, scrap PCB are prime materials for primary copper-smelting plants. The process consumes the organic content of the waste and also allows the recovery of other precious metals, such as gold or silver. However, the process is energy intensive. As a result, it is only economically viable when applied to high-grade printed circuit boards, which possess high intrinsic value due to a higher content of precious metals (Lee et al., 2004).

Mechanical treatments reduce the size of the initial scrap PCB material, and sorts it into enriched fractions, whose composition is optimised for further recycling or direct application. Dry mechanical separation includes different size reduction processes associated to metal separation by magnetic current (ferrous metals) or Eddy current (non-ferrous metals) (Cui and Fossberg, 2003). Other separation and sorting processes comprise pulverisation (size reduction), electrostatic separation, allowing the separation of the conducting fraction (Wu et al., 2008), and air table techniques, to sort the particulates by size (Zhou and Lu, 2005). For instance, the German PCB manufacturer Fuba has been operating a recycling plant since 1995, for recycling of un-populated circuit boards (Gold and Dietz 2003). The process, recovers 92-95% of the metal values from low grade un-assembled PCB, while the output polymer stream, after extrusion, finds an application as pallets for underground mining and storage, taking advantage of the flame retardant property of the material. This purely mechanical treatment separates shredded fraction, through magnetic and electrostatic separation, allowing recycling of 5000 tons/year at a beneficiary cost.

Hydrometallurgical treatment involves the use of a wet stage where solvent dissolves metals in their cationic form. Metals are then recovered under their solid form by precipitation (chemical or electrolytic). The processes can be selective or can dissolve all metals present in the waste. For example, etching solutions based on cupric chloride or ammonium sulphate (Oishi et al., 2007) are used for copper leaching. Solder (tin and antimony) can be selectively leached out by a regenerable solution based on fluoroboric acid before copper and precious metals are extracted and recovered. Pure metals can then be electrolytically recovered (Goosey and Kellner, 2003). Non selective dissolution is also possible using an electrochemically generated chlorine solution. Subsequent metal recovery is achieved by electrolytic membrane cells with discrete metal separation (Goosey and Kellner, 2003). All these examples demonstrate that chemical treatments are available for metal recovery.

Most of the PCB recycled in UK are treated through dismantling/size reduction and sorting (mechanical treatment) followed by the smelting of the precious metal-rich fraction (Goosey and Kellner, 2002). It presents the advantage of raising the intrinsic value of metal concentrated fraction, thus making subsequent smelting cost-effective. As a matter of fact, dry separation is the most attractive option, as it has a relatively low functioning cost and is easy to operate, does not generates by-products, such as used solvent or leaching solutions, and only requires noise and dust control. The only limitation is the market for the different recycled fractions, which contain mixed metals, whose content is too low for cost-effective recovery (Lee, 2004). The Fuba approach (Gold and Dietz, 2003), confirms this point, as the polymeric by-products are transformed into a sellable product for a specific and limited use. Smelting appears to be a cost-effective option for metal recovery, but it requires metal preconcentrated fraction, it destroys the polymeric phase, and it is an energy intensive process. Pyrolysis of PCBs at various temperatures (de Marco et al., 2008; Hall et al., 2007; Chiang et al., 2007) represents an alternative, and it leads to a polymer-free metal-rich pyrolitic residue, a liquid phase (very low metal content trapped) and gases. This pyrolitic treatment suffers from similar problems, namely the formation of waste byproducts, the necessity to trap brominated by-products, and generation of CO_2 and CO.

Economical cost of such processes is also crucial and, therefore, the recycling systems have to be profitable in order for them to be sustainable and have maximum chance of their adoptions by industry. For that reason, there must be a market for recycled products. Although metals are commonly recycled, as they represent the highest intrinsic value, polymeric fractions are more difficult to sell, as their purity is an issue (Goosey and Kellner, 2003). The problem can be solved by expanding the range of application for the recycled fractions, or by developing new recycling techniques that allow recovery of materials in a quality high enough to be reused in the market, at a reasonable cost.

As a conclusion, a universal treatment using a single process is not possible due to the diversity and variation of intrinsic value of end-of-life PCB, and an integrated approach, resulting in a mixed process, should be envisaged. Mechanical separation seems the best way to start, as it segregates the waste into different fractions rich in one compound that can eventually be recover or recycled. Hydrometallurgical or thermal treatments (smelting or pyrolysis) can then be used for specific recovery of a compound. These treatments, however, suffer from limitations due to high running cost or formation of by-products, and none is completely satisfactory. As a result, and considering the need to always improve existing technique to make them greener and more cost effective, new treatments should be investigated and especially hydrometallurgical treatments, as they seem to have better potential for their adoption on industrial scale.

1.1.2.2. Removal of DBDE from polymeric e-waste

Recycling plastic from WEEE is challenging, as it presents itself as a mixed shredded fraction from mechanical recovery processes. As a result, the bulk of WEEE plastic fraction contains more than 10 different polymer types, may contain hazardous heavy metals and restricted flame retardants, such as polybrominated diphenylether (PBDE). Every manufacturer proposes its own polymer formulation and incorporates a different flame retardant to pass flame safety regulation test. Although manufacturers tend to replace PBDE by other families of flame retardant, it is still present in 40% of all BFR containing housing polymer from the dismantling of computer monitor and TV sets (Schlummer and Maurer, 2007). Recycling of the polymeric fraction of WEEE includes sorting the different polymers and removing the unwanted additives, such as brominated or chlorinated BFRs. This is necessary to obtain a material that shows good mechanical properties (contamination of a polymer by another might weaken its resistance), and is exempt of restricted chemicals (to comply with the regulation).

Many ways have been investigated to recycle the polymeric fraction of e-waste, but very few proved to be a sustainable process. The first option consisted in degrading the material to eliminate the additives, such as the BFR, through pyrolysis of the polymer (de Marco et al. 2008, Blockhorn et al. 1999, Uddin et al., 2002; Mazzochia et al., 2003). This method was very efficient at eliminating bromine from the waste, and the degradation products could find an application as fuel or chemical feedstock. Although the formation of brominated dioxins or furans was not an issue (Hamm et al., 2001; Drohman et al., 2004), emission control measures had to be implemented to trap bromine, and the polymer is degraded in the process. The second approach, relying on the mechanical sorting of BFR containing plastics, was also difficult due to the limitation of the spectroscopic sorting system (Schlummer and Maurer, 2006). The third approach consisted in sorting the polymers according to their density. Initial separation followed by an additional step to eliminate the additive appeared too costly and time consuming, as all the plastics had to be independently treated for BFR removal. In addition, the content of BFR increased the polymer density, which can be used to increase the range of separation, suggesting that the elimination of additives could be done during the separation, if not after. The limitation of density separation, encountered when polymers show a similar density, could be overcome by using a multi stage “swell and float” separation system (Schlummer and Mäurer, 2006a; Schlummer et al., 2006b). Briefly, the process used a mixture of a commercial separation fluid, CreaSolv, and water. The high impact polystyrene (HIPS) fraction was swollen by the fluid, which lowered its density enough to be transferred to the float fraction while acrylonitrile butadiene styrene (ABS) was transferred to the heavy fraction. However, this process seemed limited to the isolation of upgraded quality of bromine-free HIPS from TV-set fractions, but not in the case of PC monitors (Schlummer and Mäurer, 2006a). Disposal of the waste fractions is also an issue, despite the possibility to recycle the solvent through distillation.

None of the systems used for bromine elimination seems to be totally compatible with plastic recovery from e-waste, despite a promising trial with sink and float technology applicable for HIPS recycling. Among all approaches, solvent- based separation seemed more adapted, as they allowed the migration of brominated content from one fraction to another, as well as density separation of the various polymer fractions. Consequently, the design of a solvent specifically designed to remove the BFR, and especially DBDE, from the HIPS fraction seems important in a combined approach to recycle plastics. Ionic liquids have been prepared and used for a large number of applications as designer solvents, and this thesis aims to investigate if these designer solvents can be used to recover DBDE, in addition to copper dissolution.

1.2. Aims and objectives

To solve the problem of e-waste collection and treatment, new waste treatment processes need to be developed to improve the global efficiency, selectivity, cost and environmental impact of recovery and to comply with the ambitious objectives of the EU legislations (Dalrymple et al., 2007). In this study attention was focussed to investigate a new approach for recycling copper and DBDE from WEEE. Such approach consisted in optimising the structure of a task-specific solvent (ionic liquid IL) to specifically separate copper or DBDE from the waste material. More particularly, interpretation of the results was focused on understanding how the structure and properties of such ILs influenced its characteristics, such as its ability to leach DBDE or dissolve copper.

The approach involved the syntheses and characterisation of a range of ILs, and the assessment of their efficiency at extracting or leaching the desired material. The choice of these ILs was based on the assumption that two parameters, logP and F, were important factors for material solubilisation. The study was, therefore, divided in two main sections, one for the heavy metal copper, and one for the organic DBDE. The oxidative power of ILs was not well documented, and preliminary experiments showed that they were not very efficient. In order to observe a measurable concentration of Cu in the IL, we chose to carry out dissolution tests of an oxidised species of copper, CuO, in various ILs. On the contrary, preliminary tests with DBDE showed higher miscibility with our ILs, so we chose to directly measure the efficiency of the leaching of the BFR from a polymer matrix, similar to the composition of a polymer housing unit. Consequently, three objectives were set to reflect such experimental choice, summarised below:

- Synthesising and characterising in total 18 ILs using a microwave (MW)-assisted method in a conventional MW oven
- Measuring the ability of each of the prepared ILs to dissolve CuO and compare it to the value of the three parameters: logP, F, and the type of aromatic ring
- Measuring the ability of each of the ILs to extract DBDE from a polymer matrix and compare it to logP and to the cationic aromatic ring

The thesis is divided into seven chapters including this introductory chapter where the research problem and the aims and objectives of the work are described. The second chapter deals with the literature review where the properties of ILs and previous work about IL as separation solvent are presented. The third chapter deals with the materials and methods used in this work. The results of the experimental work undertaken to verify whether ionic liquid could be used as a recycling solvent are reported in the following three chapters, each focussed on a specific phase of the work. Chapter four describes the use of microwave-assisted method for the synthesis of a range of ILs and their characterisation. Chapter five deals with the application of ILs to dissolve CuO, and chapter six describes the use of the synthesised ILs to extract DBDE from high impact polystyrene (HIPS). Finally, the seventh chapter concludes the thesis by summarising the findings and putting them in perspective of the contribution it made to the field.

2 Chapter 2: Literature review about ionic liquids in separation science

The fate of end-of-life electronic waste, as stated in the introduction chapter, is a large-scale problem which needs to be solved. Existing treatment methods have to be improved in order to comply with the recycling targets and this strategy ultimately provides incentives for researchers to explore and develop novel recycling and recovery techniques. This literature review chapter aims at summarising the specific problems associated with the two compounds investigated here, and providing information about ionic liquids (IL). In the first two sections of this chapter, recovery of copper from printed circuit boards and the extraction of decabromodiphenyl ether (DBDE) from HIPS are investigated. The third section of this chapter aims at describing ILs, and how they can be used as designer solvents. The fourth section is an extensive review of the application of IL for organic separation and partition of inorganic compounds, in order to identify the relevant parameters of the IL structure that influence partition and extraction of various substances. On-site preparation of these ILs is also necessary, so the next section describes the available synthesis route, with emphasis on MW-assisted synthesis. Finally, the information collected in the other sections of this chapter is combined to decide which IL should be synthesised for the purpose of this PhD.

2.1. Copper in printed circuit boards

Copper is a naturally abundant transition metal, essential for biological processes and of low toxicity for mammals (Fleming and Trevor, 1989). However, toxicological tolerance limit for aquatic organism is 10 to 100 fold lower than for mammals. This metal is widely used in the industry for its mechanical and conductive properties: water pipes are commonly made of copper, as are the conductive tracks on the surface of PCBs. This section aims at presenting the specific e-waste containing copper, PCB, and describe its actual recycling scheme.

Printed circuit boards are usually formed by a non conductive substrate used to mechanically support a network of electronic components interconnected through copper pathways (Coombs, 1995). The substrate is usually a composite polymer, which typically consists of a woven glass fibre matrix impregnated with epoxy resin rendered flame resistant by the addition of brominated flame retardants (BFR) in the polymer, such as Tetrabromobisphenol A (present in 96% of the PCBs) (Birnhaum, 2004). There are also other categories of polymeric substrate which are normally used for extreme applications, for example, high power radiofrequency, use in vacuum or zero gravity, or flexible PCB.

The surface of the substrate bears copper tracks, which form a conductive layer connecting the different components. More advanced PCB present a multi-layer structure, obtained by superposing several etched PCB and bonding them together (Coombs, 1995). A fully functional integrated circuit board is formed by soldering the various electronic components and integrated circuits to the PCB (populated PCB). They contain many metals, such as silicon, gold, silver, nickel, iron or aluminium (Lee, 2004). The soldering, traditionally made of an alloy tin/lead, has been replaced by lead-free alloy to comply with the RoHS directive (EU, 2002a). In some cases, other plating methods are used, like gold for edge connectors.

As a result, a populated PCB contains a mixture of organics (polymer, flame retardants, glass fibre) and metals (copper, iron, gold, silver, etc…), as detailed in Table 2.1 (Meinhart Ltd., 2002). Although gold and palladium are not major component (they count for 0.04%), they form 90% of the intrinsic value (Meinhart Ltd., 2002). Consequently, only precious-metal-rich board recycling is nowadays economically viable. PCBs are also separated in three classes depending on their intrinsic value. The 3 quality scale stretches from Grade I, which contains high value metals, up to Grade III for low intrinsic value material, like unpopulated PCBs.

Table 2.1: Average composition of printed circuit boards

Material	***Weight (%)***
Non-metallic (glass-reinforced polymer, BFR)	7
Copper	16
Solder	4
Iron, ferrite (from transformer core)	3
Nickel	2
Silver	0.05
Gold	0.03
Palladium	0.01
Other (bithmuth, antimony, tantalum etc.)	<0.01

Potential recycling of PCB should include recovery of copper, the major metallic fraction, and precious group metals, which is why dissolution of copper in IL was chosen as centre of interest for this thesis, with potential application to real PCB.

2.2. DBDE, a controversial brominated flame retardant

Another typical organic compound present in the plastic fraction of e-waste is the brominated flame retardant (BFR). Because of their fire resistance properties, this class of halogenated compound is an essential constituent in many polymers or textile products, However, their effects on human health have been strongly debated over the past years, and some legal texts, such as the RoHS directive (European Commission, 2006), ban some of them from use in the industry. Among the most common, Tetrabromobisphenol A (TBBPA) is used in printed circuit boards, and DBDE, also known as BDE 209, is widely used in polymer housing for electronic equipment, such as TV. This work was focused more on DBDE because it is currently assessed by the EU and face potential ban, which is why some manufacturers have already abandoned its use. As a result, the need to develop a recycling process involving removal of DBDE is important, if the polymer is to be recycled.

Polybrominated diphenyl ether (PBDE) is a family of brominated flame retardant widely used in polymeric material from electrical and electronic equipment (European Commission, 2007). The most common of them, DBDE (Figure 2.1), shows the lower toxicity (Birnhaum, 2004) and is of critical importance in the polymer and textile industry, with a worldwide consumption of 56,000 tons in 2001. Europe uses around 8,300 tons/year, 70% of which is used in plastic/polymer applications. DBDE is traditionally used to give flame retardancy to high impact polystyrene (HIPS), a butadiene/styrene copolymer, mostly used in TV back casing. It is usually present at a load of 10% per mass in the polymer formulation, and is always used in conjunction with antimony trioxide (European Commission, 2002c).

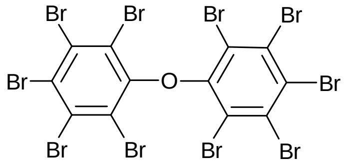


Figure 2.1: Decabromodiphenyl ether (DBDE)

DBDE works as an additive, which physically combines with the polymer. As opposed to chemically combined additives, the substance can diffuse within the polymer and eventually escape, posing a threat of environmental contamination. For this reason, these non-reactive additives have been intensively investigated, and the risk they pose has been assessed (European commission, 2002c; Wennig, 2002). The European risk assessment concluded that, although DBDE poses a low risk of exposure in water and sediment, there were still some uncertainties regarding certain class of animal, and more importantly regarding the risk posed by the less brominated degradation products. As a result, DBDE was included in the RoSH directive (European Commission, 2006), resulting in a ban from industrial use in Europe. However, due to the key economical importance of the substance in the bromine industry, its life saving application and the voluntary emissions reduction program established by the DBDE manufacturers, DBDE has been subject to an exemption from the RoSH in 2005 in the field of polymer manufacturing (70% of DBDE used), and is still being used in the industry (BSEF, 2007).

Another issue in the potential ban of DBDE is the understudied impact of the flame retardants, proposed as an alternative to DBDE. On one hand, the Danish EPA concluded that non-halogen organo-phosphorus substitutes to DBDE exist, and do not appear to have more adverse effects (Danish EPA, 2006). On the other hand, the bromine industry contested the need to replace DBDE, based on the EU risk assessment, which concluded that there is no need for further risk management measures (BSEF, 2007), whereas none of the alternatives have been subject to a similar risk assessment. A recent EU report about the alternative to DBDE in the industry (European Commission, 2007) highlighted this divergence of point of view, but also insisted on the fact that the EU risk assessment of DBDE raised many essential points such as:

- Increasing use of DBDE leading to increased intake and accumulation in the biota.
- The substance is widespread in top predators.
- Evidence of neurotoxic effects and uptake of the substance by mammals in laboratory studies.
- “Possible formation of more toxic and accumulative products such as lower brominated diphenyl ether in the environment” (European Commission, 2002c).

The report published by the European Commission in 2007 stated that there are insufficient data to determine whether the negative impact caused by the substitution outweighed the benefits or not, and recommended further work, based on the concerns with the impact of the breakdown products from some alternatives. Consequently, the legislation about DBDE ban is not definitive yet, and might change in the future, based on new evidence. In this context, some electronic manufacturers, such as Philips, Sony, Toshiba or NEC (European Commission, 2007), have decided if not to remove, at least to reduce the quantity of PBDE in their products, and removal of DBDE from waste polymeric material remains a necessity.

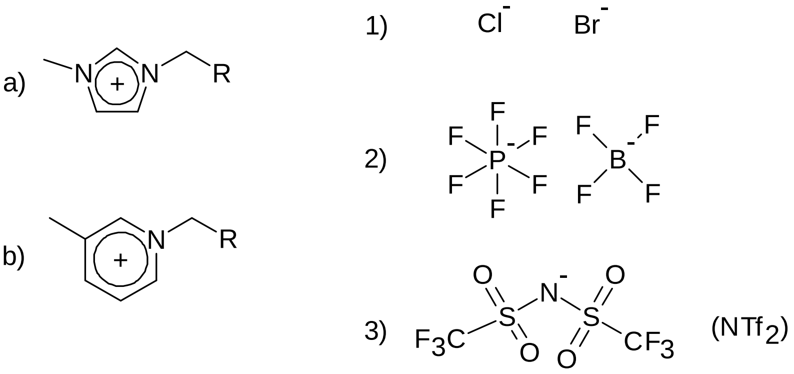
2.3. Ionic liquids: towards a green solvent

Ionic liquids (ILs) represent a class of chemicals with a great potential for novel industrial applications, because they exhibit interesting properties and are considered as green solvents for separation (Freemantle, 2000). This class of compounds, although discovered 100 years ago (Walden, 1914) have only been investigated more intensively (Wilkes et al., 1982) when air and moisture stable hydrophilic (Chan et al., 1977; Wilkes and Zaworotko, 1992) or hydrophobic (Bonhote, 1996) imidazolium-based ILs were discovered. With this breakthrough, the application of ILs as green solvent was possible, because of their very low vapour pressure, which stimulated scientific interest, with more than 8,000 scientific publications up to 2007 (Hough and Rogers, 2007). This section aims at briefly describing the background information about these novel solvents, how they are made, why they are so popular nowadays and why they are being used in a wide range of fields. In addition, some of the downside of using IL will also be presented, with emphasis on toxicity.

2.3.1. Ionic liquids: a family of promising chemical compounds

By definition, an IL is a liquid that exclusively contains ions. Although molten inorganic salts, such as NaCl (mp = 806 °C under normal pressure), fit to the definition, the modern concept of IL is limited to those salts whose melting point is below 100 °C (Malhotra and Zhao, 2003), which is also known as room temperature ionic liquid (RTIL) when the melting point is close or below ambient temperature. Such a liquid is obtained when combining a bulky asymmetric organic cation and a small anion, which results in a poorly coordinated network (Welton, 1999). The ionic pairs are chosen to minimise the charge interactions between ions, so that the energy supplied by thermal agitation at room temperature is high enough to break the crystal network. By analogy, Tom Welton (Welton, 1999) compared an IL to a “salt that doesn’t make a very good solid”.

Cations range from quaternary amine, to disubstituted imidazolium and pyridinium, whereas anions span from simple halide (Cl^-, Br^-) to aluminochloride $AlCl_x$ (Wilkes et al., 1982), and perfluorinated anions, such as BF_4^-, PF_6^- (Holbrey and Seddon, 1999) or NTf_2^- (Bonhote et al., 1996), as described in Figure 2.2. The number of ions available to make an IL is obviously much wider than what is presented in this Figure. However, only the most relevant to this work are presented here.



a) 1-alkyl-3-methylimidazolium; b) 1-alkyl-3-methylpyridinium

1) chloride and bromide; 2) hexafluorophosphate and tetrafluoroborate;

3) bis((trifluoromethyl)sulphonyl)amide NTf_2

Figure 2.2: Possible combination of cations and anions to form an IL

The main advantage of RTILs lies in a combination of properties, which justify their selection as potential green solvents. They exhibit (Welton, 1999):

- Good solvent properties for a wide range of organic and inorganic compounds
- Very low vapour pressure (evaporation is non-existent)
- Wide thermal stability range

- Immiscibility with a large range of organic solvent (they are polar alternative to aqueous solvent in biphasic systems)
- Good electrolytic properties (good conductivity and electrolytic stability over a large electrolytic window)

Such a large range of properties is the reason why ILs find applications in many fields, including solvents for extraction of organics and inorganic materials (Seddon, 1997; Zhao et al., 2005), organic synthesis (Welton, 1999; Tzschucke et al., 2002), lubricant (Weng et al, 2007), thermal fluid (Blake et al., 2006), propellant (Jones et al., 2006), etc… Their very low vapour pressure was the key advantage that encouraged researchers to use these chemicals in different applications, because they represent a versatile alternative to volatile organic solvents. There is an incredibly high number of possible anion / cation that could give a RTIL, so there is a high chance that a certain property can be achieved by finding a right combination. Some precursor work has already tried to understand and quantify the relationship between IL properties and structure (Malhotra and Zhao, 2003). Ultimately, the ionic liquid will be designed for a specific purpose, linked to a set of properties that can be obtained by engineering and design of its structure. This is the concept of Task Specific Ionic Liquid (TSIL).

2.3.2. Task-specific ionic liquids

The principle of a TSIL (Davis, 2004) is included in two observations regarding ILs:

- Certain properties can be drastically changed by changing the counterion or the cationic core. For instance, imidazolium halides are water miscible whereas imidazolium bis((trifluoromethyl)sulphonyl)amide is immiscible

- Keeping the same cationic core and the same anion, the properties of an ionic liquid can be tuned by modifying the side chain. For instance, the side chain length of dialkylimidazolium-based ILs is related to the hydrophobicity of the cation (Malhotra and Zhao, 2003)

Following these two observations, it becomes possible to envisage a design pathway, where a cation and anion are chosen as a base, and the cationic core is substituted with a side chain that influence a particular property, such as hydrophobicity or the presence of a particular functional group.

In theory, there are more than 10^{18} possible combinations (Holbrey and Seddon, 1999) that can generate different types of ILs, so the choice of starting cores should be almost infinite. In reality, very few cations and anions have been documented, and supposedly, not all the possible combinations will give exploitable ILs, due to very high viscosity, high toxicity or low stability. As a result, studying the influence of a side chain upon the properties of IL requires a cationic core and anionic core that are not only already well-documented, but also easy and safe to synthesize in addition to being stable. Among all the systems studied, imidazolium-based or pyridinium-based present most of these advantages, and could therefore represent the best starting point, according to our knowledge, to develop new designer solvents. However, these ILs might not be the ideal green solvents, as recent studies pointed out the toxicity of some imidazolium towards the aquatic environment.

2.3.3. Are Ionic Liquids toxic?

Ionic liquids were first developed because they were thought to be green alternatives to volatile organic compounds. On one hand, they are not volatile, and therefore cannot contaminate the atmosphere, but on the other hand handling and disposal, not to mention accidental spilling, might be a source of environmental contamination, especially in the case of water-soluble ILs such as imidazolium bromides (Zhu et al., 2009). In addition, fluorinated ILs containing anions such as BF_4^- and PF_6^- degrades in presence of water and produces toxic species such as hydrofluoric and phosphoric acid (Rank et al., 2007). Some ILs (especially fluorinated anion) also have a high octanol-water partition coefficient (Ropel et al., 2005; Domanska et al., 2008), which raises the question of their potential bioaccumulation.

The development of IL as an active pharmaceutical ingredient (Hough and Rodgers, 2007) is the only case where high toxicity might be a property of interest and environmentally friendly ILs should be preferentially developed. Yet, all the recent toxicity studies suggested that most of the commonly used ILs represent a significant risk to living organisms (Zhao et al., 2007). Many recent studies proved the toxicity of some common ILs for algae (Latala et al., 2005), microorganisms (Matsumoto et al., 2004a; Docherty and Kulpa, 2005; Stock et al., 2006), animals (Bernot et al., 2005, Pretti et al, 2006, Wang et al., 2009; Yu et al., 2009) or to human cells (Stepnowski et al., 2004). For instance, exposure of goldfish embryo to [C8MIM][Br] led to embryonic malformation and higher mortality rate (Wang et al., 2009).

In all cases, the nature of the cation seemed to be an essential factor that influences the toxicity. As a result, ILs show a large range of toxicological behaviour depending of the structure. The impact of ILs on living organisms can be similar to those obtained for

VOC such as methanol, phenol or toluene (Wells and Coomb, 2006, Stepnowski et al., 2004), less toxic (Stepnowski et al., 2004) or even more toxic (Docherty and Kulpa, 2005). The length of the sidechain is an important factor that governs toxicity, and longer alkyl chains always lead to higher toxicity (Stepnowski et al., 2004; Docherty and Kulpa, 2005; Wells and Coomb, 2006). For instance, imidazolium and pyridinium-based ILs were found more toxic to *V. fischeri*in than toluene, when the alkyl chain was longer than 6 carbons (Docherty and Kulpa, 2005). The nature of the ring is also important, as a QSAR model predicted that toxicity slightly increases with the number of nitrogen in the cycle (Couling, 2008), pyridinium being less toxic than imidazolium. The anion is another important factor of toxicity, as suggested by a study about the cytotoxicity of IL to rat leukemia cell line (Stolte et al., 2006). The authors concluded that most of the tested anions showed no noteworthy effects, except 10 of them, including perfluorinated anions such as bis((trifluoromethyl)sulphonyl)amide. Most of these studies pointed out the potential threat that imidazolium and pyridinium based ILs pose to the environment, and more especially the risk associated with aquatic systems (Wang et al., 2009).

Biodegradability is also a cause of concern, since ILs are usually designed to be stable in order to be used in cycles, where they are regenerated for reuse. Unfortunately, alkyl substituted ring-based ILs, such as 1,3-dialkylimidazolium or 1-alkylpyridinium, show little to no biodegradation (Wells and Coombe, 2006), although the addition of hydrolysable groups in the alkyl chain improved the biodegradability (Garcia et al., 2005). Photodegradation of imidazolium ILs with longer alkyl chains was also found difficult (Stepnowski et al., 2003). However, recent work carried out by Docherty et al. (2006) proved that biodegradation of imidazolium and pyridinium ILs by activated sludge is possible, and depends on the length of the alkyl chain and the nature of the cation (Docherty, 2007), the degradation rate increasing with the length of the side chain. More particularly, degradation was only observed for longer chains of 6 or 8 carbons, and only pyridinium led to total degradation as opposed to imidazolium, which only partial degraded. Biodegradation of shorter chains is however possible, as [C4MIM][BF4] was found to degrade in soil after 4 month (Modelli et al., 2008). Finally, biodegradation of [C4MIM][PF6] was also possible using a fungi, Fusarium sp (Esquivel-Viveros, 2009).

One of the easiest ways to obtain a non-toxic, biodegradable IL is to use a natural feedstock as precursor (Zhao et al., 2007), such as natural amino-acids (Tao et al., 2006), further functionalisation still being possible afterwards. Biodegradability can be achieved by incorporating ester and amide groups (Gathergood et al., 2004), or use non toxic precursors such as saccharin and acesulfame (Vidis et al.,2005).

As a conclusion, ILs show a significant toxicity to various organisms, especially in aquatic environment, and their biodegradation is difficult, although effort are being made to develop adequate degradation treatments. The future development of IL should emphasis the design of environmentally benign ILs selected for their biodegradability and low toxicity, which include using greener precursors. Imidazolium-based ILs, despite being the most studied, also showed higher toxicological effect, and should therefore be replaced with more environmentally friendly ILs.

2.4. IL for specific extraction

Extracting a substance from an inert material can be achieved in several ways and mainly depends on the physical state of the material under investigation. In the case of

WEEE, waste is likely to be in the form of small size granulated material, so they can be treated by solid/liquid extraction (leaching) to separate recoverable substances. Leaching can be straightforward, when the extract is soluble in the extraction solvent, or more complex, when the extract has to chemically react with an extractant before migrating to the liquid phase. In both cases, the systems are heterogeneous because they involve transfer of materials through a solid/liquid interface. The transfer mechanism is crucial, as it determines the specific properties a solvent needs. Since copper and DBDE are different in nature, their extraction mechanism, although similar, present some differences described in the next subsections, and lead to different design strategies. Moreover, the interactions of the IL with its solute are of prime importance to improve separation.

2.4.1. Interactions in IL

Because they are composed of poorly coordinated ions, ILs are usually regarded as polar and non-coordinating solvents, even if they are able to provide both polar and non-polar interaction with a solute (Keskin et al., 2007; Singh and Kumar, 2008). As a result, ILs show an amphiphilic behaviour, and can be used not only for partition of polar substances, but also for non polar solute. In addition, specific interactions can be introduced by introducing a particular functional group in the structure of the IL. More particularly, gas chromatography characterisation of ILs (Anderson et al., 2002; Han and Armstrong, 2007), revealed that dipole-dipole, hydrogen bond basicity and dispersion forces provide the most important contribution to these interactions. Extensive HPLC investigations on alkylmethylimidazolium tetrafluoroborate (Studzinska et al., 2007) highlighted the importance of π-π interactions and van der Waals dispersive forces. Although each interaction could theoretically be quantified separately by characterising them using their retention time with different GC columns, it is more convenient to use a different parameter, hydrophobicity, quantified by the octanol / water partition coefficient K_{ow} (sometimes represented by P) or its logarithmic form logP. This parameter, which reflects the affinity of a compound with an aqueous or organic phase, can be accessed experimentally using the shake flask method (OECD, 1995) or the HPLC characterisation method (OECD, 2004). Depending on the type of solute, it is necessary to optimise one specific interaction to promote extraction or leaching.

2.4.2. Design of a TSIL for leaching of copper

Developing an IL to extract a specific heavy metal is not a new idea, and has been already investigated in liquid / liquid partition of aqueous solutions (Dietz, 2006). Although leaching was at the centre of our work, other types of extraction represented an essential source of information (especially liquid/liquid extraction), as they provided data about metal extraction mechanism and extracted species nature and stability. Such information provides the knowledge to identify the key structural requirement needed for the production of successful extractive solvents based on ILs.

2.4.2.1. Mechanism of extracting copper from PCB

In Printed Circuit Boards (PCB), copper is present on the surface, as metallic tracks. Once the PCB is ground to increase the contact area, the waste material consists of grain of small size containing metallic or slightly oxidised copper in the surface. If copper was to be leached into a solution, it needs to be fully oxidised first, and then it can be leached out by using a suitable solvent. Figure 2.3 illustrates the 5 different steps necessary to leach the copper out (Habashi, 1999), which are summarised below:

1. Diffusion of the leaching reagent through the diffusion layer
2. Adsorption of the reactant on the solid
3. Chemical reaction between reactant and the solid
4. Desorption of the product from the solid
5. Diffusion of the leaching product through the diffusion layer

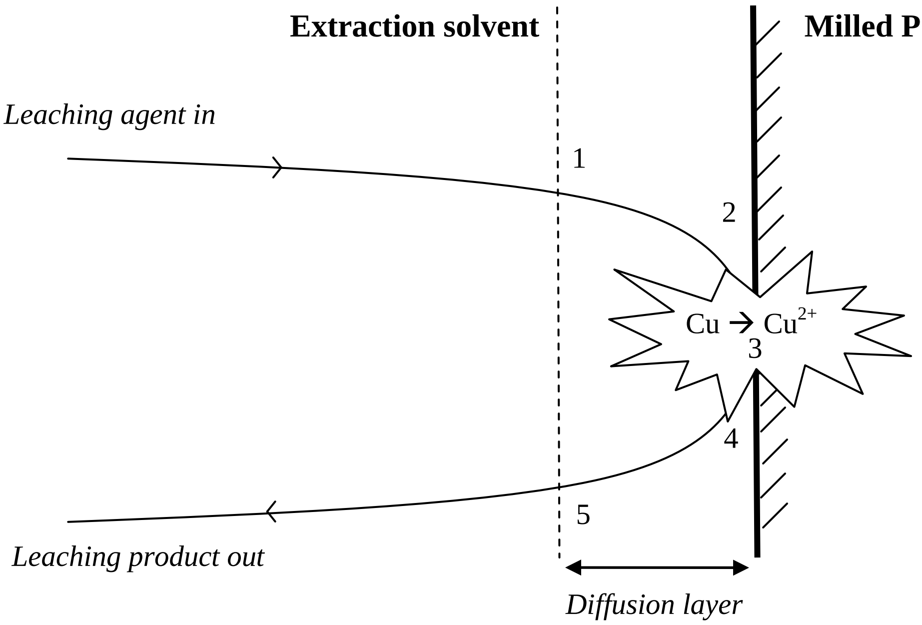


Figure 2.3: Schematic representation of the copper leaching process

As a result, an IL capable of leaching copper must be designed to fulfil several tasks:

- Oxidation of copper
- Formation of an extractable copper species that will migrate in the liquid phase
- Facilitate the access of the IL molecule to the surface of the polymer
- Regenerate the IL by removing its copper content, leaving it ready to perform another extraction cycle

Due to the limited amount of time the research was focused on the second task: formation of an extractable copper species. Although other target properties will not be investigated, their fulfilment is potentially achievable. For instance, oxidation could be done by altering the structure of the IL to incorporate a regenerable oxidising group either in the cation or in the anion. However, it adds an extra step to the extraction process to regenerate the oxidising group in addition to recover copper. It might be better to rely on the solubility of oxygen in IL (Anderson et al., 2007), since oxygen dissolved in the IL could act as an oxidizing agent. Recovery of dissolved copper could then be done by electro-precipitation, because ILs are very good electrolyte (they are liquid ionic compounds) or by chemical precipitation.

2.4.2.2. *Extraction using a complexing agent*

Extraction of metals in a hydrophobic liquid has been widely investigated in the past 10 years. At first, linear 1-alkyl-3-methylimidazolium hexafluorophosphate (Vidal et al., 2004) were found not to be a good solvent for partition of free dissolved metals, such as Cu^{2+} or Zn^{2+}, although changing the anion to the more fluorinated nonafluorobutanesulphonate (NfO) allowed very high extraction of lanthanide from aqueous solution (Kozonoi and Ikeda, 2007). As the latter study pointed out, the extraction mechanism occurred mainly through cation exchange with partial transfer of non charged species. Although the study did not test the partition of heavy metals, the authors observed that cations with large hydrated radii are more effectively partitioned.

Extraction rates could be improved by the addition of a complexing agent, which could either be integrated in the structure of the solvent, or be an external molecule, such as an extractant, or a chelating agent (Han and Armstrong, 2007). On one hand, using an extraction agent (Dai et al, 1999; Visser et al. 2000a, 2003) led to interesting result, with partition coefficients much higher than with conventional solvents such as chloroform. Extractant molecules were either charged or neutral, and formed a complex with the metal ion which migrates in the RTIL phase, due to its hydrophobic nature. Pioneer studies have proven the efficiency of the method using two extractants, 1-(2pyridylazo)-2-naphtol and 1-(2-thiazolyl)-2-naphtol in hydrophobic 1-hexyl-3-methylimidazolium hexafluorophosphate [HMIM][PF_6] to extract Fe^{3+}, Co^{2+} and Cd^{2+} (Visser et al., 2001b). Very high extraction of strontium was also possible using crown ethers (18C6 and its dicyclohexano- and di-tert-butylcyclohexano- analogs) as an extractant in various 1-alkyl-3-methylimidazolium hexafluorophosphates (Dai et al, 1999; Visser et al. 2000a, 2003). On the other hand, complexing agents, such as EDTA (Sun et al., 2008), also showed promising results to selectively extract yttrium(III) from heavy lanthanides in [C_nMIM][PF_6]/[NTf_2]. Metal extraction, in these examples, also occurred through a cation exchange process, where the RTIL cation was exchanged for the charged complex, and was lost in the aqueous phase. Although the use of EDTA as a complexing agent seemed to improve the extraction yield and reduced the RTIL cation transfer in the aqueous phase (Sun et al., 2008), the RTIL lost remained an issue, considering the cost of the solvent, and its potential toxicity when released in the environment (Section 2.3.3). In an attempt to overcome this loss, neutral complexes of mercury and o-carboxyphenyldiazoamino-p-azobenzene were extracted from a basic solution into the very hydrophobic 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate [C_4tmsim][PF_6] (Li et al., 2007a). The superiority of [C_4tmsim][PF_6] over [C_4MIM][PF_6] was due to its lower solubility in water, and to the fact that the extraction mechanism involves the transfer of a neutral species from the aqueous media to the hydrophobic IL. Recovery of IL can be executed by stripping the

Hg^{2+} with an acidic solution, which protonates the chelating agent, thus decreasing its coordination ability.

2.4.2.3. Extraction using TSIL

Another way of overcoming the loss of cation in the aqueous phase consisted in integrating the complexing moiety directly into the structure of the ionic liquid (Davis, 2004). For instance, 3-butylimidazolium hexafluorophosphate bearing a thiourea and urea substituted butyl sidechain showed a remarkable efficiency (partition coefficient of 300) at extracting Hg^{2+} and Cd^{2+} (Visser et al., 2001a, 2002), due to the Lewis basicity of the O and S in the functional groups. In another study (Papaiconomou et al., 2008), IL based on substituted 1-methylpiperidinium, 1-methylpyrolidinium and 4-methylpyridinium showed a very high extraction for mercury, but required the presence of a functional group, such as nitrile or disulphide, to show a noticeable extraction of other metals (Na^+, Mg^{2+}, Fe^{2+}, Co^{2+},Cu^{2+}, Zn^{2+}, Cd^{2+}, Ti^+, Pb^{2+} and Sn^{4+}). The functional groups were appended at the end of the sidechain containing 4 carbon atoms and, although the presence of a nitrile group shifted the selectivity towards silver and palladium, the disulphide groups induced complete partition of copper and mercury. The authors of the study also highlighted the difference observed between IL cations, as a piperidinium cation reduced the partition coefficient for all the metal cations. In all those experiments, loss of IL cation in the aqueous phase was not detectable, which suggested the method to be adapted for cation partition, without additional molecule.

2.4.2.4. Dissolution of oxides in IL

Several TSIL have been specifically designed to dissolve metals which are either in the form of ores (Whitehead et al., 2007) or oxides (Abbott et al., 2006; Nockenheim et al., 2006). It has been observed (Whitehead et al., 2007) that 1-butyl-3-methyl-imidazolium hydrogen sulphate [C4MIM][HSO_4] can be successfully used to leach copper out of chalcopyrite ($CuFeS_2$). An increase in the concentration of IL in the leaching solution not only increased the extraction of Cu (85%) but co-extraction of iron (<8%) was also observed. The hydrogen sulphate anion was believed to stabilise the copper through ion pairing process. Other factors were also thought to be responsible for this increase, such as increased solubility of Cu in the IL, increased solubility of oxygen in the IL (oxygen solubility is higher with larger anion), and increase in ionic strength with increasing IL fraction. The presence of oxygen, especially, reduced the sulphide ions into sulphur, suggesting that the redox processes happening in such IL are comparable to those in water. The study also reported the use of extractants (thiourea) to leach gold and silver in [CxMIM][HSO_4], x = 4, 5, 6,7 and 8. Leaching was more efficient compared to water because of a better stabilisation of thiourea and the inhibition of silver sulphide re-precipitation. Longer alkyl chains decreased the amount of metal leached, because of increased viscosity.

In another attempt to develop an IL-like system for oxide dissolution (Abbott et al., 2006), alternative eutectic solvent were explored. More particularly, it was discovered that choline chloride (2-hydroxyethyl)trimethylammonium chloride) could form a liquid, with properties very similar to RTIL, when mixed with a hydrogen-bond donor, such as urea or malonic acid. As a result, very high metal solubilisation (up to 14,000 ppm for CuO at 50 ºC) has been achieved in malonic acid/choline chloride mixture (1:1). The nature of metal complexes were identified (Abbott et al., 2005, 2006), and it was inferred that the hydrogen bond-donor species (acid group) played an active role in the solubilisation process.

Finally, later work on a protonated betaine derivate (Nockeman et al., 2006) led to the preparation of carboxymethyltrimethylammonium bis(trifluoromethylsulphonyl)imide [Hbet][Tf_2N]. This hydrophobic ionic liquid was able to selectively dissolve oxides like ZnO, CdO, HgO, NiO, CuO and PbO, provided water is present as trace. The surface of oxides being hydrophilic, water helped to decrease the high hydrophobicity of the IL, which improved contact at the solid/liquid interface. Aqueous complex of this TSIL and Cu^{2+} were isolated and studied using X-ray crystallography, revealing they were formed by two cations: $[Cu(bet)_4(H_2O)_4]^{2+}$ where the copper is coordinated with four carboxylate oxygen at the basal plane and two weak contact to water ligands, and $[Cu_2(bet)_4(H_2O)_2]^{4+}$ where the four carboxylate groups are coordinated to the dimer Cu-Cu, forming a bridge between the two cations, one aqua ligand being in the coordination sphere of each copper. The two species were maintained together by hydrogen bounding between aqua ligands. In this case, complexation was due to the deprotonation of the carboxylic group, which provided a negatively charged electron-donor site. In a similar approach, EDA (ethylaminediacetic acid $-(CH_2)_2N(COO^tBu)_2$) substituted methylimidazolium hexafluorophosphate (Harjani et al., 2006) was used to form a complex with copper (II). The deprotected form of the EDA $\{-N(COO^-)_2\}$ provided the electron-donor sites to complex the metal. The procedure, however, could not be used for extraction, as the counterion PF_6^- is removed during the complex formation and prevented the regeneration of the complex.

2.4.2.5. Conclusion: what types of ILs are suitable for copper extraction?

As a summary, stability of a metal complex seemed to be the key to metal leaching. Forces involved with the stabilisation of a metal complex, involving an external leaching agent or a functionalised IL, were therefore of primary importance. Principal stabilisation forces are reported to be:

- H-bound (presence of H-bound donors, thiourea, malonic acid)
- Ion pairing (presence of HSO_4^-)
- Dipolar interactions (presence of a highly polar group, electron-donating group)

While some strategies successfully relied on the use of an external extraction agent to provide these interactions, other focused on modifying the structure of the IL cation or anion to provide specific interactions. The most promising approach included functionalisation of the sidechain from imidazolium or pyridinium, with a group exhibiting H-bond, electron-donating ability or chelating ability. The length of the sidechain also seemed to be a determinant factor, as a shorter length was reported to increase the amount of metal leached, because either hydrophobicity or viscosity of the IL decreased.

2.4.3. Design of TSIL to leach DBDE from HIPS

DBDE is present as an additive in HIPS (copolymer of styrene and polybutadiene), often used in conjunction with antimony trioxide as an enhancement agent. It is a physical additive, which means it is not chemically bound to the polymer and can be leached out. Similarly to copper leaching mechanism, the process can be divided into several steps (Figure 2.4).

1. Diffusion of the solvent through the pores of the solid
2. Desorption of the solute
3. Transfer of the solute to the bulk of the solution

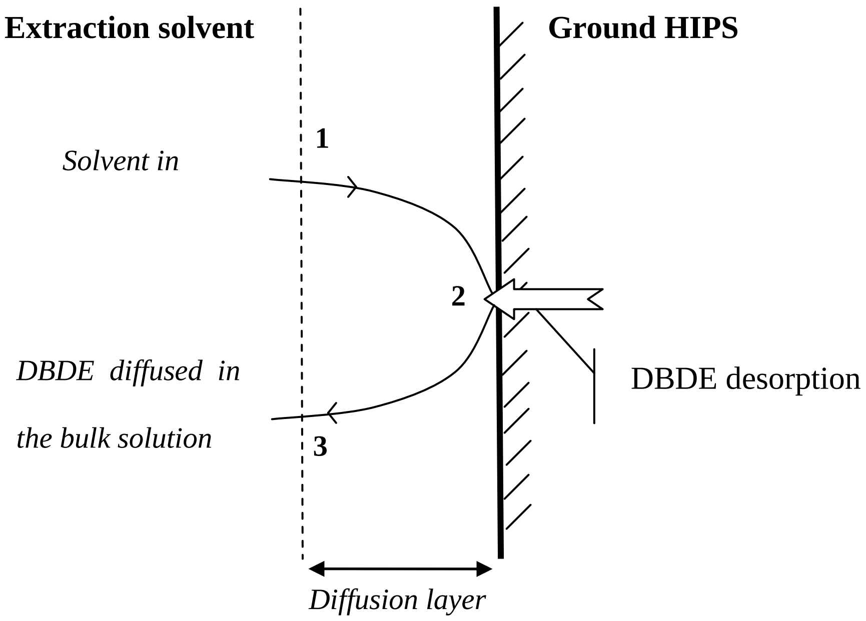


Figure 2.4: Schematic process of leaching DBDE from its HIPS matrix

2.4.3.1. Extraction of organics in IL

Considering IL to replace organic solvent in organic extraction has been investigated for more than ten years (Huddleston et al., 1998) and widely reviewed (Zhao et al., 2005; Han and Armstrong, 2007; Berthod et al., 2008). As mentioned earlier, RTIL represent an alternative choice to replace volatile organic solvent, since these very stable compounds exhibit a very low vapour pressure, and provide both polar and non-polar interactions with a solute. As a result, they have a very good affinity with organic molecules (Carda-Broch et al., 2003; McFarlane et al., 2005), showing good partition coefficients for phenolic compounds (Huddleston et al., 1998; Bekou et al., 2003; Vidal et al., 2004; Khachatryan et al., 2005), dyes (Visser et al., 2000b; Li et al., 2007b; Pei et al., 2007), amino acids (Gu et al., 2004; Smirnova et al., 2004; Wang et al., 2005), carbohydrate (Spears et al., 2002; Pletnev et al., 2003; Liu et al., 2005; Swatloski et al., 2002), organic acids (Matsumoto et al., 2004b, Yan-Ying et al., 2007), biofuel such as butan-1-ol (Fadeev and Meagher, 2001), antibiotics (Cull et al., 2000), enzymes (Shimojo et al., 2006), DNA (Wang et al., 2007), hydrocarbons (Munson et al., 2002; 2003; Smith et al., 2004) and various aromatic compounds (Gmehling and Krummen, 2003; Letcher and Reddy, 2004; Acre et al., 2007; Domanska et al., 2007; Meindersma et al., 2005, 2007).

Extraction strategies depended on the nature of the solute, whether it was charged, neutral, or associated with an extractant. This allowed for pH dependant extraction (Visser et al., 2000a), where the species was transferred into the organic phase. Extractants, such as crown ether dicyclohexano-18-crown-6 (DC18C16), were investigated for extracting amino acid (Smirnova, et al., 2004), organic acids (Matsumoto et al., 2004b) or reactive dyes (Li et al., 2007b). Their use was guided by the need of a selective extraction, where the extraction agent promoted the complexion of a solute prior to its partition in the IL phase. For other purpose, only the direct partition of a molecule from the aqueous phase to the IL was tested.

In all cases, hydrophobic IL were used, containing simple fluorinated anions, such as PF_6^- and BF_4^-, or more complex, such as bis((trifluoromethyl)sulphonyl)imide Ntf_2^-. Such anions were mostly chosen to limit the solubility of the IL in water, which not only improved the efficiency of the separation, but also minimised the loss of IL in the aqueous phase. Although various cationic structures were investigated, 1-alkyl-3-methylimidazolium remains the most studied. Compounds in their neutral form were usually more easily extracted in IL, and charged species, such as amino-acid, often required the use of a chelating agent such as crown ether (Carda-Broch et al., 2003). It was found that the interactions responsible for organic extraction are mostly hydrophobic, but could also be dipolar, with interaction between IL and phosphate

(Wang et al., 2007). This fact is reflected by higher partition coefficients associated with an increase in the cationic side chain for dyes (Visser et al., 2000b), butyl alcohol (Fadeev and Meagher, 2001) and benzene (Arce et al., 2007). Higher hydrophobicity increases the difference of polarity between the two solvents, hence the partition. However, this trend was not always verified, as a longer side chain might lead to unfavourable interactions. For instance, more detailed NMR investigation about partition of folic acid or caffeine between water and [C4MIM][PF6] (Ying-Yang et al., 2007) confirmed that the major interactions behind the partition of solute in IL were dispersive forces and H-bond. In that case, the hydrogen-bond between the H on the second C of the imidazolium ring and the fluoride from the anion was weakened by the presence of a bulky solute, such as folic acid. The resulting streric hindrance was greater when the cation sidechain was longer, thus the higher efficiency of short chains.

2.4.3.2. Aromatic and aliphatic separation in IL: influence of the aromatic ring

Very high interest has recently been shown about the use of IL to separate aromatics from aliphatic compounds (Munson et al., 2002, 2003; Gmehling and Krummen, 2003; Letcher and Reddy, 2004, 2005; Smith et al., 2004; Meindersma et al., 2005, 2007; Dormanska et al., 2007; Smiglak et al., 2007; Acre et al., 2007). Such work is extremely interesting, as it not only investigated the IL / solute interactions necessary for the design of a TSIL, but also aromatic interactions, such as π - π interaction between aromatic rings. These studies more particularly focused on the partition of aromatics such as benzene, toluene or xylene, from linear non saturated hydrocarbons such as hexane, heptane or octane.

Among other, research work has been focused on the application of ILs to the separation of aromatics from the heptane/toluene system (Meindersma et al., 2005, 2007). Such study revealed that the cation, and also the type of anion influences the partition. The aromatic character of the imidazolium cation is weaker than that of pyridinium, so the selectivity (ability to extract the aromatic instead of the aliphatic compound) and partition coefficient for aliphatic and aromatic were lower. A shorter side chain was found to increase the selectivity, as it enhances the aromatic character of the cation, but also decreases the partition. Distribution coefficients of heptane and toluene in [C2MIM][X] increased in the following order for X: $(C_2H_5)_2PO_4^- > CH_3SO_3^- > BF_4^- > C_2H_5SO_4^- > HSO_4^-$. The selectivity followed the opposite order, because the solubility of heptane increased faster than that of toluene. However, it was noticed that [C4MIM][BF_4] exhibited a singular behaviour, since it exhibited higher selectivity and distribution ratio for toluene and heptane. In later work (Meindersma et al., 2007), a quantum chemical approach was used to predict various parameters such as the surface charge, calculated from the dielectric continuum (COSMO-RS) model. The interactions between IL and solute were successfully predicted using the surface charge profile of the molecules, and rendered possible the screening of IL for separation. Another study about the separation of linear hydrocarbon from aromatic revealed that the addition of an alcohol group at the end of one ethyl chain from diethyldimethyl-ammonium bis(trifluoromethyl)sulphonyl-imide resulted in an increase of selectivity for the aromatic.

2.4.3.3. *Conclusion: best qualities of a TSIL as organic extraction solvent*

As a conclusion, TSIL have been used to extract many organic compounds because of the unique set of interactions they provide. The main interactions were dipolarity, hydrogen bond basicity and dispersion forces (Anderson et al., 2002), but other specific forces were present, such as specific aromatic π - π interactions or steric hindrance. In general, increasing the length of the sidechain of the cationic moiety of the IL resulted in increasing the solubility of the organic, except when specific forces, such as steric hindrance, weakened attractive interactions. The functionalisation of the side chain has also been investigated, but seemed to bring improvement only in specific cases, when better selectivity is required for instance. Finally, quantum models have been successfully used to roughly predict the behaviour of IL with certain solute, and attempts have been made to correlate solvent parameters to solubilisation behaviour.

2.4.4. How to quantify hydrophobicity and polarity of a functional group

These two parameters were chosen to reflect a combination of various interactions that the IL ions provide with the solutes. Hydrophobicity of a compound can be reflected by a physical measure, logP, while the polarity of a functional group can be approximated using a derivate from the Hammet constant, as explained in the next two paragraphs.

2.4.4.1. Hydrophobicity

Hydrophobicity is the affinity of a compound with water. According to IUPAC definition (van de Waterbeemd, 1997), “hydrophobicity is the association of non-polar groups or molecules in an aqueous environment which arises from the tendency of water to exclude non-polar molecules”. It results from hydrophobic interactions, attributed to influence of hydrocarbon-like groups on the water-water interactions according to the IUPAC definition (Muller, 1994). In Quantitative Structure Activity Relationship (QSAR) methods, the lipophilicity (similar to hydrophobicity) of a compound is represented by the octanol/water partition constant K_{ow} (P), or more commonly its logarithm, logP. Two official methods are available to measure it, the shake flask method (OECD guideline, 1995), or the HPLC determination (OECD Guideline, 2004). Shake Flask is the most simple, as the solute is introduced in a water/octanol system, and shaken for a certain time. The concentration of solute in both phases is then measured, and the coefficient P is calculated using Equation 2.1.

$$P = \frac{[A]_{octanol}}{[A]_{water}} \quad \text{(A is the solute)} \qquad \textbf{Equation 2.1}$$

$$k' = \frac{t - t_0}{t_0} \quad \text{(t is the retention time, } t_0 \text{ is the dead time)} \qquad \textbf{Equation 2.2}$$

$$\log P = \alpha + \beta \log k' \quad (\alpha \text{ and } \beta \text{ are constants}) \qquad \textbf{Equation 2.3}$$

This method, although it gives good results for non neutral compound, is highly dependent on the nature of the solute. Moreover, it is time consuming, and requires few replicates to be validated so HPLC methods have been developed in order to automate the process. Chromatography relies on the separation of solute by successive adsorption/desorption of the solute from a mobile to a stationary phase, so the retention time of a solute is proportional to the strength of the interactions with the stationary phase. Using a highly hydrophobic stationary phase, such as C18, allows relating the intensity of the hydrophobic interactions to the retention factor k’ (Equation 2.2). Subsequent regression allows k’ to be related to P using Equation 2.3. The use of reference compounds is essential and must be close to the logP measured, in order to determine the factors α and β. The method, however is limited to logP between 0 and 6, as hydrophilic compounds are not retained enough to produce a measurable k’, and highly lipophilic compounds imply a retention time too long to be applicable.

Shake flask method (Chapeaux et al., 2007) or HPLC method (Stepnowski and Storonial, 2005; Studzinska et al., 2006, 2007) have both been successfully applied to determine various interaction parameters for IL. Hydrophobicity of imidazolium based IL has been more particularly investigated using reverse phase HPLC (Stepnowski and Storonial, 2005). The chromatographic method consisted of a reverse phase C8 column eluted by a blend of two solvents, water (20 mM of triethylammonium phosphate at pH=6.5) and methanol, at a flow rate of 1 ml.min^{-1}. The effect of the IL counterion was averaged because the concentrated buffer provided excess of phosphate anions. As a result, the estimation of logP based on this method was limited to the cation and did not depend on the type of counteranion. In order to measure only hydrophobic interactions, k' was determined with different mobile phases containing a decreasing percentage of methanol, and extrapolated at 0% methanol. As too little data was available for LogP in IL, the parameter had to be estimated (Stepnowski and Storonial, 2005) using the ClogP3 algorithm (Leo, 1993; Hansh and Leo, 1995). Such algorithm was based on a fragment method, where the molecule structure was divided into small fragments of atoms. The estimated logP for a molecule was the sum of the contribution of smaller fragments and correction terms, accounting for the interactions between fragments (Equation 2.4). Linear regression of the predicted logP vs. logk' led to a high correlation ($R^2 > 0.99$), thus confirming that the predicted values for logP are in accordance with the experiment.

$$\log P = \sum_i a_i f_i + \sum_j b_j F_j$$ **Equation 2.4**

f_i is a fragment constant, F_j a correction term (factor), a_i and b_j corresponding to the frequency of occurrence.

As a conclusion, the HPLC method described above was able to provide reliable values for logP. However, direct experimental values obtained from the shake flask method cannot be compared with HPLC, as the IL, in the latter case, was completely dissociated, masking the effect of the anion on lipophilicity. As a result, a chemometric method was identified as the simplest way to obtain values for logP of the IL cations synthesised in this work, provided these estimated values were confirmed by the experimental k’ values. The set of data had to be correlated in order to determine weather the model we used was appropriate or not. The fact that the effect of the anion was not tested by this method was not essential, as not only did all the IL have bromide as a counteranion, but also only the effect of the cation was investigated in this work. Since we didn’t have access to a ClogP3 prediction software, we realised on a free on-line package provided by Molinspiration (milogP 2.2 – November 2005), which relied on a similar group contribution methodology (Molinspiration, 2008).

2.4.4.2. Field constant as a measure of polar contribution of a group

The polarisation of a functional group could be quantified by measuring its effect on a chemical property such as reactivity. More particularly, the field, inductive and mesomeric effects of a substituent directly influence the rate of many reactions. Field and inductive effect are very similar, since they both are the result of intramolecular coulombic interactions between an isolated unipole or dipole (atom or a functional group) and the centre where the effect is applied. The field effect is propagated through space while the inductive effect propagates through chemical bond (Muller, 1994). As a result, stronger field and inductive effects are caused by greater coulombic forces, hence greater dipolar moment.

The QSAR methodology consists in relating the chemical structure of a molecule to its toxicological activity (van de Waterbeemd et al., 1997). The chemical structure of a compound can be characterised using a set of various parameter quantifying interactions such as steric, hydrophobic, hydrophilic, hydrogen-bonding and more particularly electronic, such as field and inductive effects. The measurement of the complete set of parameters would take a long time and poses many experimental problems, so computational techniques were developed to predict them. For instance, the inductive effect was obtained from the empirical approach of Hammet (1937). The so-called Hammett constant σ (σ_m or σ_p) was calculated as the logarithmic difference between the ionisation constant of benzoic acid and of its substituted counterpart (meta or para). Such constant denoted the global electron donating or electron withdrawing effect of a group, although subsequent work used the data to separate the field/inductive effect, F and the mesomeric effect, R (Taft and Lewis, 1958; Swain and Lupton, 1968). Higher F means strong inductive effect and stronger field generated by the functional group, which can be explained by a stronger polarisation of such a group. Later correlation of F with σ_m and σ_p allowed the calculation of F for an extensive range of substituents (Hansch et al., 1991) including cyano, hydroxyl, carboxyl and ethyl.

2.5. Microwave-assisted synthesis of ionic liquids

At present, a large number of ILs are available in the market but they are still essentially being synthesised at laboratory scales for specific research applications. Due to the high number of possible ILs, many synthesis pathways exist, related to a particular ionic base. However, the scope of this work is limited to imidazolium and pyridinium halide formation reaction, which is fairly straightforward. The reaction can be improved using non-conventional methods, such as microwave (MW) irradiation (Leveque et al., 2007).

Besides its qualities, MW-assisted synthesis as a route to prepare imidazolium halide is subject to debate, since the pathway does not appear particularly green, as developed in the last paragraph of this section.

2.5.1. Mechanism of synthesis for imidazolium salts

The synthesis of substituted imidazolium halide can be performed through a simple nucleophilic substitution. In the common case (Leveque, 2007), the aromatic nitrogen from imidazole or pyridine, which possesses a basic character, attacks the carbon in α position of the halogen, thus forming the corresponding halide salt, as shown in Figure 2.5 (Dupont et al., 2002).

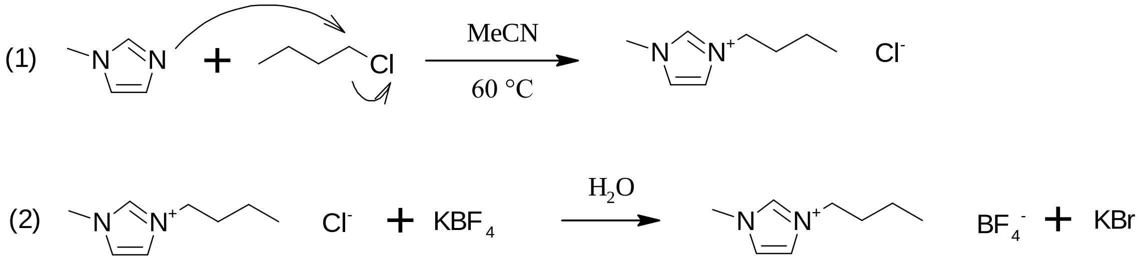


Figure 2.5: Synthesis of 1-butyl-3-methylimidazolium bromide and tetrafluoroborate

This quaternisation of the heterocyclic nitrogen can be followed by metathesis, which consists in exchanging the halide with the counteranion from another salt (potassium, sodium or ammonium). For instance, the IL halide (Br^-) reacts with the salt (KBF_4) to form a new salt (KBr), which remains in aqueous phase, while the newly formed hydrophobic IL migrates to an organic phase (Figure 2.5), facilitating their separation. An extended range of IL can be prepared this way, showing different properties, such as a water immiscible ionic liquid when the counterion contains fluorine atoms (BF_4^- or

PF_6^-) (Wilkes et Zaworotko, 1992). Halogen-free pathways were developed, but were restricted to different heterocyclic rings (Quek et al., 2006; Tommasi and Sorrentino, 2005; Holbrey et al., 2002), hence are not of interest here.

Most of the imidazolium-based IL can be synthesised this way, including TSIL, providing the starting alkyl halide is available. The reaction itself satisfies few principles of green chemistry (Lancaster, 2002), such as atom economy. However, the procedure presents a few drawbacks, such as the necessity to use a solvent for amine quaternisation, and long heating time, ranging from 72 h for imidazolium chloride to 6 h for imidazolium bromide (Wilkes et al., 1982). In order to develop a greener synthesis pathway, non-conventional activation methods have been successfully applied to heterocyclic IL synthesis, which is the subject of the next section.

2.5.2. An alternative activation method: MW-assisted synthesis

Green chemistry, and especially green chemical synthesis, has become very important nowadays, in the field of sustainable development. Twelve principles have been listed that summarise the good practice for green synthesis (Lancaster, 2002). In order to satisfy as much of these 12 criteria, a reaction should:

- Minimise or eliminate waste
- Maximize the amount the incorporation of all materials used in the final product
- Limit the toxicity of the materials used and produced
- Minimise or eliminate the use of organic solvent
- Minimise the amount of energy spent
- Use starting material from renewable source
- Etc…

Quaternisation of heterocyclic nitrogen is interesting, as it obeys to the atom economy rule, but energetic and solvent-free criteria are not met. Switching to a renewable feedstock is possible but the capacity of preparing a range of similar ionic liquids substituted with various alkyl chains becomes more difficult. For instance, aromatic five-member heterocyclic nitrogen-containing rings could be derived from glucose (Handy et al., 2003), but functionalisation involved further reaction steps. In order to improve the existing imidazolium synthesis pathway, based on thermal activation methods, it has been proposed to use non-conventional activation methods, such as MW irradiation for polar compound, or ultrasound. MW-activation, in particular, has been applied for various nitrogen quaternisation reactions (Varma and Namboodiri, 2001; Khalidar and Rebeiro, 2002; Namboordiri and Varma, 2002), successfully reducing reaction time, and avoiding the use of reaction solvent.

MW-assisted synthesis relies on the use of a MW irradiation at 2.5 GHz used for domestic MW, the rest of the frequency range (0.3 to 30 GHz) being used for telecommunication (Whittaker, 1994). The reaction activation is possible through the combination of heating effect and non-thermal microwave-specific effects (de la Hoz, 2005). Firstly, heating is due to the interaction of the high frequency radiations with a polarised molecule: The molecule tends to align with the field by rotation and provided the frequency is right, will dissipate energy through intercollision, thus generating heat. Secondly, MW activation induces specific effects (Stuerga and Gaillard, 1996, de la Hoz, 2005), because the energy is directly (rapid, uniform and energy-efficient heating) and selectively (non-polar molecules are not affected) transferred to the sample, and because it allows the superheating of a polar liquid (the compound remains liquid above its evaporation temperature). Therefore, the MW-assisted activation method is greener, because it accelerates the reaction rate and it improves the chemical yield under relatively mild conditions and lower energy consumption.

Heating behaviour of IL during MW irradiation has already been studied (Hoffman et al., 2003; Habermann et al., 2005) and, due to the polar nature of the imidazolium salts, their formation reaction could be activated by MW irradiation. An extra step of metathesis or acid-base reaction could be added to exchange the halide with another anion, as summarised in Figure 2.6 (Deetlefs and Seddon, 2003).

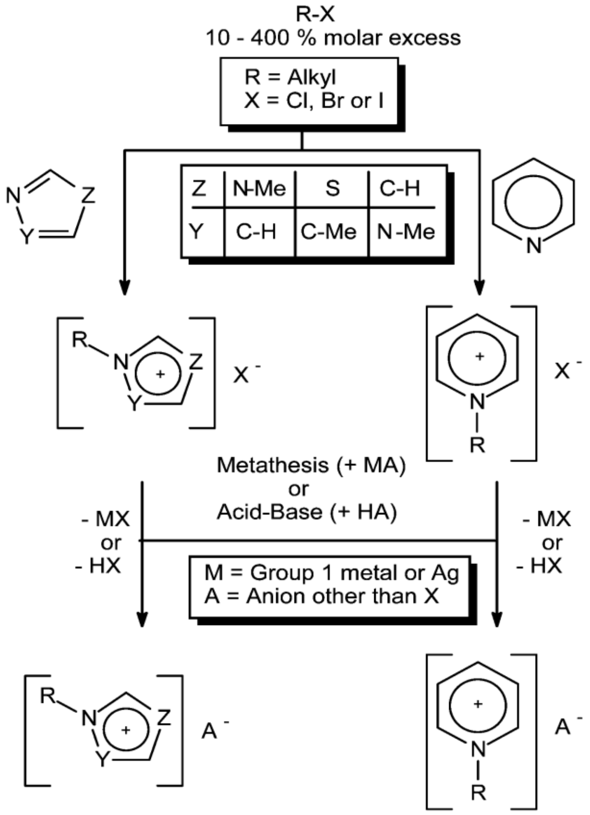


Figure 2.6: Generic pathway for MW-assisted synthesis of heterocyclic IL

More specifically, Imidazolium-based ILs have been prepared without solvent in an unmodified microwave oven (Varma and Namboordiri, 2002). At a low power (240 W), the reactants (alkylhalide and imidazole) were mixed in an open glass container and irradiated by successive shots of 30s separated by 10s mixing time (average mixture temperature of 100 °C), because continuous irradiation led to partial degradation of the products. As the ionic liquid formed, the polarity of the reaction media increased, which enhanced the heating effect from MW irradiation and contributed to the acceleration of the reaction. The technique was suitable for long chain alkyl halide, as the shorter chain (like bromobutane) have a low boiling point and might evaporate, requiring being present in excess to avoid a lower yield. The reactivity of haloalkanes followed this order: $I^{-}>Br^{-}>Cl^{-}$ (Varma and Namboordiri, 2001, 2002; Khadilkar and Rebeiro, 2002). As a result, the preparation of brominated IL required less irradiation time than chloride, and consequently less energy to be carried out.

Several issues were associated with the use of the solvent-less procedure in open vessel (referred to as open container technique): heat dissipation was not effective, because no solvent was present, and the produced salt was more polar than the starting materials, which could lead to local overheating and degradation. In addition, a 10% excess of haloalkane (Varma and Namboordiri, 2001) was necessary to obtain high yields. The procedure was later modified by immersing the reactor into a water bath preheated at 60 °C (Law et al., 2002). Being more polar than the starting materials, the bath absorbed more radiations than the reaction mixture and heated up to 80 °C. As the salt appeared, the reaction mixture became more polar than the water phase and absorbed the energy. Any heat excess from the reaction medium was absorbed through heat exchange with the water mantle. MW irradiation pattern had to be carefully controlled, as degradation was observed when the mixture was initially irradiated at a high power, or for too long. In another attempt to overcome these drawbacks, imidazole- and pyridine-based ionic liquids were prepared in a closed vessel inside a microwave digester (Khalidar and Rebeiro, 2002). At a power of 300 W, and a temperature kept at around 150 °C (pressure around 0.6 to 1 Mpa), the ionic liquid formed with a yield comparable to the open container technique. Similar results were achieved in a microwave reactor (Deetlefs and Seddon, 2003). The use of a MW digester allowed close control of the temperature (the MW received by the reaction media was regulated by the temperature, no need to mix the mixture), avoided reactant loss, and reduced the need for haloalkane excess, so much that the procedure could theoretically used for larger scale synthesis.

2.5.3. Purification: an issue for MW synthesis

Purity of the aforementioned ILs is an issue, when considering MW synthesis. Local overheating might lead to partial degradation and introduce contaminants which can affect some properties of the IL, such as the melting point strongly influenced by traces of water (Bonnet and Kariuki, 2006). Besides, removal of unreacted materials often involves the use of a washing solvent which dissolves the starting materials but not the final product. The combination of solvents for purification differed from one synthesis to another. The simplest relied upon diethyl ether to wash halogenated ILs (Law et al., 2002), whereas more complex ones involved washing the IL / ethanenitrile phase with ethyl ethanoate (Deetlefs and Seddon, 2003). Hydrophobic IL, such as 1-butyl-3-methylimidazolium hexafluorophosphate, required a less polar solvent, such as dichloromethane containing anhydrous magnesium sulphate to trap the water resulting from the anion exchange process (Dupont et al., 2002). In order to limit the environmental impact of the procedure, the amount of remaining starting material or degradation products should be minimised to reduce the amount of solvent used.

The procedure involving an open-vessel in a household MW oven (Namboordiri and Varma, 2002) led to potentially lower purity (Leveque and al., 2007) due to less control over radiation power and media temperature, and because the hot hygroscopic reaction mixture strongly absorbs water. Extended purification was needed, including solvent extraction, and 4 to 8 h of drying under vacuum (Law et al., 2002), but traces of starting materials might still be present, as well as colour impurities generated during any IL synthesis (Tang et al., 2008). Closed vessel procedure may appear the preferred method, as the control of the reaction conditions reduced overheating and the need for a high excess of one reactant, while keeping high yields. However, it still involved washing and vacuum drying steps, without a significant difference in purity, as the open-vessel method afforded imidazolium chloride and bromides already highly pure (Varma and Namboordiri, 2001). As a result, since contaminants were undetected after purification in both cases, and if the excess of reactant is not an issue, then the two methods have similar impact, and open-vessel might be easier to implement.

2.6. What choice of IL for experimentation?

2.6.1. The best IL for property tuning

Choosing a cation and an anion as a base for property tuning through alkyl chain substitution is not an easy task. More particularly, a compromise between an IL that is readily available, easy to synthesise, and easy to substitute, and an IL that show non-toxic, biodegradable attitude needs to be found.

In order to fulfil the research objectives, it is important to answer two questions regarding the choice of IL we make:

- Which cationic base is better suited for substitution / properties
- What would be the most adapted synthesis methodology

In order to take a decision, several key requirements have to be taken into account, including:

- Suitability of the properties linked to the type of IL
- Simplicity of the reaction of the substituted IL formation
- Availability of the reactants
- Green impact of the preparation and use of the IL, including product purification and impact of synthesis

Clearly, none of the organic salts mentioned earlier are likely to meet all the criteria mentioned above, and the final choice requires a compromise between green environmental impact on one hand, and process simplicity and availability on the other hand. Green IL mentioned in section 2.3.3 might seem right for a starter, but would require some extra work to develop synthesis, and lack of data about their stability. As a result, imidazolium and pyridinium bromide are better suited for the synthesis of a large range of substituted IL in limited time, mostly because they are stable to moisture and air, but also because the halogenated IL can be synthesised in one pot, thanks to the availability of substituted haloalkanes as starting materials.

Various synthesis methods are available, and the choice again depends on a compromise between green procedure and ease of application. According to section 2.5, MW-assisted synthesis appears much greener than conventional method (referring to the reactor heated by hot plate and oil bath), because of the polar nature of organic salts, and because no solvent and less energy are required. As for the methods, closed vessel might not be the best option, in spite of an advantage such as controlled reaction conditions, because it required a MW reactor. Intermittent irradiation involved in the open-vessel aimed at keeping the temperature of the mixture low enough to avoid local overheating and degradation, and despite the loss of reactant, the final purity of the product is comparable, as mentioned in section 2.5.3. The boiling point of the reactants used in this case (such as 1-bromobutane) was above 100 °C, so evaporation should not affect the final purity with reactants of higher boiling points, providing the intermittent irradiation pattern is applied and an excess of alkyl halide is added. Only the final quality of the IL is important, since the objective of this PhD is not optimising the synthesis but rather using a method that can be adapted to a large range of starting materials, not only easily but also at low cost.

In addition, the nature of the halogen in the alkyl halide reactant affects the reaction rate. A compromise has to be made between price of the reactants and fast reaction rate. Although iodine possesses the highest reactivity, it remains the most expensive. On the contrary, chlorides are cheaper and wildly available, but they react slower. As a result, bromides offer a compromise with fast reaction rate and average cost (At the date of writing this thesis, Aldrich online pricing for 1L of 1-halobutane (Reagent Plus, 99%) is £17, £26, £109 for respectively Cl, Br and I). For all of these reasons, imidazolium and pyridinium bromide were chosen as a base for the substituted IL used in this work, which will be prepared through MW-assisted synthesis in an open vessel using a household oven.

2.6.2. Which IL to dissolve copper

The leaching solvent must not only overcome the diffusion layer, but also allow desorption of the solute and its migration into the bulk solution (Section 2.4.2.1). The latter is not an issue, since an energetic stirring of the solution provides instant mixing. Overcoming the diffusion barrier can be trickier, as it requires a solvent fluid enough to allow fast diffusion of material and polar enough to lower the interfacial energy and promote good contact between solid and liquid. Although brominated IL might be too viscous when used at room temperature, their viscosity decreases greatly at the higher temperature used for leaching. As a result, the most important issue to address is the desorption step, which revolves around the stability of the complexed metal in the IL. IL can provide a whole range of specific stabilising interaction with any solute, such as dipolarity, H-bound basicity and dispersion forces (Anderson et al., 2002). Most of these interactions have contributed to the stability of various metals in studied TSIL (section 2.4.2). It would have been very difficult to study all these interactions due to time constrain and the attention was focused to study the impact of only two sensitive parameters upon the stabilisation of copper complex in IL. In order to do so, the amount of copper dissolved in an IL, after 10 min of contact with CuO, was quantified using flame atomic absorption spectrometry. High amount of copper present in the IL would indicate the presence of a more stable copper complex.

Previous work done with liquid/liquid extraction of copper and CuO dissolution in IL (Section 2.4.2) confirmed that the side chain length of the cation and the presence of a monodental or bidental ligand in the cation were required to achieve good copper extraction. These two structure modification can be translated into measurable parameters, hydrophobicity (related to the sidechain length) and polarity of the sidechain.terminal group. Three common functional groups were retained, because of their availability: cyanide (-CN), alcohol (-OH) and carboxyl (-COOH), while the alkyl chain length varied from 2 to 8 carbons (Figure 2.7).

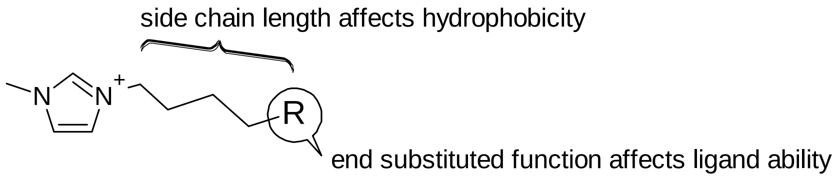
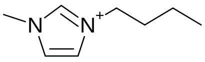
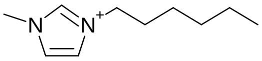
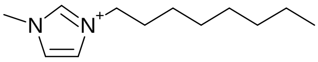
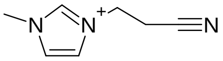
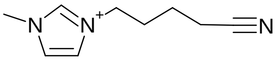
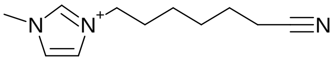
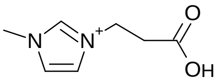
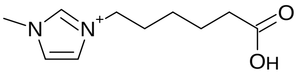
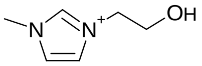
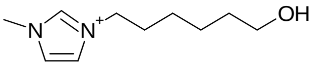
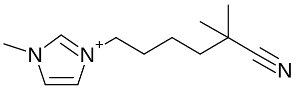
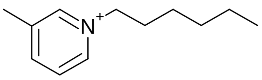
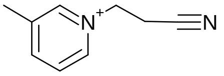
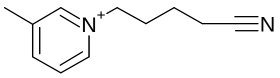
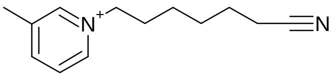


Figure 2.7: View of a tunable IL cation

In order to explore how the amount of copper dissolved depends on these parameters, we decided to test 16 RTIL (Table 2.2). The full names of the ILs were abbreviated for better clarity, using brackets containing the abbreviation from the cation in the left part, and the anion in the right part. The cation name was abbreviated using the chemical formula of the functional group at the end of the side chain (CN, OH or COOH), the number of carbons in the sidechain (C4, C6 or C8), and the cation aromatic ring system (MPy or MIM). The anion was always bromide Br.

Table 2.2: IL tested for copper extraction

Abbreviation used	Name of the Ionic liquid	Formula of the ionic liquid
[C4MIM][Br]	1-butyl-3-methylimidazolium bromide	
[C6MIM][Br]	1-hexyl-3-methylimidazolium bromide	
[C8MIM][Br]	1-octyl-3-methylimidazolium bromide	
[CNC2MIM][Br]	1-(2-cyanoethyl)-3-methylimidazolium bromide	
[CNC4MIM][Br]	1-(4-cyanobutyl)-3-methylimidazolium bromide	
[CNC6MIM][Br]	1-(6-cyanohexyl)-3-methylimidazolium bromide	
[COOHC2MIM][Br]	1-(2-carboxyehtyl)-3-methylimidazolium bromide	
[COOHC5MIM][Br]	1-(6-carboxyhexyl)-3-methylimidazolium bromide	
[OHC2MIM][Br]	1-(2-hydroxyethyl)-3-methylimidazolium bromide	
[OHC6MIM][Br]	1-(6-hydroxyhexyl)-3-methylimidazolium bromide	
[CN(CH$_3$)$_2$C5MIM][Br]	1-(5-cyano-4,4-dimethylpentyl)-3-methylimidazolium bromide	
[C6MPy][Br]	1-hexyl-3-methylpyridinium bromide	
[CNC2MPy][Br]	1-(2-cyanoethyl)-3-methylpyridinium bromide	
[CNC4MPy][Br]	1-(4-cyanobutyl)-3-methylpyridinium bromide	
[CNC6MPy][Br]	1-(6-cyanohexyl)-3-methylpyridinium bromide	

2.6.3. Which IL for DBDE extraction? Importance of hydrophobicity

Most of the work undertaken previously focused on liquid/liquid extraction of organics into a hydrophobic IL phase (section 2.4.3). Nevertheless, these studies provide enough information on the type of interactions that can be expected between an IL and an organic solute. In our case, the solute we wish to extract, DBDE, is integrated into a polymeric matrix, HIPS, which was formulated in the laboratory in order to contain a typical amount of DBDE. According to our model (section 2.4.3), the solvent must have certain characteristics.

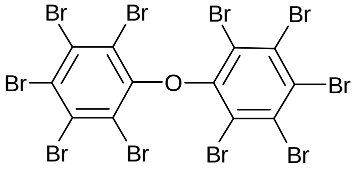
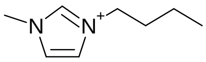
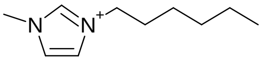
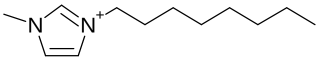
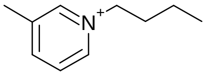
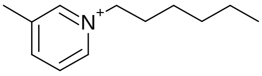
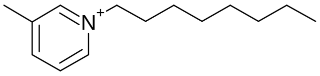
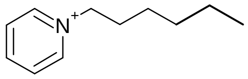


Figure 2.8: Formula of DBDE

First of all, it must provide better stabilising interactions than the solid matrix. DBDE is a bicyclic, fully brominated ether (Figure 2.8). As such, it has a strong polarity and is able to undergo aromatic interaction, such as π - π. According to section 2.4.1, ILs exhibit good ability for these particular interactions, making them ideal candidates for BFR extraction. Linear aromatic ILs seem to be the better candidates, as they are simple to synthesise, and already proven to be efficient for the extraction of various organics. Anions have an effect, too, but as the purpose of the PhD was not to investigate them, then therefore all of the ILs will be bromide, because they are easy and quick to synthesise. Finally, due to the aromatic character of DBDE, two cationic rings were investigated: pyridinium and imidazolium, the latter having more aromatic character. Several side chain lengths were considered, ranging from 4 to 8 carbons, to reflect the influence of the hydrophobic interactions of the cation, since longer carbon chain increases the hydrophobicity of the IL (Welton, 1999). Table 2.3 summarise the various ILs retained for this work.

Table 2.3: IL tested for DBDE extraction

Abbreviation used	Name of the Ionic liquid	Formula of the cation
[C4MIM][Br]	1-butyl-3-methylimidazolium bromide	
[C6MIM][Br]	1-hexyl-3-methylimidazolium bromide	
[C8MIM][Br]	1-octyl-3-methylimidazolium bromide	
[C4MPy][Br]	1-butyl-3-methylpyridinium bromide	
[C6MPy][Br]	1-hexyl-3-methylpyridinium bromide	
[C8MPy][Br]	1-octyl-3-methylpyridinium bromide	
[C6Py][Br]	1-hexyl-pyridinium bromide	

Secondly, leaching is a surface process, because the polymer is not soluble in the IL. It has already been proved that PS (Bento and Brazel, 2002; Winterton, 2006) is insoluble in [C4MIM][PF6] and [C4MIM][Cl]. HIPS being a copolymer of PS, neither should it be soluble in the ILs. In addition, HIPS is not soluble in [CXMIM][Br] (X = 4, 6, 8) and [C6Py][Br] (Lateef et al., 2008). It seemed reasonable to assume that the ILs investigated here wouldn't solubilise HIPS, since they were of the same family as those mentioned earlier. Such fact implies that only the fraction of DBDE present in the surface layer of HIPS is transferred in the solvent. Supposedly, the inner DBDE can be transferred in the surface through diffusion in the polymer, although the diffusion is a slow process here. As a result, two options were investigated to improve the quantity extracted:

- Grinding the polymer finely to increase the surface area to increase the extraction of DBDE
- Increase the temperature enough to increase DBDE diffusion in the polymer

Finer polymer particles are more difficult to handle, as they tend to float on top of the IL when mixed, are highly electrostatic and can easily become airborne. Besides, the grinding process we used could hardly produce enough material smaller than 1mm in diameter. Consequently, our effort was focused on two experiments: leaching test of DBDE at a constant temperature using different IL to assess the influence of the structure, and leaching with the same IL at various temperatures to determine the influence of diffusion in the polymer. Several methods were examined to measure the amount of DBDE dissolved in the IL. Although GC-MS (Eslami et al., 2006; Raff and Hites, 2007; Carroll and al., 2008) provided a better and quicker way to quantify DBDE, the presence of IL might affect column life, because of their high viscosity and very low vapour pressure. Quantification of BFR by XRF was also investigated, but didn’t lead to satisfactory results. Therefore, it was decided to use HPLC (Bonin et al., 2003; Eriksson et al., 2004; Pohleim et al., 2005), and more particularly a method adapted from previous work (Riess and van Eldik, 1998).

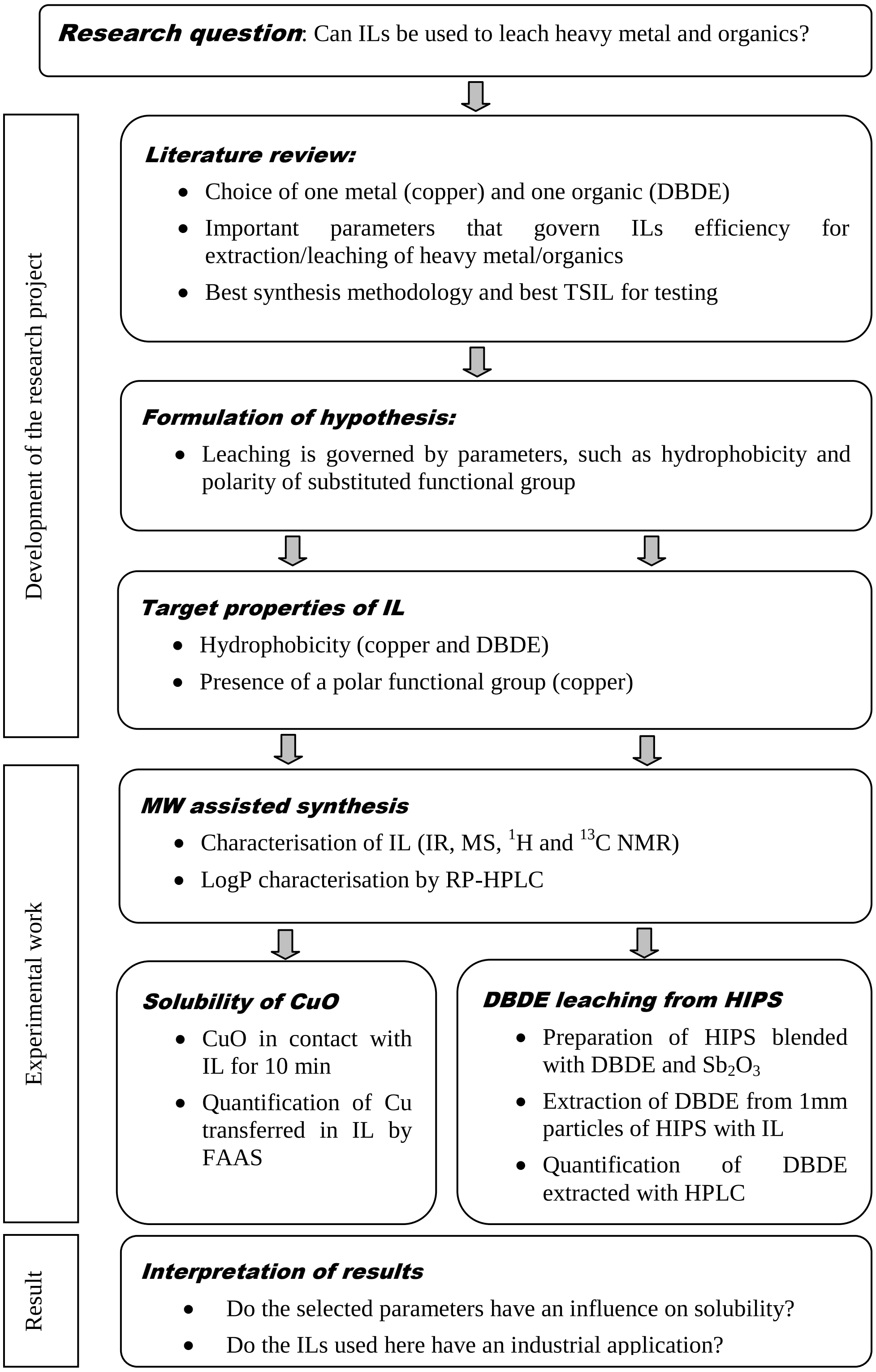
3 Chapter 3: Materials and Methods

The experimental work associated with the methodology adopted in this thesis can be divided into three distinct phases (Figure 3.1). The first phase consisted in limiting the scope of the research question, and defining clear aims and objectives. Extensive literature review was necessary to narrow down the research subject, and select the most adapted methods (parameters investigated, IL synthesis method, IL selected, solubility test, etc…). All the chemicals used in the experimental work were obtained either from Sigma-Aldrich (Gillingham, UK) or Fisher Scientific (Loughborough, UK) and were used without purification. Ultrapure water (18.2 MΩ) was obtained from a Millipore system, and all solvents were of HPLC grade. All the ILs used in the leaching tests were synthesised and characterised in the IFE lab.

The second phase involved the actual experimental work, divided into three sections:

- Synthesis and characterisation of the IL
- Experimental solubilisation of CuO in various IL
- Experimental leaching of DBDE from the polymer

In the final phase, the experimental values of solute (DBDE or copper) leached into the IL were analysed and compared to the parameters investigated, F and logP, in order to determine if a direct effect of the IL structure could be observed.



Research question: Can ILs be used to leach heavy metal and organics?

Development of the research project

Literature review:

- Choice of one metal (copper) and one organic (DBDE)
- Important parameters that govern ILs efficiency for extraction/leaching of heavy metal/organics
- Best synthesis methodology and best TSIL for testing

Formulation of hypothesis:

- Leaching is governed by parameters, such as hydrophobicity and polarity of substituted functional group

Target properties of IL

- Hydrophobicity (copper and DBDE)
- Presence of a polar functional group (copper)

Experimental work

MW assisted synthesis

- Characterisation of IL (IR, MS, ^{1}H and ^{13}C NMR)
- LogP characterisation by RP-HPLC

Solubility of CuO

- CuO in contact with IL for 10 min
- Quantification of Cu transferred in IL by FAAS

DBDE leaching from HIPS

- Preparation of HIPS blended with DBDE and Sb_2O_3
- Extraction of DBDE from 1mm particles of HIPS with IL
- Quantification of DBDE extracted with HPLC

Result

Interpretation of results

- Do the selected parameters have an influence on solubility?
- Do the ILs used here have an industrial application?

Figure 3.1: Organisation of the project

Detail of the protocols used to carry out the research work is given in the three sections, each focussed successively on synthesis and characterisation, dissolution of CuO in IL, and leaching of DBDE from ILs.

3.1. Synthesis and characterisation of ILs

A total of 19 imidazolium and pyridinium based ILs were prepared and characterised using appropriate analytical methods and techniques. The protocols used were straightforward, since the syntheses of ILs involved the quantitative reaction of only two compounds, with theoretically no by-products formed. The usual characterisation techniques were applied, involving mass spectrometry (molecular mass of the primary cation), IR spectrophotometry (identification of the functional groups) and ^{1}H and ^{13}C NMR (structure of the cation and contamination). The conditions of synthesis and the different analyses adopted for their characterisation are summarised in the next subsections.

3.1.1. Protocol of synthesis

Chemical reactions were carried with the help of an unmodified household microwave oven (900W Panasonic NT552W equipped with Inverter Technology) set up on defrost position (30% power, 270 W).

The syntheses of the different types of ILs were carried out using the same protocol and designed to prepare 15 g of IL. It was necessary to add one of the reactant in excess, to account for the loss of reactant by evaporation. A the bromoalkane was added in 10% excess unless it was in a solid form, in which case a 10% excess of the aromatic nucleophile (1-methylimidazole or 3-methylpyridine) was used. The adequate reactants were mixed in a 250 mL round flask and irradiated, following a pattern adapted from previous work (Varma and Namboordiri, 2002). The pattern consisted of successive heating periods gradually increasing from 30 to 90 s, separated by 10 s of manual shaking. When a single clear phase was observed, the reaction media was left to cool down at room temperature, washed 3 times with 20 ml of ether and dried for 2 h at 70 °C and reduced pressure (0.05 mmHg) before characterisation. The detailed information regarding the irradiation patterns, and the quantities of different reactants needed for the synthesis of various types of ILs is given in Table 3.2, Table 3.1 and Table 3.3 (// indicated the moment when the clear single phase appeared).

Table 3.1: Protocol of synthesis for methylimidazolium-based IL

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Table 3.2: Protocol of synthesis for methylpyridinium-based IL

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Table 3.3: Protocol of synthesis for pyridinium-based IL

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3.1.2. Analytical instruments and methods used in characterisation

Routine characterisation of various types of ILs was done using Infrared spectrometry (IR) and mass spectrometry (MS) analysis in the Institute for the Environment. Liquid IR samples were analysed between two NaCl crystal plates, placed in a Fourier Transform Perkin Elmer RXI NIR spectrometer. The MS spectra were obtained from a Perkin Elmer SCIEX API 365 equipped with a Turbospray source and controlled via the Applied Biosciences Aanalyst 1.4.2 software. After a rapid optimisation of the method, a set of parameters was selected and remained the same for all ILs (Table 3.4). Infused sample consisted of IL diluted in water (~ 100 mg.L^{-1}), and the fragments were identified by scanning the mass/charge ratio interval from 40 to 400 amu every second.

Table 3.4: Operating condition for the MS characterisation of IL

Parameter	***Value***
Nebuliser Gas	9
Curtain Gas	8
Turbospray Voltage	+4000 V
Temperature of Nebuliser	80 °C
Declustering Potential	30 V
Focusing Potential	60 V

Parameter	***Value***
Entrance Potential	4 V

NMR analyses of these ILs were performed at the Department of Chemistry, Queen Mary University, London. Samples were prepared by diluting one or two drops of IL in deuterium oxide D_2O, followed by ^{13}C and ^{1}H spectra acquisition on a Bruker AV600, at a frequency of 600 MHz.

3.1.3. HPLC characterisation of logP

The relative hydrophobicity of the cations was characterised by reverse phase HPLC. The method has been described elsewhere (Stepnowski et Storoniak, 2005), and consists in measuring the retention factor (k’) of the cation at different percentage of eluent A (water and 20 mM of triethylammonium phosphate at pH = 6.5) and B (methanol). Only the extrapolated value of k’ at 0% B is of interest to measure the hydrophobicity. As a result, the retention time of an IL was measured four times in isocratic mode, at different percentage of B. Linear regression of logk’ vs %B gives access to the hydrophobicity, represented by logk’ at 0% B. For more hydrophilic cations, the percentages of B chosen to carry out the regression (Table 3.5) were < 20%. However, the ILs bearing longer chains showed long retention times (> 1 h 30 min) at low %B, incompatible with the timescale of the experiment. Instead, it was decided to use a % B in the range 40 to 70 % for these specific ILs. The logarithm of k’, extrapolated at 0% methanol, was then compared to the logarithm of the octanol/water coefficient, logP, using the Molinspiration software (Molinspiration, 2008).

The HPLC work was carried out on a PE 200 series equipped with a binary gradient pump, a UV detector and a vacuum degasser. Sample was injected with the help of a Gilson model 231 autosampler, fitted with a loop of 100 μl, and separated on a Supelco Kromasil C8 5 μm (250 x 4.6 mm) at a flow rate of 1 ml.min^{-1}. The various k' were measured, using the point at which the first positive signal is recorded as t_0.

Table 3.5: Elution method for the characterisation of logP

	Percentage of MeOH								
	70	***60***	***50***	***40***	***30***	***20***	***15***	***10***	***5***
[OHC2MIM][Br]						x	x	x	x
[CNC2MIM][Br]						x	x	x	x
[CNC2MPy][Br]						x	x	x	x
[COOHC2MIM][Br]						x	x	x	x
[C4MIM][Br]					x	x	x	x	x
[CNC4MIM][Br]			x	x	x	x		x	
[CNC4MPy][Br]			x	x	x	x		x	
[C6MIM][Br]			x	x	x	x		x	
[CNC6MIM][Br]			x	x	x	x		x	
[C6MPy][Br]			x	x	x	x		x	
[CNC6MPy][Br]			x	x	x	x		x	
[COOHC5MIM][Br]			x	x	x	x		x	
[OHC6MIM][Br]			x	x	x	x		x	
[CN(CH3)2C5MIM][Br]			x	x	x	x		x	
[C8MIM][Br]	x	x	x	x					
[C8MIM][NTf2]	x	x	x	x					
[C8MPy][Br]	x	x	x	x					

3.2. Dissolution of CuO in IL

Two experimental tasks were operated in the phase of CuO dissolution. First task involved the dissolution tests, whereas the second task involved the assessment of the test, done by quantifying the amount of copper dissolved with FAAS. The protocols of both tasks are described in this section.

3.2.1. Protocol of dissolution

The dissolution experiment was designed to measure the amount of copper dissolved after a short amount of time. The characterisation of copper in neat IL was difficult, so it was decided to add a solvent (water or acetonitrile), in which CuO is not soluble but the IL is, and determine the copper content with flame atomic absorption (FAAS).

The test were designed to keep a ratio IL / CuO of 10 / 1, hence 100 mg of CuO for every g of IL. In the case of [CNC2MIM][Br], the ratio was increased to 200 mg of CuO per g of IL because this particular IL solubilised all the copper from the initial ratio. Consequently, 2 g of IL was weighed in a 100 ml beaker fitted with a stirrer at medium speed (5 out of 10) and placed on a hot plate conditioned at 70 °C. 200 mg of CuO (or 400 mg in the case of [CNC2MIM][Br]) was added, and after 10 minutes of contact under vigorous stirring, around 30 ml of water or acetonitrile was added slowly to the mixture, still under stirring. The solution was then removed from the heat source and filtered over Buchner using a Whatman No. 3 qualitative filter paper. Finally, the filtrate was collected in a 100 or 25 ml volumetric flask, and the final volume was adjusted using the same solvent (water or acetonitrile). The test was repeated twice for each IL.

3.2.2. Quantification of copper

The solutions obtained from dissolution tests were often too concentrated to be analysed directly through FAAS, and had to be diluted 100 to 2,500 times with water depending on the concentration. Copper quantification was performed on a Perkin Elmer AAnalyst 100 equipped with an impact bead and a copper hollow cathode lamp. Operating parameters are summarised in Table 3.6.

Table 3.6: Operating parameters of the FAAS

Parameter	***Setting***
Wavelength	324.8 nm
Flame	air / acetylene Blue, oxidant
Calibration standards	1, 2, 3, 4 and 5 ppm
Measurement replicates	3

3.3. Extraction of DBDE with IL as a solvent

Before attempting any extraction, it was necessary to quickly examine the solubility of DBDE in the various IL selected. Such a test consisted simply in mixing 30 mg of DBDE with 1 g of IL and stirring the mixture. It was observed that a white, very viscous liquid formed upon agitation, indicating that solubility was high enough to allow the extraction of 9 mg of DBDE contained in 200 mg of polymer, into 2 g of IL. As a result, it was not judged necessary to investigate the solubility in detail.

In order to develop the leaching protocols, a sample of waste polymeric material (HIPS) containing DBDE was necessary. Access to such a sample was very difficult, so it was decided to prepare a polymeric sample within our own laboratory using a commercial HIPS sample (supplied by Aldrich, Gillingham, UK). In that way, the exact composition of the polymer chosen (HIPS) was known, which rendered easier the assessment of extracted species. The second problem was that an analytical procedure to measure the concentration of DBDE in the IL had to be developed, since very little information was available from the literature.

3.3.1. Preparation of HIPS

The pure poly(styrene-co-butadiene) was obtained from Sigma-Aldrich (Gillingham, UK). This particular type of HIPS contains 4% of butadiene in weight. In order to obtain a formula close to what can be found in the EEE industry, two additives were incorporated, DBDE (98% in fine powder) and antimony trioxide (99%, 5 μm powder), a synergetic agent commonly used with BFR. The polymer formulation consisted in 5% in weight of DBDE and 2.5% of Sb_2O_3 mixed in a Winkworth mixer 2Z.EL.JKT. First of all, 201.25 g of HIPS was softened for 4.5 min at 200 °C before addition of the additives (10.31 g of DBDE and 5.04 g of Sb_2O_3). After 15 min of mixing between the two V shaped blades, the resulting paste was taken out in a mould with the help of a spatula and pressed for 10 min at 1.5 tons per cm^2 with an upstroke Moore press. The final product consisted of a sheet of polymer (around 150 g) roughly 5 mm thick. In order to assess the actual content of DBDE from the polymer, the HPLC method developed previously was applied to a sample of HIPS. Prior to analysis, however, it was necessary to dissolve 20 mg of polymer into 200 ml of ethyl acetate. Further addition of 300 ml of toluene helped to keep the DBDE in solution. The resulting solution was injected and a concentration of 3.51 $mg.l^{-1}$ was measured, which translated into a massic content of 4.4% of DBDE in HIPS.

As a grinding machine was unavailable, it was decided to use a domestic coffee grinder to perform the size reduction of the polymer into different fractions. The polymer sheet was first cut into smaller pieces (1 cm of diameter) with the help of pliers, and ground for several minutes in a DeLonghi KG39 coffee grinder. The resulting powder was sorted using three sieves and only the intermediate fraction (between 1 and 2 mm) was kept for analysis because the others proved to be either too big or too small to ensure an easy separation from the IL. Eventually, the coarse fraction had to be ground again to produce more intermediate fraction.

3.3.2. Techniques used to quantify DBDE

After preparing the test polymer, the second priority was to develop the method to measure the amount of DBDE extracted from the polymeric matrix. Several methods were investigated from the easiest to the most complicated. Since DBDE molecules absorb UV light, it was decided to investigate the possible use of UV/Vis spectroscopy to quantify the amount of DBDE in IL. The second method was based on analysing the concentration of Br using X-ray fluorescence (XRF) technique. The third method was based on analysing the concentration of DBDE using an HPLC technique.

3.3.2.1. UV/Vis spectroscopy

UV/Vis spectra were recorded on a Perkin Elmer Lambda 25, from 200 to 800 nm. Sample were analysed in double beam subtractive mode, using a reference cell containing solvent. Typical experiment consisted in measuring the absorption spectrum of a mixture of known DBDE, IL and solvent at different concentrations. Toluene was chosen as a solvent, because it solubilised DBDE. However, the IL tested, [C8MPy][Br], was not completely soluble in toluene, and the mix IL/DBDE/toluene required additional methanol to form a homogeneous solution. In subsequent experiments, it was decided to use 5 ml of toluene and 1 ml of MeOH to completely dissolve DBDE in order to get a solution containing a single clear phase.

Various samples were prepared (Table 3.7), consisting of DBDE standards in toluene at different concentrations in absence of IL. More standards were prepared in presence of [C8MPy][Br] adding methanol to avoid partition of toluene and the IL. The spectra were analysed and correlation of peak intensity to concentration of DBDE at one or two wavelength was attempted.

Table 3.7: Sample prepared for the development of UV-Vis spectroscopic quantification method

[DBDE] (mg.l^{-1})	***[C8MPy][Br] (mg.l^{-1})***	***Methanol (ml)***	***Toluene (ml)***
200	-	-	5
400	-	-	5
500	-	-	5
500	40000	1	5
16.5	1800	1	5
33.0	1800	1	5
41.2	1800	1	5

3.3.2.2. X-ray fluorescence

The second analytical technique used to quantify DBDE was X-ray fluorescence (XRF). It was hoped to link the intensity of the signal corresponding to bromide and antimony ions to their respective concentrations. In order to exclude the signal due to bromide ions from the IL, the tests were also conducted with [C8MPy][Cl]. Analytical work was carried out with an Oxford Instruments XR2000 energy dispersive X-ray fluorescence spectrometer. Three sets of sample were prepared. The first batch of samples investigated the quantification of the bromine content of HIPS, and consisted of a simple analysis of the polymer powder (700 mg to 1 g of material) after grinding. The second batch assessed the quantification of DBDE in liquid sample, and checked the linearity of the calibration curve. Accordingly, DBDE standards were prepared in toluene (100, 200, 300, 400 and 500 mg.l^{-1}). Finally, the last batch of sample was designed to measure an experimental sample from a leaching test. The extraction procedure, explained in section 3.3.3.1, consisted of leaching 200 mg of HIPS with 2 g of [C8MPy][Cl]. Regularly, 50 mg was taken from the extraction media and diluted in 5 ml of toluene and 1 ml of methanol.

3.3.2.3. HPLC

The last analytical technique used for the analysis of DBDE was based on HPLC. Separation and quantification were performed with the help of a PE 200 series chromatographic system equipped with a binary pump, UV detector, vacuum degasser, Gilson model 231 autosampler, and a ACE5C18 column (Hichrom, Berkshire). This method was adapted from the previous work (Riu, 2006) by changing the isocratic eluent ratio (methanol:water) to 90:10 to shorten the retention time of DBDE, at a flow rate of 1 ml per min. All samples were prepared in methanol and toluene (1:5 ratio). Method development involved the choice of the best monitoring wavelength, selected by measuring all 0.5, 1 and 100 mg.l^{-1} at 210, 250 and 280 nm. In order to assess the reproducibility of the measurements at the most suited wavelength, another set of standards (0.5, 1, 2.5, 5 and 10 mg.l^{-1}) was injected several time. Finally, experimental sample, consisting of two or three drops of IL with a small amount of DBDE were accurately weighted in 1 ml of methanol and 5 ml of toluene, and were analysed.

3.3.3. Protocol of DBDE extraction

Each leaching experiment was divided into two steps:

- Leaching of DBDE from HIPS
- Preparation of samples to determine the concentration of DBDE using the HPLC method described above.

3.3.3.1. Extraction experiment

During the leaching experiments, the polymer containing DBDE was kept in contact with the extraction solvent (the IL) for up to 24 h. Small amounts of sample were taken periodically to determine the concentration of DBDE in the IL. In each experiment, 200 or 300 mg of polymer was introduced in a round bottom flask containing 2 or 3 g of IL respectively, and equipped with a condenser and a magnetic stirrer. The resulting assemblage was heated in an oil bath, whose temperature was controlled with a thermometer (Figure 3.2).

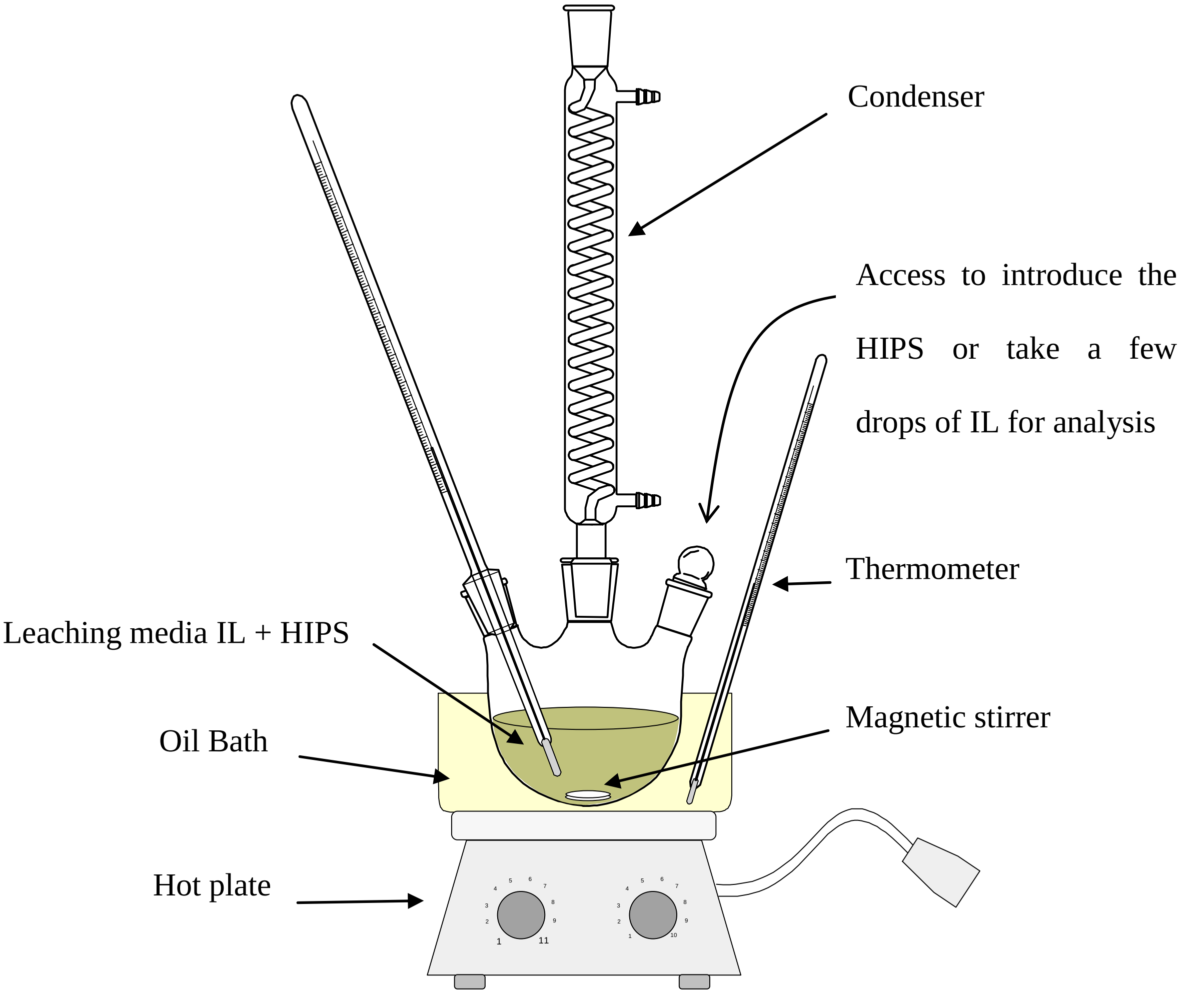


Figure 3.2: Schematic of the leaching experiment

3.3.3.2. Preparation of sample for DBDE quantification

During the extraction process, a few drops of liquid phase were withdrawn periodically from the reaction flask with the help of a Pasteur pipette and weighed accurately in a 10 ml tube. Special care was observed not to withdraw any polymer grains from the reaction flask during the sampling process. This was achieved by interrupting the stirring process for 10 to 15 minutes before taking the sample to allow the polymer particles to float on top of the IL. The Pasteur pipette was then introduced at the bottom of the flask to take a small quantity of IL, which was diluted with 1 ml of methanol and 5 ml of toluene in the tube. The solution was homogenised and transferred into a sealed HPLC crimp vial. At the end of the experiment, the leaching media was filtered using a Buchner flask over a fritted glass under mild vacuum. Few drops of the filtrate were transferred in a 10 ml tube and were diluted with 1 ml of methanol and 5 ml of toluene.

4

Chapter 4: Microwave assisted synthesis of ionic liquids

This chapter is focused on the first section of the experimental work: preparation and characterisation of imidazolium and pyridinium based ILs, as well as measuring their relative hydrophobicity. The method of synthesis adopted in this work has been described in section 2.5, which also stated the advantages of MW heating over conventional heating. The main objectives of the work described in this chapter are to:

- Synthesise the ILs in good yield;
- Characterise them to ensure they correspond to the expected product and are pure enough for the purpose of this work;
- Measure the hydrophobicity, parameter needed for leaching studies.

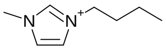
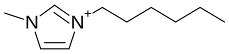
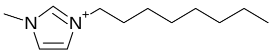
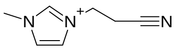
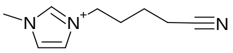
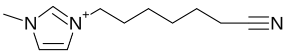
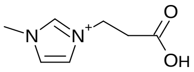
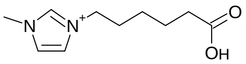
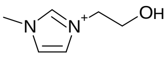
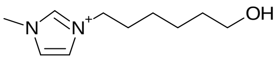
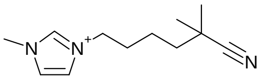
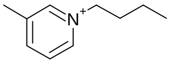
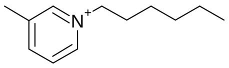
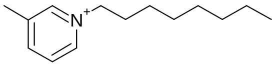
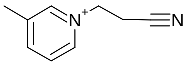
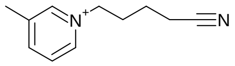
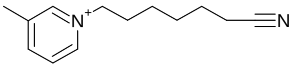
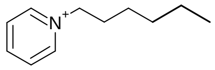
This chapter is divided into four sections. The first section aims at reporting and commenting on the outcome of the syntheses in term of yield and reaction time. The second section is focussed on the characterisation of IL with IR, MS and NMR spectroscopy. Some irregularities observed in NMR are also analysed and explained in order to prove that all compounds were fully characterised in a purity state suitable for further leaching tests. The third section reports the determination of the hydrophobicity and its correlation with the predicted logarithm of the octanol/water partition coefficient. Finally, the concluding section investigates how well the experimental results compare to the literature and specifies the key outcomes of the chapter.

4.1. Synthesis of ILs

Following the experimental protocols described in Chapter 3, the different ILs studied in this work were prepared. Table 4.1 summarises the synthesis time and final yields, but the full description of the synthesis protocols are given in Annex A.

No major problems were encountered during the synthesis of these ILs and in most cases > 90% yields were obtained. Reaction time, representative of the reaction rate, varied from 4 min for [OHC2MIM][Br] up to 30 min for [C6Py][Br]. Unsubstituted ILs were usually synthesised faster except for [OHC2MIM][Br]. In the case of [CNC2MIM][Br] and [COOHC2MIM][Br], the electron withdrawing functional group might have weakened the electron density around the bromide atom through inductive effect, resulting in a less favourable nucleophilic substitution reaction. In addition, pyridinium derivates required twice as much reaction time as imidazolium. Presumably, the Lewis acidity of the nitrogen in the pyridinium cycle is lower than in the imidazolium ring, because of the stronger charge delocalisation in the 6 member ring. As a result, the nucleophilic substitution would be more favourable in the case of imidazolium derivates. Once synthesised, the compounds were identified and characterised using a range of techniques, in order to verify that the product of synthesis correspond to the IL expected. The outcome of such characterisation is presented in the next section.

Table 4.1: Irradiation time and yield of the organic syntheses

Ionic Liquid	*Cation*	*Total (min)*	*Yield (%)*
[C4MIM][Br]		7’40	97
[C6MIM][Br]		6’20	95
[C8MIM][Br]		9’10	97
[CNC2MIM][Br]		14’20	89
[CNC4MIM][Br]		8’00	90
[CNC6MIM][Br]		8’40	94
[COOHC2MIM][Br]		13’20	100
[COOHC5MIM][Br]		11’30	90
[OHC2MIM][Br]		4’00	86
[OHC6MIM][Br]		8’00	95
[CN(CH$_3$)$_2$C5MIM][Br]		11’30	91
[C4MPy][Br]		22’40	88
[C6MPy][Br]		17’40	95
[C8MPy][Br]		17’30	98
[CNC2MPy][Br]		17’50	91
[CNC4MPy][Br]		11’00	87
[CNC6MPy][Br]		16’10	92
[C6Py][Br]		32’50	88

4.2. *Characterisation of ILs*

The ILs were characterised by three techniques, including NMR, IR and mass spectroscopy. A collection of the full spectra for NMR and IR can be found in Annex B and C respectively. Infrared and MS analysis provided unambiguous results (Section 4.2.1). Interpretation of NMR spectra was straightforward for most compounds (Section 4.2.2) but required specific interpretation in some case (Section 4.2.3) in order to identify the structure of the cation.

4.2.1. Confirmation of the IL structure by IR and MS

Infrared spectra of the pyridinium (MPy) and the imidazolium-based (MIM) ILs were relatively easy to explain. A typical spectrum (Figure 4.1a) for MIM showed a massif of peaks between 3200 and 2800 cm^{-1}, which correspond to C-H stretching from the aromatic ring, the methyl attached to the aromatic nitrogen and the CH_2 groups from the sidechain. Aromatic C=C stretching (1571 cm^{-1}), CH_2 bending (1466 cm^{-1}) and C-N stretching (1170 cm^{-1}) were also observed in all the spectra of MIM-based ILs.

The presence of O-H stretching (3360 cm^{-1}) was also observed in most cases, which tend to indicate the presence of water in the IL at room temperature, because of their hygroscopic nature. The characteristic peaks of the functional groups were also observed where expected, such as 2200 cm^{-1} (C≡N stretching) or 1720 cm^{-1} (C=O stretching).

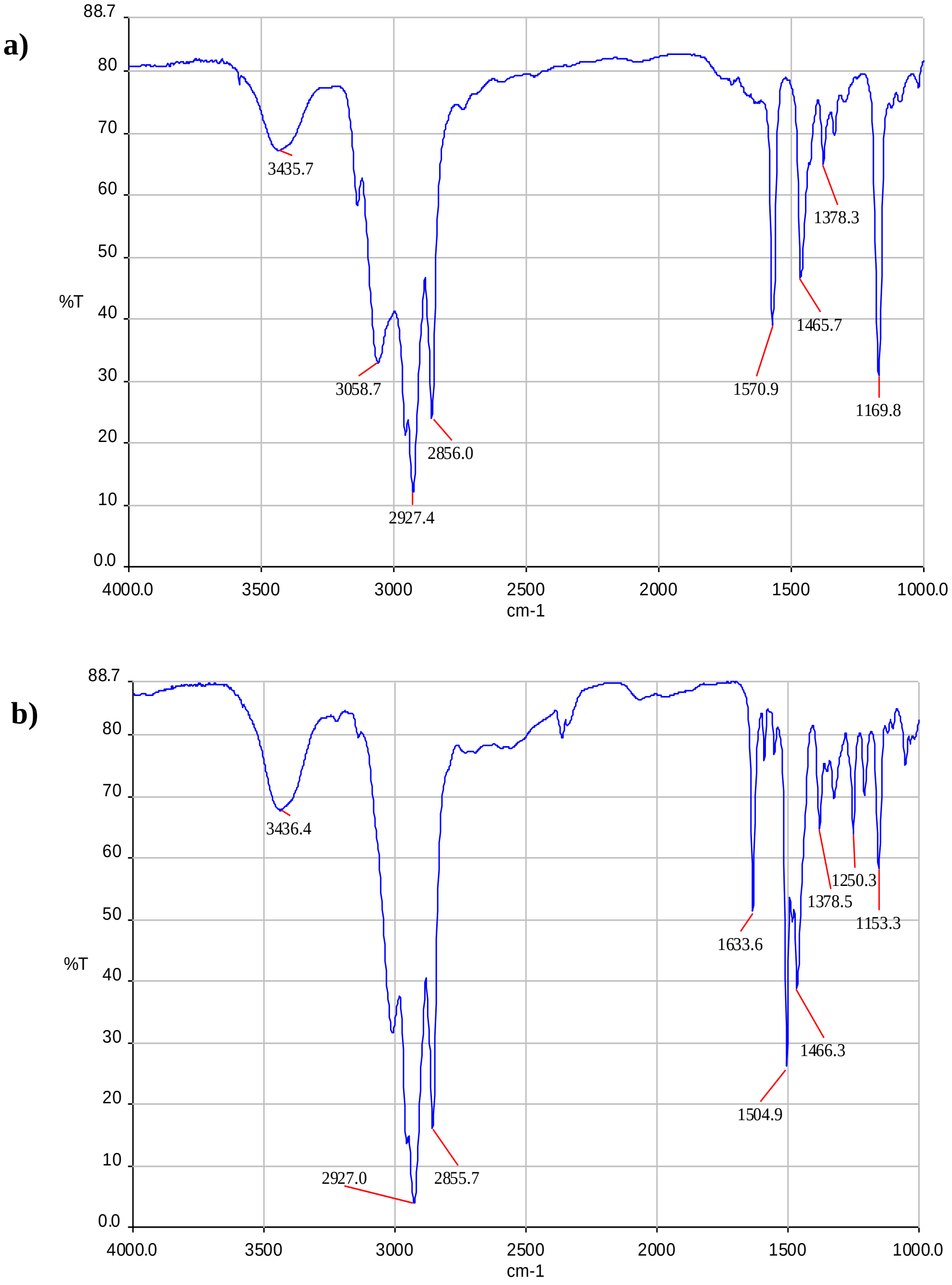


Figure 4.1: IR spectra of a) [C8MIM][Br] and b) [C8MPy][Br]

Pyridinium-based IR spectra (Figure 4.1b) were extremely similar to imidazolium, with a peak massif in the region 3000 to 2850 cm^{-1} (aromatic and aliphatic C-H stretching), a peak at 1634 cm^{-1} (C=C stretching), 1504 cm^{-1} (C-C skeletal vibrations), 1466 cm^{-1} (CH_2 bending), 1250 cm^{-1} (CH_3 bending), 1153 cm^{-1} (C-N stretching). The difference observed is due to the variation of interatomic distance in the two different heterocycles, which affects the vibration energy associated with the interatomic bounds.

Mass spectra were also very simple, since the MS method was optimised to limit fragmentation because the main constituent of the IL were ions already. Two major peaks could be observed, one at 83 amu (atomic mass unit) for the MIM fragment (or 94 amu for the MPy) and a peak corresponding to m/z ration of the IL cation, which was reported in the result section. Nonetheless, two particular facts were observed. First of all, the intensity of the first peak (corresponding to the cation without the sidechain) varies from one IL to the other. This could be explained by the stability of the IL in the MS, as shorter chains brake down more easily, leading to higher fragmentation of the mother ion. Secondly, peaks corresponding to adduct were also observed (for instance two cations and a bromide), which had already been observed (Alfassi et al., 2003). As a result, the two analyses confirmed the nature of the ILs prepared.

4.2.2. Confirmation of the cation structure ^{1}H and ^{13}C NMR of ILs

Some imidazolium and pyridinium ILs have already been synthesised and characterised elsewhere. More particularly, the NMR chemical shifts measured for unsubstituted imidazolium and pyridinium bromides have already been reported (Varma and Namboordiri, 2001) corresponded to the NMR spectra obtained in this work. In such case, the peaks could be attributed by referring to the data already available, but substituted ILs required more interpretation.

4.2.2.1. Interpretation of ^{1}H NMR spectra of imidazolium ILs

A typical spectrum (Figure 4.2) showed that the hydrogen atoms present in the aromatic ring (position 2, 4 and 5) have a stronger chemical shift (δ = 8.69, 7.45 and 7.40 ppm) due to the electron delocalisation and aromatic ring current effect. The CH_2 and CH_3 groups in α of the aromatic nitrogen atoms had a lower δ (4.18 and 3.82 ppm respectively) because the influence of electron delocalisation is not as strong. Finally, the hydrogen atoms present in the sidechain had usually very low δ (between 0.5 and 2 ppm) except when located next to a polarised functional group (3.18 ppm for hydrogen in alpha of CN, 2.97 ppm in alpha of COOH or 4.31 ppm in alpha of OH). Peak multiplicity corresponded to the number of hydrogens neighbours, but two consecutive signals sometimes possessed a close δ and thus formed an indistinct multiplet with an intensity of 7 or more equivalent hydrogens (position 9 to 11 in [C6MIM][Br] from Figure 4.2).

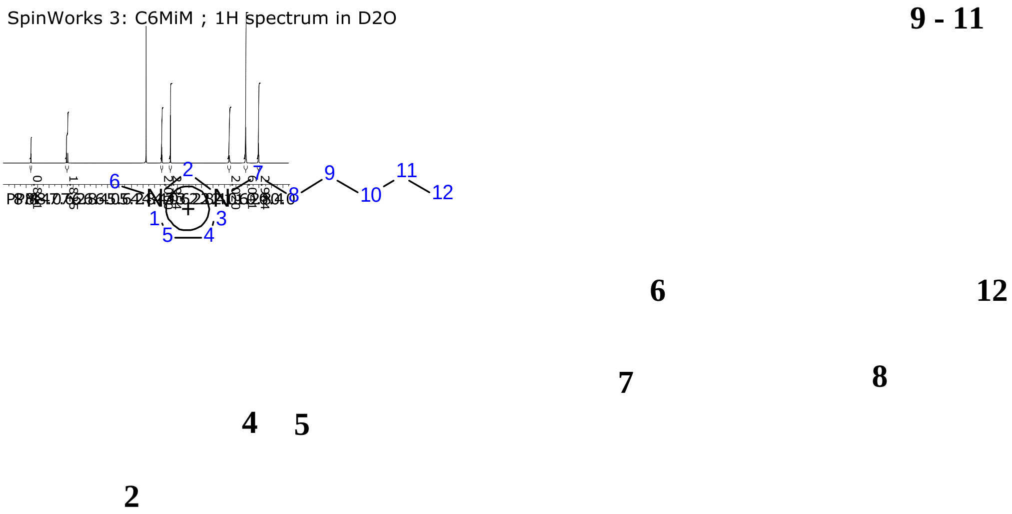


Figure 4.2: Proton NMR of [C6MIM][Br]

4.2.2.2. Interpretation of ^{1}H NMR spectra of pyridinium ILs

Pyridinium NMR spectra were significantly different from imidazolium (Figure 4.3), because the chemical shifts for the aromatic hydrogens were higher (8.68, 8.62, 8.36 and 7.94 ppm for H in position 1, 5, 3 and 4 respectively) due the stronger delocalisation of the electrons in the pyridinium ring. The H in positions 3 and 5 corresponded to a doublet and the H in position 4 to a triplet, confirming that they have interaction with 1 hydrogen, or 2 hydrogens in the case of position 4. The CH_2 in α of the nitrogen showed a triplet at 4.6 ppm, while the rest of the hydrogens displayed low chemical shifts between 1 and 2 ppm, very similar to what was observed for imidazolium IL.

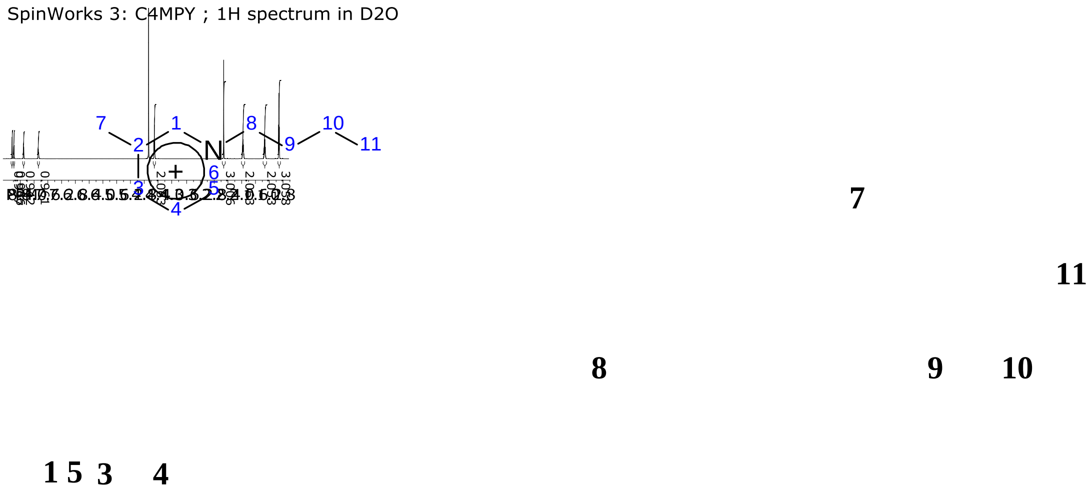


Figure 4.3: Proton NMR of [C4MPy][Br]

4.2.2.3. Interpretation of ^{13}C NMR spectra of ILs

The interpretation of decoupled ^{13}C NMR spectra (Figure 4.4) was more difficult, as the chemical shift is the only parameter available: all peaks are singlets, and their intensity is not proportional to the molar quantity of carbon. Furthermore, an artefact could be observed in most spectra, at 127.0 ppm. Such a peak was generated by the instrument, and was consequently ignored in the data treatment. Their interpretation led to the identification of the carbons from the aromatic cycle at a high chemical shift (135, 123 and 122 ppm for MIM, 146, 143, 141 and 139 ppm for MPy). Once more, the aromatic character of the ring was held responsible for the high shifts observed, and higher δ values for the pyridinium ring could be explained by the higher electron delocalisation (higher aromatic character). Non aromatic carbons showed lower δ, except those linked to the functional groups (174 to 179, 117 to 122, or 60 to 61 ppm for COOH, CN and COH respectively).

Figure 4.4: ^{13}C NMR of a) [C6MIM][Br] and b) [C4MPy][Br]

4.2.3. Interpretation of more complex NMR spectra for short chain IL

Although the spectra of linear ILs corresponded to the literature, a couple of singularities were detected. First of all, the hydrogen in α of the two cyclic nitrogen atoms (position 2 in Table 4.2) was not present in a few spectra, such as those of [C4MIM][Br], [OHC6MIM][Br] and [CN$(CH_3)_2$C5MIM][Br], which was confirmed by the absence of the corresponding carbon in ^{13}C NMR (Table 4.2).

Table 4.2: Comparison of NMR peaks for [C6MIM][Br] and [C4MIM][Br]

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The problem was inherent to the NMR technique, because the instrument cannot detect nuclei whose spins are perpendicular to the magnetic field, which was presumably the case of the proton and carbon in position 2. The rest of the spectra confirmed the structure expected, and further evidence of the expected data was given by MS characterisation, with a molecular ion at the same mass/charge ration as expected from the IL cation. As a result, the disappearance of the signal was considered normal and didn't interfere with the full identification of the IL cation.

Moreover, proton NMR of short, substituted chain such as [CNC2MIM][Br], [CNC2MPy][Br], [OHC2MIM][Br] or [COOHC2MIM][Br], showed the presence of two sets of peaks, one very intense (set 2 in Figure 4.5) and one less intense (set 1 in Figure 4.5).

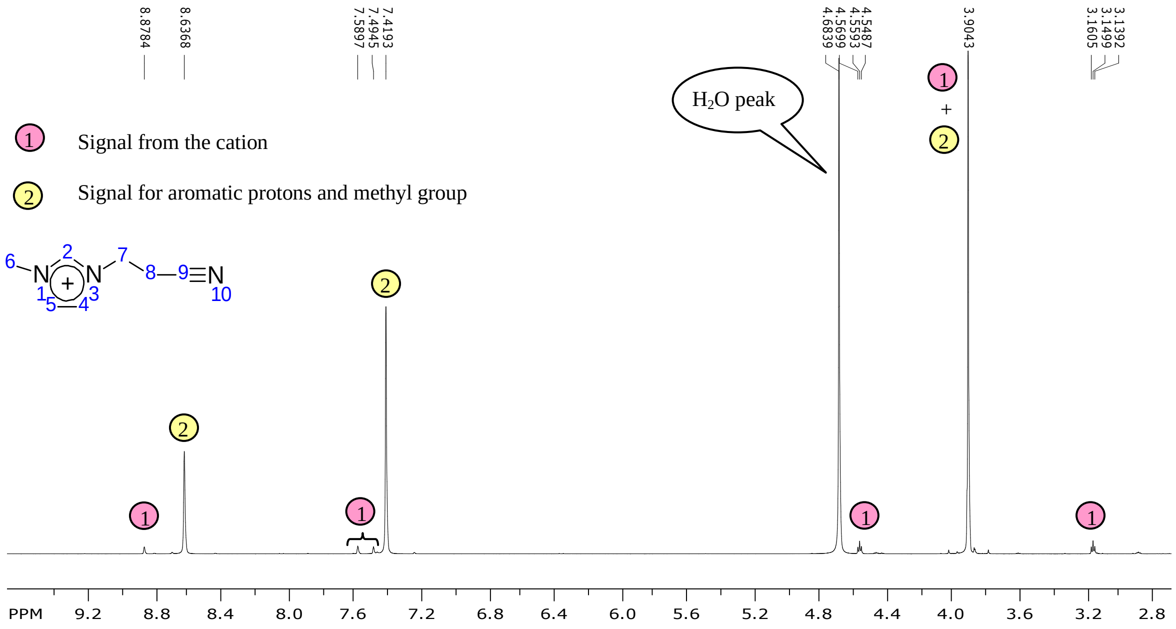

Figure 4.5: ^{1}H NMR spectrum of [CNC2MIM][Br] in D_2O

The signal from aromatic hydrogen atoms was split into two sets, because some of these protons (position 2, 4, 5 and 6 in Figure 4.5) aligned themselves with the magnetic field applied during precessional movements, which greatly increased the intensity of resonance compared to the signal of other protons. Because of this specific magnetic interaction, the chemical shifts of the aligned protons 2, 4 and 5 were different (8.64 and 7.42 ppm) from the unaligned protons (8.88, 7.50 and 8.60 ppm). The methyl protons were less affected but their intensity still remained very high. As a result, the high signal from set 2 shouldn't be mixed with the normal signal from the cation (set 1). Furthermore, in some instances, a very low signal corresponding to the starting material was observed. The relative intensity was so weak (ratio of 1:20 or more) that the starting materials were only present as traces that couldn't be removed by the purification process. Therefore, the major compound synthesised was the IL, and the starting materials were present in such a low concentration that they could not affect the outcome of the dissolution and extraction tests.

4.3. Measurement of hydrophobicity of the cation

The hydrophobicity of the cation was determined by measuring the retention factor k’ at different composition of eluent and comparing it with the octanol/water partition coefficient logP, estimated by a prediction algorithm. Experimentally, k’ was estimated using the retention time t_R and the first positive signal observed in the chromatogram t_0 (Figure 4.6).

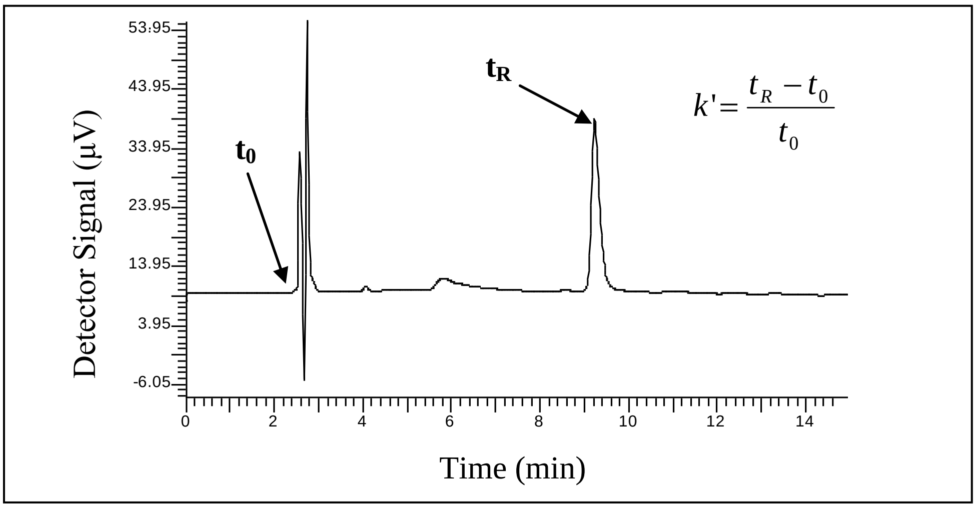

Figure 4.6: Chromatogram of [C8MIM][Br] at 50% MeOH isocratic elution

4.3.1. Estimation of log k'

The detailed values of k' and extrapolation to 0% MeOH are given in Annex D. Briefly, the k' were measured at different ratio of eluent (methanol/water). The logarithms of k' were calculated and extrapolated at 0% methanol to account for only hydrophobic interactions of the solute (IL) with the stationary phase. A typical regression curve is represented in Figure 4.7.

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Figure 4.7: Regression of log k' and interpolation at 0% MeOH for [C6MIM][Br]

Regressions showed a good linear trend with $R^2 > 0.88$, except for CNC2MIM where R^2 was 0.47 (Annex D). It is because the cation is more hydrophilic than the others and was not well retained in the chromatographic conditions used. Finally, the values of logk' were averaged between the two replicates and compared with the logP values calculated from Molinspiration (Table 4.3).

Table 4.3: Comparison of experimental logk' and logP

Ionic Liquid	logk' (average)	RSD	logP (calculated)
[C4MIM][Br]	0.6	4%	-2.0
[C6MIM][Br]	1.6	0%	-1.0
[C8MIM][Br]	1.9	6%	0.0
[C6MPy][Br]	1.7	1%	-0.7
[C8MPy][Br]	2.1	3%	0.4
[CNC2MIM][Br]	-0.2	-73%	-4.0
[CNC4MIM][Br]	-0.2	-32%	-3.2
[CNC2MPy][Br]	-0.2	-74%	-3.6
[CNC4MPy][Br]	-0.1	-75%	-2.9
[CNC6MPy][Br]	1.0	0%	-1.9
[COOHC2MIM][Br]	0.6	15%	-4.0
[COOHC5MIM][Br]	0.1	13%	-2.7
[CN(CH2)2C5MIM][Br]	1.0	1%	-1.5
[OHC6MIM][Br]	0.1	33%	-2.6

4.3.2. Correlation of log k' and the calculated logP

The linear correlation of logP with logk' was tested using the coefficient of determination R^2 with 14 points (Figure 4.8). High R^2 of 0.86 demonstrated the existence of a significant linear relationship between the two series. For more hydrophilic cations (bearing short side chain), the difference observed between two replicates was higher, because retention times were too short to be measured more accurately.

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Figure 4.8: Correlation between experimental logk' and calculated logP

As a result, logP and logk’ are considered collinear and the values of logP were representative of the actual hydrophobicity measured by k’. Although some ILs were not tested for logP because of time constraint, the estimated logP was still considered accurate, because the relationship was established using a representative group of IL, including substituted and non-substituted ILs possessing imidazolium or pyridinium rings. Furthermore, these values corresponded to previous work that demonstrated the increase in hydrophobicity provoked by a longer side chain length (Malhotra and Zhao, 2003). LogP values, however, were different from other published work, because of the different algorithm (ClogP3) used (Stepnowski and Storoniak, 2005). Nevertheless, the relative magnitude of the calculated logP remained the same.

4.4. MW-assisted synthesis is an advantageous method for preparing ILs

4.4.1. Comparison with other MW-assisted synthesis of IL

The data were consistent with the previous work on MW-assisted synthesis of ILs . For instance, the yields obtained were in the same range as what was already observed, 92% for open vessel (Namboordiri and Varma, 2002) and 91% for closed vessel (Khandilar and Rebeiro, 2002) for the synthesis of [C4MIM][Br]. Reaction time was longer (22 min) in the case of the closed vessel method possibly because the closed vessel provided more control over the reaction conditions. In spite of presenting less control over the reaction, because atmospheric pressure, temperature and hygrometry were not controlled, the open vessel method presented many advantages. The reaction procedure was robust and easy, no particular and no costly control method was implemented, and the final quality of the product was satisfactory in terms of yield and purity. However, such method would not be acceptable for large scale preparation, and remained limited to immediate, local preparation of a small quantity of IL.

4.4.2. Key outcomes of the syntheses

In spite of the difficult interpretation of some of the NMR spectra, the ILs were successfully identified. Although NMR inevitably showed traces from the starting materials in the final product, the IL remained the major compound synthesised and contamination from external products was negligible. Reaction yields were high (from 86 to 98 %) regardless of the chain length or the type of substituents. The measure of the hydrophobicity for IL showed a correlation to the estimated logP, and the use of logP predicted from the Molinspiration software could therefore be used as a parameter in Chapter 5 and 6. To prevent any subsequent degradation of the IL, or any absorption of atmospheric water, it was decided to prepare them shortly before the dissolution or extraction tests. Furthermore, they were kept in desiccators at room temperature to prevent any contamination with water. In summary, the objectives set up at the beginning of this chapter are successfully met:

- A range of MIM and MPY based ILs were successfully synthesised in high yields
- They were characterised by a range of techniques that confirmed that the reaction product was same as expected
- The analysis confirmed that the synthesis products were pure enough for the purpose of the leaching studies

- The hydrophobic properties of these IL was successfully measured and compared to the estimated logP

5

Chapter 5: Dissolution of CuO in ionic liquids

The ability of various IL to dissolve copper oxide is investigated in this chapter. A selection of IL (Table 5.1) has been made to reflect a variation of the hydrophobicity, the type of aromatic ring, and the presence of a polarised functional group. These parameters have been identified through the literature review of the previous work on the subject (Chapter 2).

Table 5.1: Acronyms of the ILs used for CuO dissolution tests

IL acronym	*IL name*
[C4MIM][Br]	1-butyl-3-methylimidazolium bromide
[C6MIM][Br]	1-hexyl-3-methylimidazolium bromide
[C8MIM][Br]	1-octyl-3-methylimidazolium bromide
[CNC2MIM][Br]	1-(2-cyanoethyl)-3-methylimidazolium bromide
[CNC4MIM][Br]	1-(4-cyanobutyl)-3-methylimidazolium bromide
[CNC6MIM][Br]	1-(6-cyanohexyl)-3-methylimidazolium bromide
[CN(CH2)2C5MIM] [Br]	1-(6-cyano-5,5-dimethylpenthyl)-3-methylimidazolium bromide
[COOHC2MIM][Br]	1-(2-carboxyethyl)-3-methylimidazolium bromide
[COOHC5MIM][Br]	1-(5-carboxypentyl)-3-methylimidazolium bromide
[OHC2MIM][Br]	1-(2-hydroxyethyl)-3-methylimidazolium bromide
[OHC6MIM][Br]	1-(6-hydroxyhexyl)-3-methylimidazolium bromide
[C6MPy][Br]	1-hexyl-3-methylpyridinium bromide
[CNC2MPy][Br]	1-(2-cyanoethyl)-3-methylpyridinium bromide
[CNC4MPy][Br]	1-(4-cyanobutyl)-3-methylpyridinium bromide
[CNC6MPy][Br]	1-(6-cyanohexyl)-3-methylpyridinium bromide

More particularly, this chapter aims to test the following two hypotheses:

- IL can be used to dissolve CuO
- The magnitude of dissolution is influenced by hydrophobicity and polarisation of the functional group (represented by F)

The chapter is divided into four sections, the first of which reports the results from the dissolution tests of CuO in the various ILs. The second section reports the work undertaken to identify the complex that forms when a diluent is added. The effect of the two parameters, hydrophobicity and polarity of the substituent are examined in the third section, and the final section concludes this chapter by summarising the key findings.

5.1. Results of dissolution tests

The same procedure, described in section 3.2, was applied to test the ability of 15 ILs to dissolve copper oxide. Briefly, the powder of CuO was added to the IL at 70 °C for 10 minutes. A diluent solvent was then added to solubilise the IL/CuO slurry and allow the determination of the amount of copper dissolved by FAAS. Table 5.2 reports the concentration of copper dissolved in the IL with the standard deviation between the two replicates measured for each IL. Initial qualitative observations indicated that IL formed a coloured, dark, thick slurry when high amount of CuO (roughly more than 8.5 $mg.g^{-1}$) was dissolved. In such case, the solution formed after the addition of water or acetonitrile, took an intense colour, suggesting the formation of a complex.

Table 5.2: Quantity of copper dissolved in various IL, calculated from FAAS data

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The FAAS technique used always provided very linear standard curves ($R^2>0.99$) for all batches of sample measured (calculation details are reported in Annex E). The variance associated with the triplicate measurements from FAAS was always very low, with a maximum of 1% of RSD. Moreover, the measure of the control sample (1 ppm) at the end of each run was always accurate (less than 6% difference in signal with the 1 ppm standard), indicating that the technique produced reliable measurement. The %RSD associated to the duplicate experiments were higher, up to 12 % in some cases, because of random error associated with parameters such as external temperature, hygrometry or atmospheric pressure and couldn’t be eliminated, since these experiments have been designed to be as simple as possible.

In general, unsubstituted MIM dissolved less than 2 $mg.g^{-1}$ of copper whereas short, substituted IL, dissolved up to 74.5 $mg.g^{-1}$ of copper in the case of [CNC2MIM][Br]. Both the length of the chain and the presence of a polarised substituent have an effect. Long, substituted ILs dissolved similar amount than their unsubstituted analogues, and in such case, the concentration of copper was higher in MPY-based ILs.To the contrary, MIM-based ILs dissolved more copper for short, substituted sidechain. As a result, [CNC2MIM][Br] was the most appropriate candidate for solubilisation of copper oxide.

It is also apparent from the data (Table 5.2) that the choice of the solvent used to dilute the IL/copper slurry had an impact on the quantification of copper. Nevertheless, both datasets, in water and acetonitrile, showed a similar pattern in the relative magnitude of the dissolution. The investigation of the two diluents is carried out in section 5.2.

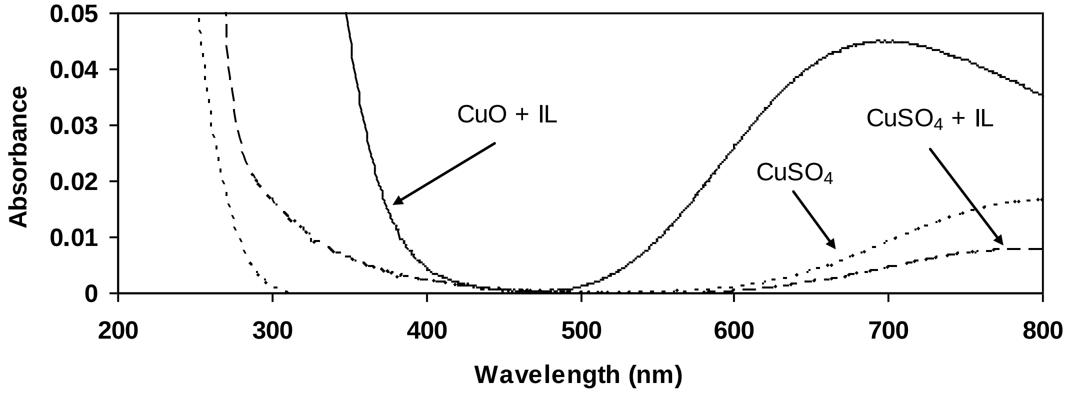
5.2. Effect of the dilution solvent: formation of complexes

The first series of tests were carried out using exclusively water, because it is a very good solvent for all ILs and it doesn't dissolve CuO. However, a white precipitate formed during the addition of water to the Cu/IL slurry. This could be due to low solubility of Cu/IL in water. As a result, it was decided to use an organic solvent such as acetonitrile, which instantly formed a dark brown solution with the slurry. The formation of coloured solution with the addition of the diluent suggested that the solubilisation of the Cu/IL slurry lead to the formation of a copper complex. In principle, if the IL is not a good coordinating agent, copper would not be dissolved, and would therefore remain intact in the form of solid CuO after the addition of the diluent. In order to identify the complex, few experiments were carried out with the IL that dissolved the most copper, [CNC2MIM][Br]. Such experiments involved ligand exchange, monitored by UV spectroscopy, and characterisation by mass spectrometry.

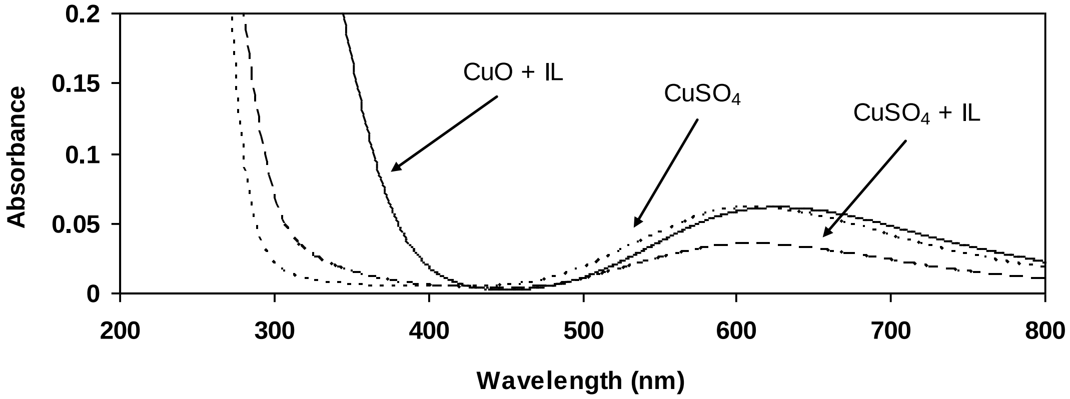
5.2.1. Identification of copper/IL complex with UV spectroscopy

UV-visible spectrophotometry was used for characterising the coloured complexes formed when the slurry [CNC2MIM][Br]/CuO was diluted. The presence of a copper complex was indicated by the dark blue colour of the solution formed in presence of water, and by an intense brown colour in presence of acetonitrile. Using water as diluent, the ligands were exchanged with ammonia while monitoring the change in colour. The effect of the IL was investigated using an aqueous solution of copper sulphate in the presence or absence of [CNC2MIM][Br]. The copper sulphate complex in the presence of IL was prepared by dissolving $CuSO_4.5H_2O$ in [CNC2MIM][Br] and diluting the slurry in water. The data (Figure 5.1a) showed a clear difference between the maximum absorption of CuO (700 nm) and $CuSO_4$ (800 nm) in IL. In addition, no notable difference was observed between $CuSO_4$ in water or in presence of IL in the visible range, so it seemed that the IL was not present in the coordination sphere of copper sulphate.

a. in water



b. in water and NH3 excess



c. in acetonitrile

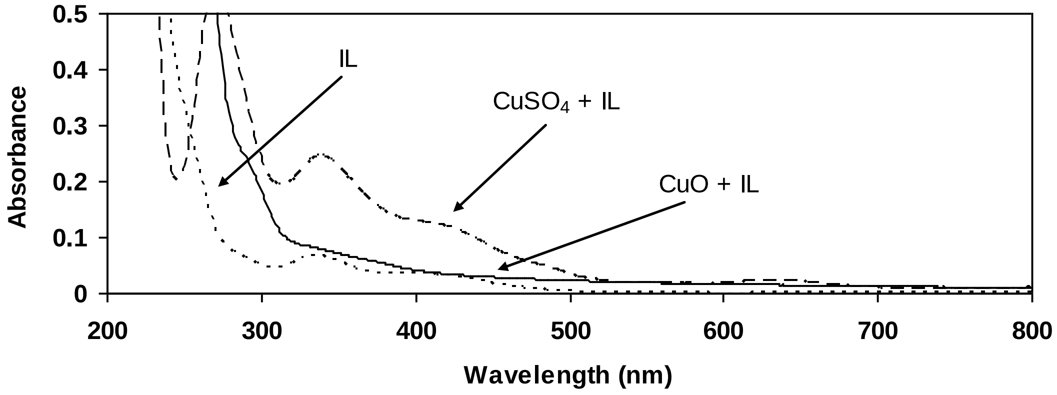


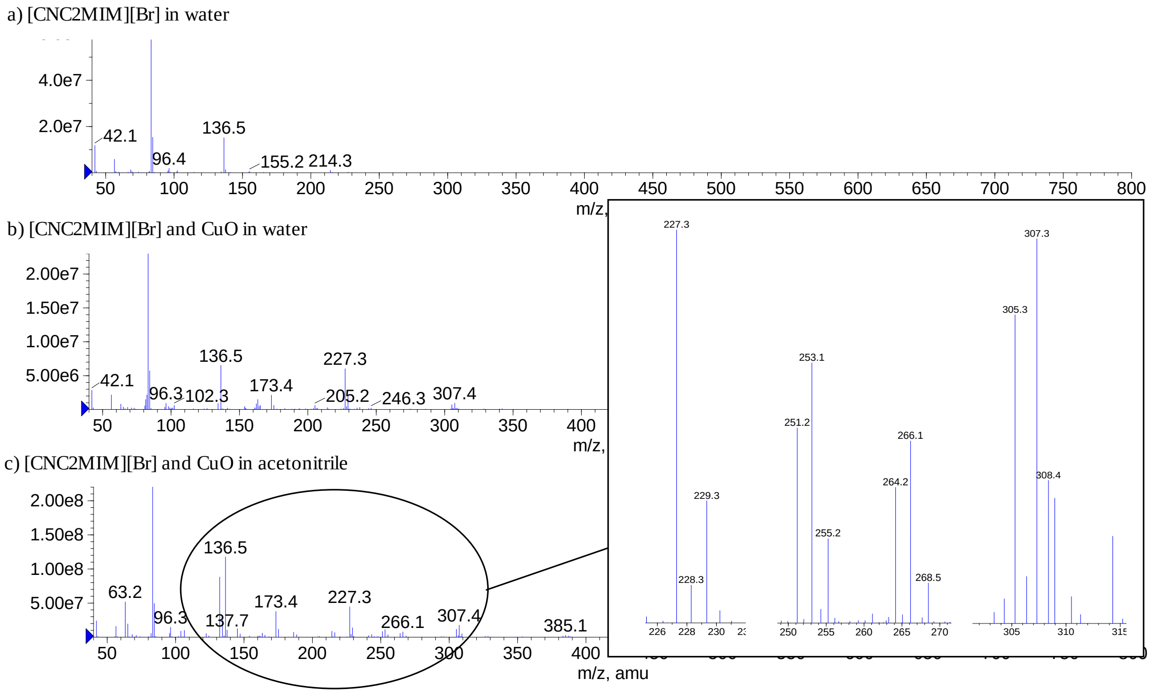
Figure 5.1: Absorption shift of copper complex in [CNC2MIM][Br] induced by a) different copper salts in water; b) ammonia ligand exchange in water; c) different copper salts in acetonitrile

The addition of ammonia (Figure 5.1b) shifted the maximum visible absorption from 700 or 800 nm to the same wavelength (625 nm) in water, reflecting the transition from blue to purple. As a result, CuO dissolved in IL and water formed a complex, but had the same coordination sphere as $CuSO_4$ with excess ammonia (all ligands were replaced by ammonia). It can also be deducted that the two complexes had different ligands, prior to the addition of ammonia, which suggested that the IL was present in the coordinating sphere of copper when dissolving CuO.

Finally, in the visible range, the solution in acetonitrile (Figure 5.1c) absorbed the lower wavelength but no sharp absorption peaks, often associated to the presence of a coloured complex, were observed. However, peaks were found in the near UV region (270 nm), which were not present in the spectrum of IL alone, implying the presence of a transition complex which absorbs in UV and in the shorter visible wavelength. Consequently, UV spectroscopic analysis brought evidence of the presence of a complex involving the IL molecule.

5.2.2. Characterisation of copper/IL complex with Mass Spectrometry

Identification of the complex was attempted via mass spectrometry, supposing that the complex did not break in the turbospray source, and that its molecular weight remained in the range of analysis. The resulting spectrum of [CNC2MIM][Br] was acquired in positive mode, with or without CuO in water and acetonitrile (Figure 5.2).



a) [CNC2MIM][Br] in water

b) [CNC2MIM][Br] and CuO in water

c) [CNC2MIM][Br] and CuO in acetonitrile

Figure 5.2: Mass spectra of [CNC2MIM][Br] in presence of copper

Interpretation of such spectra was very difficult, because of the little information available. However, it seemed that CuO dissolved in IL and diluted in solvent led to the presence of extra peaks at 227, 251, 254 and 305 amu, not visible in the simple spectrum of IL in water. These peaks were present regardless of the solvent used (water or acetonitrile). The resolution of the spectrometer was not high enough to allow the attribution of a formula for these peaks, but the presence of copper in the ion fragments could be inferred. Indeed, the peaks at 227 and 229 had an intensity ratio of 75 / 25 close to the theoretical isotope distribution of copper 63 and 65 (70 / 30). Furthermore, other peaks show a triplet, such as 251, 253 and 255 with a ratio of 35 / 50 / 15, close to the theoretical isotope distribution of a species containing Br and Cu (35 / 50 / 15). However, none of the attempts made to attribute a fragment to a molecular formula were successful, hence the attribution of a formula to such fragment was impossible in absence of more accurate MS measurement. If these fragments came from the original complex, the presence of the ligands from the solvent should have been observed, and the resulting spectrum in water or acetonitrile should have been different. As a result, there was a great chance that the observed fragments were formed during the ionspray phase, when the solvent completely evaporated to leave only the ionic species, which combined together, to include Cu or Br atoms in addition to other organic fragments.

5.2.3. Kinetic of complex formation in water and acetonitrile

Although the results from MS and UV investigations were inconclusive to characterise the complex, they still represented evidence of the involvement from the IL molecule. The choice of solvent to create such a complex had a great influence on the amount of copper transferred into solution from the original slurry that [CNC2MIM][Br] formed with CuO. In all cases, acetonitrile led to a higher concentration of Cu than in water despite the fact that the solutions were prepared from the same amount of IL+CuO. Experimental observation indicated that the slurry almost instantaneously went into solution after addition of acetonitrile while it took a longer time to solubilise in water, which may be due to the kinetics of complex formation in water. In order to verify such a hypothesis, water was added dropwise under vigorous stirring to a slurry of CuO+IL, allowing the time for the complex to form (the addition of 50 ml of water took 30 min). The resulting dark blue solution contained around 100 mg.L^{-1} of copper, very close to the results in acetonitrile. As a result, the values of the test in acetonitrile represented the true amount of copper dissolved in the IL whereas the tests in water underestimated these values. Supposing that the kinetic of solubilisation in water was similar for all the IL, the two datasets should be equivalent for qualitative analysis. However, investigation of the link between [Cu], logP and F required regression work, which can only be carried out with the true amount of copper dissolved. Consequently, only the dataset in acetonitrile will be used for regression purposes.

5.3. *Effect of structural parameters on the copper dissolved*

Qualitative interpretation of the two datasets for water and acetonitrile confirmed that the amount of CuO dissolved in ILs depended strongly on their structure (from 1 mg.g^{-1} for [C8MIM][Br] up to 74.5 mg.g^{-1} for [CNC2MIM][Br]). The purpose of this section is to investigate if there is a quantifiable link between two parameters, which were chosen to reflect the variation of structure, and the amount of copper transferred in the IL phase. Each parameter, hydrophobicity, represented by logP, and the polarity of the functional group, represented by F, is investigated independently in section 5.3.1 and section 5.3.2. Then the conclusion summarises the key points of the results.

5.3.1. Low hydrophobicity: prerequisite for high extraction

Figure 5.3 represents a plot of the amount of copper dissolved versus the logP of the IL, as predicted by Molinspiration. Qualitative analysis of the results in water and acetonitrile revealed the presence of two groups of ILs. The first group contained the more hydrophilic ILs (logP < -2.9), whereas the second group contained the more hydrophobic ILs (logP > -2.9). This separation was operated because group 1 dissolved more than 10 mg.g^{-1} of Cu in acetonitrile, and more than 2 mg.g^{-1} in water, as opposed to group 2 which dissolved less than 10 mg.g^{-1} of Cu in acetonitrile (less than 2 mg.g^{-1} in water). Very similar patterns were observed when the Cu/IL slurry was diluted in water and in acetonitrile. The values in acetonitrile were higher because only a fraction of the CuO originally dissolved in IL formed a complex in water, regardless of the type of IL used (section 5.2.3) so only the values in acetonitrile were used for regression.

a)

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Figure 5.3: Influence of logP upon the amount of copper dissolved in ILs using a) acetonitrile or b) water as dilution solvents

Group 1

The ILs from group 1 consisted of substituted MIM or MPy-based ILs bearing short chains. Such ILs achieved much better solubilisation of CuO, showing a concentration of dissolved copper in IL ranging from 14 to 74.5 mg.g^{-1}. Group 2 was mainly composed of long chain MIM or MPy-based ILs, substituted or unsubstituted. As a result, the ability to dissolve copper oxide resulted from the synergy of two factors, low hydrc ity, and presence of a polarised functional group.

b)

5.3.1.1. LogP in unsubstituted ILs

In order to study the influence of the hydrophobicity alone, qualitative analysis of the unsubstituted ILs was performed. These linear ILs were all found in group 2, because they displayed a lower ability to dissolve CuO. Figure 5.4 represents a plot of the hydrophobicity of linear MIM-based series versus the copper concentration.

Group 1

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Figure 5.4: Quantity of Cu dissolved in linear MIM-based ILs

Shorter ILs such as [C4MIM][Br] are more hydrophilic, which facilitates the contact with the hydrophilic surface of copper oxide (Nockemann et al., 2006). With more hydrophilic solvent, the diffusion layer is easier to overcome because the dispersive forces at the surface are stronger. As a result, dissolution of the species at the interface is easier, which led to better solubilisation. However, the magnitude of the copper dissolved (from 1 mg.g^{-1} to 1.8 mg.g^{-1}) remained lower compared to than other ILs, which was expected according to chapter 2.

5.3.1.2. LogP in substituted ILs

The influence of hydrophobicity can also be studied using two series of substituted MIM- and MPy-based ILs bearing the same cyanide group, but with a different chain length. In that case, one parameter (the functional group) was kept constant while the other parameter (hydrophobicity) varied, in order to study the effect of hydrophobicity in the presence of a polar group. Interestingly, the ILs studied in this section belonged to both group 1 and group 2.

These cyano substituted ILs behaved in a very similar way as linear MIM, since more hydrophilic ILs dissolved more copper (Figure 5.5a). Similarly to section 5.3.1.1, hydrophilic ILs facilitates the contact between solvent and CuO particle, thus improving the solubilisation. The main difference with linear MIM lies in the greater magnitude of the increase of copper concentration with logP. Consequently, linear regression of log[Cu] and logP was performed (Figure 5.5b).

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Figure 5.5 (a)Cu dissolved in CN-substituted ILs and (b) regression using log [Cu]

Both of the series investigated showed a linear relationship between logP and log[Cu] with high correlation (R^2>0.99). Such relationship could be related to the free energy associated with the solubilisation reaction ($\Delta G^{\Theta}=RTln[Cu]_{eq}$), which implied that, within the same series, the free energy associated to the solubilisation of CuO is directly related to the hydrophobicity. As a result, the solubility constant of CuO is proportional to the octanol/water partition coefficient so the dissolution mechanism is directly influenced by hydrophobicity.

As a conclusion, logP has an influence on the amount of copper dissolved because lower hydrophobicity increases the dispersive interactions at the interface, which is reflected by higher solubility. However, this influence became much greater when a functional group is present. Next section investigates the effect of the functional group in order to determine which parameter is the most important for dissolving CuO in IL.

5.3.2. Adding a functional group to enhance dissolution of CuO

The effect of a functional group was more visible for short chain. In acetonitrile for instance, the addition of a cyanide group to MIM-based ILs with six carbon sidechain led to the dissolution of twice as much copper as [C6MIM][Br]. When considering a four carbon sidechain, the IL dissolved 8 times more copper when a cyanide group was added. However, the maximum effect of the subsituent was observed for two carbon side chain, so this section will focus on the study of those substituted ILs.

5.3.2.1. Effect of the field coefficient

A linear regression was carried out (Figure 5.6), using the field coefficient of three functional groups, $-CH_3CH_2$, $-COOH$ and $-CN$, as a function of the amount of copper dissolved in the corresponding IL. With a coefficient of determination of 0.99, there was evidence of a linear relationship, hence a direct influence of the type of substituent upon the amount of copper dissolved.

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Figure 5.6: Field coefficient vs. quantity of copper dissolved in ILs

The field coefficient is representative of two similar withdrawing effects: the field effect, which is the dipolar interaction through space, and inductive effect, which is the dipolar interaction through interatomic bonds. The latter becomes very weak, when the distance between the source and the site is more than two carbons. Since an effect was seen with 4 carbon sidecain, it could not be attributed to the inductive effect, but to the pure field effect. Comparison of the behaviour for the two aromatic systems, conducted in the next section, was necessary to assess the order of such effect.

5.3.2.2. Influence of the aromatic system

Table 5.3 summarises the data obtained for cyano substituted ILs with various sidechain length and aromatic core. Pyridinium systems solubilised more copper than imidazolium systems for longer chains (>4 carbons), but imidazolium was more efficient in the case of short chain (2 carbons).

Table 5.3: Comparison of copper dissolved in MIM and MPy ILs (mg.g^{-1})

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The chemical shifts δ from protons in NMR are good indicator of the local electronic density around them. Table 5.4 reports the chemical shifts of some aromatic protons, and protons from the sidechain, in order to relate the effect of the substituent and the sidechain to the electronic density. Higher chemical shifts, observed for H_1 in the case of MIM, suggested that the positive charge was mainly located around the carbon in alpha of the two cyclic nitrogens. In the case of MPy, the chemical shift was stronger for H_1, H_2 and H_3, which suggested that the positive charge was mostly delocalised around the two carbons in α of the quaternary nitrogen, and in position 3. (Figure 5.7).

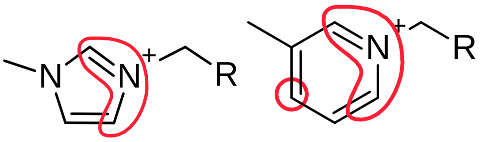

Figure 5.7: Aromatic charge delocalisation in aromatic rings

Table 5.4: Chemical shifts of H in alpha of the quaternary nitrogen in the IL ring

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For 6 carbons chains, the substituent has little to no effect on the chemical shifts regardless of the aromatic system. The values were higher for H_1 in the MIM system, but lower for all the other aromatic carbons, suggesting that the electronic configuration of the pyridinium system is more suited for copper complexation. However, in the case of shorter chain, the δ are shifted downfield, which suggested that the substituent, for short chain, has an important electron withdrawing effect on the ring, which might be responsible for the better ability to dissolve copper for substituted short chain MIM.

5.3.2.3. Field effect responsible for CuO solubilisation

When the spacer between the functional group and the aromatic ring increased from 2 to 6 carbons, the δ of H_1 was shifted downfield from 8.67 ppm to 8.88 ppm in the case of MIM (Table 5.4), which is characteristic of a withdrawing effect. The greater increase of the chemical shift from H_1, observed for short chain (from 8.71 ppm in [CNC4MIM][Br] to 8.88 ppm in [CNC2MIM][Br] compared to long chain (from 8.67 ppm in [CNC6MIM][Br] to 8.71 ppm in [CNC4MIM][Br]) reflected directly this assumption, as the field effect increased exponentially with this distance. As a result, the cation may take a conformation where the functional group get closer to the aromatic ring (Figure 5.8)

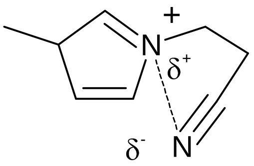

Figure 5.8: Proposed conformation of [CNC2MIM][Br]

The ring also influenced the electron density in the sidechain, but the effect was higher in the case of MPy systems. Hydrogens in α of the cyanide, H_4 or H_5, were shifted downfield because of the withdrawing effect of the positive charge of the aromatic ring, but MPy systems were more shifted ($\delta(H_5) = \delta(H_4) + 0.15$ ppm for the cyanoethyl ILs). Consequently, the local electronic density in the sidechain is higher in the case of the MIM ring, which might explain its better ability to dissolve CuO. Similar behaviour was observed with other functional groups such as −OH and −COOH, where short chains led to stronger electron delocalisation and higher copper dissolved. This supports the implication of the withdrawing effect from the functional group, as the cyanide has stronger withdrawing effect, and interacts more with the ring compared to other groups.

In conclusion, the ability to dissolve copper oxide resulted from a combination of two factors:

- The type of aromatic ring, because more delocalisation led to more copper dissolved;
- The functional group, which acted as an electron withdrawing group that decrease the electron density in the ring, and also acted as a dipolar group, inductively influenced by the charge of the ring.

The field effect tended to be the main driving force in the case of short chain, because of the supposed special rearrangement of the cation, and explained why [CNC2MPy][Br] dissolved less copper than [CNC2MIM][Br]. In long chains, the main effect came from the aromatic ring, which explained why MIM systems dissolved less copper, and why all systems were less efficient when no withdrawing group was present. Such microscopic considerations could be summarised using two parameters, one being logP (which accounts for the length of the sidechain) and the second being the field effect F which is directly proportional to the withdrawing effect that the functional group exert on the ring.

5.4. Conclusions

5.4.1. Summary of the findings and hypotheses verification

The investigation of the dissolution of CuO in IL was successful, since a link between structure and effect was demonstrated. Although the effects observed were difficult to explain, it appeared that hydrophobicity and the type of substituent took part in the process of solubilisation, which happened via the formation of a complex with the IL. Regression showed a direct influence of logP and F on the amount of Cu dissolved (related to the dissolution constant), and further analysis highlighted the importance of the presence of a strong electron withdrawing functional group to rearrange the electron density in the IL cation. To that extent, a combination of short chain, a polar cyanide group and an imidazolium ring were necessary to obtain a specific conformation of the cation that led to better solubilisation of copper oxide.

Initial hypotheses were successfully verified:

- Up to 74.5 $mg.g^{-1}$ of copper was dissolved in IL
- Hydrophobicity influences directly the ability of IL to dissolve copper
- The presence of a strong electron withdrawing group also directly increase the amount of copper transferred in the IL phase
- When the two parameters were combined, the interactions between the ring and the functional group were weaker in the case of MIM, which led to more copper dissolved
- As a result, [CNC2MIM][Br] was found to be an excellent solvent for the extraction of copper

5.4.2. Importance of the findings and recommendations for future work

Despite the success of these tests, the IL showed almost no ability to dissolve copper (metal) as explained in chapter 2, so direct application to copper recycling is not possible. However, the information about the structural requirement for ionic copper solubilisation could be used for future design of specific IL leaching agent. Many obstacles are yet to be overcome, including better understanding of selectivity toward a specific metal, incorporation of an oxidizing agent to facilitate the formation of a complex or even the toxicological issues associated with the use of pyridinium or imidazolium ILs.

Unfortunately, the duration of my PhD did not allow the investigation of other leads, which would have greatly complemented the set of data available. For instance, it would have been interesting to test more functional groups, such as amine to further investigate the influence of inductive effect. The use of a carboxylic function also seemed encouraging, as it showed good ability to solubilise CuO, and it can also be deprotonated in basic environment, leading to potentially stronger electron donating ability. More intermediate sidechain length could also bring more confirmation about the trend observed here. Other anionic systems could be investigated such as hydrophobic (NTf_2^-) or more common (HSO_4^-) to improve a hypothetical separation step. Proton donor ions such as HSO_4^- are extremely interesting, as they have the ability to oxidize metals. Using such IL, copper has been successfully leached from ore (Whitehead et al., 2007). This aspect of metal solubilisation is also crucial, and other solutions should be investigated, such as the use of oxygen dissolved in the IL as an oxidant to leach copper metal from both primary and secondary sources. Finally, the results obtained and the implication for the structure of IL cations could be applied with other systems, aromatic or not, and especially with biodegradable ILs.

6

Chapter 6: Application of ionic liquids to extract DBDE from HIPS

This chapter focuses on DBDE, and on its leaching from its polymer matrix, high impact polystyrene (HIPS) by ILs. This chapter more particularly aims at investing the effect of the IL cation structure on the extraction efficiency to identify the important structural features that lead to the best solvent for leaching DBDE. DBDE was selected because it is a brominated flame retardant (BFR) used in the production of electrical and electronic equipments (EEE), and might be banned in the future (Chapter 2). Two hypotheses are meant to be tested:

- IL can be used to extract DBDE from HIPS;
- Hydrophobicity of the cation and the type of aromatic ring can affect the extraction ability of IL.

In order to test these two hypotheses, a methodology to measure the concentration of DBDE extracted from the polymer had to be developed together with an extraction/leaching protocol. A total of seven ILs were chosen (Table 5.1) as they all reflect a variation in hydrophobicity (linked to the length of the sidechain) and the variation of the aromatic system (pyridinium or imidazolium).

In this chapter, the attention was focused on three tasks:

- Developing an analytical method which can be used for the analysis of DBDE extracted in IL
- Assessing the efficiency of the selected ILs to extract/leach DBDE from a polymeric matrix (HIPS)
- Comparing the influence of cation hydrophobicity on the extraction of DBDE

Table 6.1: Acronyms of the ILs used for DBDE leaching tests

IL acronym	*IL name*
[C4MIM][Br]	1-butyl-3-methylimidazolium bromide
[C6MIM][Br]	1-hexyl-3-methylimidazolium bromide
[C8MIM][Br]	1-octyl-3-methylimidazolium bromide
[C4MPy][Br]	1-butyl-3-methylpyridinium bromide
[C6MPy][Br]	1-hexyl-3-methylpyridinium bromide
[C8MPy][Br]	1-octyl-3-methylpyridinium bromide
[C6Py][Br]	1-hexylpyridinium bromide

The chapter is divided into five sections. The first section deals with the determination of the best analytical method to quantify DBDE in the IL. In the following section, the leaching abilities of the ILs are compared in order to identify which parameter has the most influence. Other external factors, investigated to improve the extraction efficiency, are investigated in the third section. The fourth section reports the implication of the results in the development of a full recycling process involving the IL leaching. Finally, the last section concludes this chapter by summarising the key results.

6.1. Evaluation of techniques for quantification of DBDE

Three analytical techniques were investigated: UV/visible spectrometry, X-ray fluorescence (XRF) and high performance liquid chromatography (HPLC). The results of these investigations and the process that led to the choice of HPLC as the most suited technique to measure DBDE are presented in the next three subsections, each describing one technique.

6.1.1. Limitations of UV/Vis spectrometry for DBDE quantification

The first technique evaluated was UV/visible spectroscopy, as DBDE absorbs in the UV region. Figure 6.1 represents three UV spectra of DBDE in toluene with IL (2 and 3) or without IL (1). The comparison of 1 and 3 showed that both DBDE and IL absorbed in the UV-visible region, which posed a serious problem to separate their respective signal. Toluene is a good solvent for DBDE at the concentrations involved in this work, and was tested to transfer the DBDE from the IL to the toluene phase by liquid/liquid extraction. However, an undefined amount of IL also migrated in the toluene phase, which affected the absorption spectra (spectrum 2), because all brominated ILs absorbed in the same UV region as DBDE.

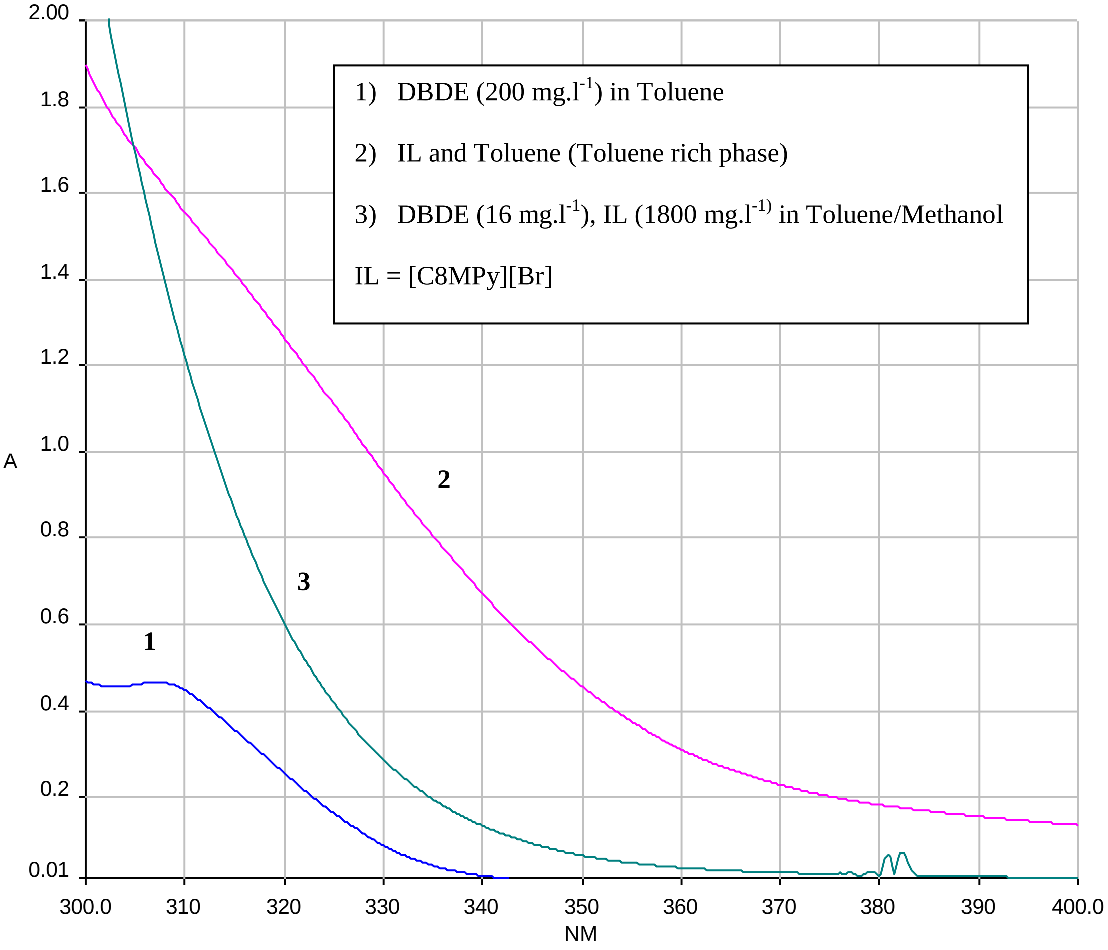

Figure 6.1: UV spectra of DBDE in the presence or absence of [C8MPy][Br]

Complete solubilisation of the IL/DBDE mix was achieved by adding methanol to the toluene solution. However, further measurements of DBDE at various concentrations in IL and such a toluene / methanol solvent mix were not conclusive, as the concentration of IL varied slightly from one sample to another. The result of these experiments, compiled in Table 6.2, were analysed assuming that the total absorbance was a linear combination of the signal from DBDE and from the IL according to the Beer-Lambert law, in the form $A(\lambda) = \varepsilon_1(\lambda)\cdot[\mathrm{DBDE}] + \varepsilon_2(\lambda)\cdot[\mathrm{IL}] + A_0(\lambda)$. By combining the expression at two different wavelengths λ_1 and λ_2, it was hoped to afford a linear relationship $[\mathrm{DBDE}] = a(\lambda_1, \lambda_2)\cdot A(\lambda_1) + b(\lambda_1, \lambda_2)\cdot A(\lambda_2) + c(\lambda_1, \lambda_2)$ where a, b and c are coefficients calculated through linear regression using data in Table 6.2. The simple regression performed with the LINEST function from Microsoft Excel gave reasonable $R^2 > 0.95$, and good relative standard deviation (2 to 6 %) for a few combination of wavelength, especially in the case of the combination of 380 and 340 nm (2 %). Using such wavelength, the calculated value for the unknown (33 mg.l^{-1}) was found to be 34 mg.l^{-1}.

Table 6.2: Absorbance of DBDE in presence of IL at various wavelengths

[DBDE] (mg.l^{-1})	***IL (mg)***	***A (330 nm)***	***A (340 nm)***	***A (350 nm)***	***A (360 nm)***	***A (370 nm)***	***A (380 nm)***	***A (390 nm)***
0.0	110	0.25	0.10	0.04	0.02	0.13	0.01	0.00
16.5	102	1.40	0.92	0.58	0.37	0.25	0.19	0.15
33.0	116	1.21	0.75	0.46	0.29	0.26	0.15	0.12
41.2	104	1.68	1.04	0.64	0.37	0.25	0.18	0.14
unknown	-	0.92	0.60	0.39	0.24	0.17	0.12	0.10

However, the measurement of extracted DBDE from a simple leaching experiment with the IL, [C8MPy][Br], produced a very low response, which showed a relative standard deviation of more than 75% between three replicates. As a result, a technique with a lower detection limit and more precision was needed.

6.1.2. Limitations of XRF for DBDE quantification

The second method of analysis was based on the use of XRF spectroscopy. Two strategies were explored, one investigating the quantification of residual DBDE in the polymer, and the other assessing the concentration of DBDE in the IL solution. However, several major limitations were encountered in the application of this technique. First of all, the determination of residual bromine in the polymer was not possible with good accuracy. The bromine content of three samples of the same HIPS (Table 6.3) showed a relative standard deviation of 10% because the signal depended on the quantity of polymer in the sample holder. As a result, the characterisation of the DBDE left in the polymer required careful weighing of the quantity exposed to the XRF spectrometer.

Secondly, the quantification of DBDE in the IL was evaluated using a liquid sample (Toluene + DBDE and DBDE in [C8MIM][Cl]). It was necessary to synthesise a non brominated IL, as the presence of Br in the structure of the solvent would have accounted for the total intensity of the XRF signal, and isolating the component of the signal belonging to the bromine from the BFR would have been difficult. Compared to the measurement of Br in HIPS, the results were more accurate, because a constant volume of sample (5 ml) was used for each run. A regression using the 5 standard, 100 to 500 mg.l^{-1} (Table 6.3) produced a linear curve (Figure 6.2).

Table 6.3: XRF signal for bromine atom in various samples

Sample description	***Net Cps (Br)***
HIPS + DBDE + Sb_2O_3 (1st sample)	12163
HIPS + DBDE + Sb_2O_3 (2nd sample)	13460
HIPS + DBDE + Sb_2O_3 (3rd sample)	14837
Toluene + DBDE (100 mg.l^{-1})	384
Toluene + DBDE (200 mg.l^{-1})	309
Toluene + DBDE (300 mg.l^{-1})	516
Toluene + DBDE (400 mg.l^{-1})	773
Toluene + DBDE (500 mg.l^{-1})	841
DBDE in [C8MIM][Cl] after 30 min	3
DBDE in [C8MIM][Cl] after 1 h 00 min	-16
DBDE in [C8MIM][Cl] after 1 h 30 min	10
DBDE in [C8MIM][Cl] after 2 h 00 min	17
DBDE in [C8MIM][Cl] after 2 h 45 min	18

However, the counts/second (Cps) signals produced by the 5 extraction sample (DBDE in [C8MIM][Cl]) was 20 to 100 times lower than the signals for the 100 mg.l^{-1} standard. This very low value (less than 18 cps) didn’t allow the quantification of DBDE in the extraction solutions. Added to the fact that only DBDE in chlorinated ILs could be measured, and that the technique required several ml of sample every time, it was decided to abandon XRF in favour of HPLC method.

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Figure 6.2: Calibration of DBDE using XRF signal

6.1.3. Quantification of DBDE in IL by HPLC

A typical chromatogram of a solution containing 1 mg.l^{-1} of DBDE produced a signal at a retention time of 23.5 min (Figure 6.3). Preliminary analysis of solutions containing 25 mg.l^{-1} of DBDE at 250 nm wavelength produced stable baselines and a response suitable for DBDE measurements at appropriate concentration.

Figure 6.3: Chromatogram of DBDE at 1 mg.l^{-1}

The calibration curve was then tested with six standards (0.5, 1, 2.5, 5, 10 and 25 mg.l^{-1}). The result (Figure 6.4) showed a linear trend up to 10 mg.l^{-1}, and it was observed that peak area produced better regression than peak height.

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Figure 6.4: Preliminary calibration curve for DBDE

Preliminary experiments to extract DBDE in [C8MIM][Cl], performed during the optimisation of DBDE detection method based on XRF spectroscopy, showed that less than 2 mg.l^{-1} of analyte was detected in each of the sample. So it was decided to limit the calibration curve to 5 mg.l^{-1}. Reproducibility was tested by successively measuring two sets of standard (0.5, 1, 2.5 and 5 mg.l^{-1}). Least square regression was applied to these results (Annex F), and led to a R^2 value higher than 0.999, which proved the reproducibility of the measurements and the linearity of the calibration curve. Furthermore, all the calibration curves obtained in this work were found linear, with $R^2 \geq 0.990$. In addition, a control sample (1 mg.l^{-1}) was always injected at the end of each batch and always produced a value very close to 1 mg.l^{-1} (maximum 10% deviation but overall 3% to 4 %), which confirmed the suitability of this method.

As a conclusion, the results obtained from the fist two techniques, UV/Vis spectrometry and XRF, could not be used for quantification. On the contrary, HPLC was found to provide accurate and precise enough measurements for the need of this work.

6.2. Effect of the IL structure on their ability to leach DBDE

Leaching of DBDE was carried out in various ILs, according to the procedure described in section 3.3.3. Access to a sample of waste HIPS was difficult, so it was decided to prepare the polymer within our own laboratory using a commercial HIPS (supplied by Aldrich, Gillingham, UK). In that way, the exact composition of the polymer (4.4% of DBDE in mass according to section 3.3.1) was chosen and determined by the HPLC method developed in section 6.1.3. Furthermore, initial tests proved that the solubility of DBDE in all ILs tested was high enough to eventually dissolve all the DBDE from the polymer in case the leaching ability of the IL is very good (section 3.3). Consequently, the tests were carried out, and this section aims at reporting the difference observed in the leaching ability of the ILs, and how it can be related to the variation of structure. This section is divided into four subsections. Section 6.2.1

qualitatively compares the results of the tests, and section 6.2.2 describes the kinetics of leaching observed for all ILs. The next two subsections report the effect of hydrophobicity, and the effect of the aromatic ring.

6.2.1. DBDE extracted in various IL

The first set of experiment mainly aimed at investigating the ability of the different IL to extract DBDE after 2 h 45 min of leaching at 90 °C. These conditions were chosen for practical use, as 2h45 of exposure allowed for more kinetics to be recorded, and the temperature was easy to set up. The results of these tests are presented in Table 6.4.

Table 6.4: Quantity of DBDE extracted from HIPS by IL

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A few observations can be made:

- All ILs extracted less than 10% of DBDE from the polymer matrix
- Some differences were observed between them, which can be related to the difference of structure
- The magnitude of the change of [DBDE] is greater in the case of MIM
- Pyridinium based ILs showed a very similar %DBDE extracted

Higher %RSD in the case of [C6Py][Br] and [C8MPy][Br] might be linked to the viscosity of the polymer. All the extractions followed similar kinetics, as described in the next section.

6.2.2. Influence of the kinetics of leaching

A typical pattern followed by the kinetic of leaching is represented in Figure 6.5. The quantity of DBDE extracted, in all cases, was under 10%, which remained very low.

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Figure 6.5: Kinetic profile for the extraction of DBDE from HIPS in [C8MIM][Br]

A rapid increase in concentration of DBDE in the IL is observed during the first hour of extraction. The curve slope then seemed to gradually decrease until 1 h 30 min of experiment and reach a plateau (Figure 6.5). In order to verify if the maximum of extraction was reached after 2 h 45 min, the length of the experiment was extended to 48 h (Figure 6.6).

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Figure 6.6: Kinetic profile of 48 h extraction of DBDE in [C8MIM][Br] at 90 °C

The kinetic profile indicated a change in the rate of extraction, which was fast at first and then slowed down up to the point where it reached a plateau. Possibly, slower diffusion of solvent through the pores of the polymer particulates was responsible for such behaviour, as the DBDE in the exterior was leached fast, whereas less accessible brominated flame retardant, inside the macro pores, required longer time. As a result, [DBDE] reached a plateau at 9.6 % after 18 h, because all the DBDE in contact with the surface layer of the particulates had been leached. The remaining DBDE was probably still trapped inside the bulk of the polymeric matrix, which couldn’t be reached by the solvent. Indeed, the transition temperature (polymer softening point) was 104 °C. Accordingly, the polymer was in a phase where diffusion of species is extremely low, so that the DBDE could not migrate from the interior to the surface despite the high concentration gradient.

In conclusion, the extraction reaction does reach the equilibrium between 8 and 20h of reaction. In practical, such reaction time would involve very long experiments, which was incompatible with the timeline of the project. Therefore, the reaction times were set at 2 h 45 min for each IL.

6.2.3. Effect of hydrophobicity

Figure 6.7a represents the amount of DBDE extracted in the IL versus logP. Linear regression using the dataset led to a R^2 of 0.42, so there was no evidence of a linear correlation, probably because of the low percentage extracted and uncertaincy in analysis of such close concentrations. However, a global trend was identified, where higher logP led to higher %DBDE extracted.

a)

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Figure 6.7: LogP vs. percentage DBDE extracted in a) the 7 ILs and b) MIM or MPy based IL

b)

The series of IL with the same cationic core were investigated in Figure 6.7b. The three methyl pyridinium based (MPy) IL, [C4MPy][Br], [C6MPy][Br] and [C8MPy][Br], extr average of 6.0, 6.7 and 6.9 % DBDE, respectively. These extraction values were ose to each other and the line fitted through least square regression led to an inconclusive coefficient of determination R^2 of 0.60. The reason was that the standard deviation for the two replicates of extraction in [C8MPy][Br] appeared higher (12.7 %), possibly because of random experimental conditions that couldn't be avoided, such as external temperature or pressure which affected more MPy, because they are more viscous.

The MIM-based ILs [C4MIM][Br], [C6MIM][Br] and [C8MIM][Br], showed high correlation between the linear regression and the dataset (R^2 = 0.95). In this case, hydrophobicity had an influence, and longer chain led to better extraction. The formation of HIPS involves copolymerisation of styrene and butadiene, which arrange themselves in a core / shell type structure where cores of polybutadiene are surrounded with a polystyrene matrix (Demirors, 2000). The polymer material is not soluble in the IL which means that during the extraction process, a liquid/solid interface will be established between the IL and the solid polystyrene matrix. More hydrophobic IL would improve wetting of the polymer, because of higher Van der Waals interactions between the cation bearing longer chains, and the hydrocarbonated styrenic polymer. On one hand, the various cavities and pores of the polymer grains were accessed faster by the solvent, increasing the amount dissolved, and on the other hand, the energy necessary for DBDE to cross the interface was lowered, facilitating dissolution. Moreover, hydrophobic interactions between DBDE and hydrophobic IL would be more favourable, leading to more DBDE dissolved in the IL.

In summary, higher hydrophobicity led to more DBDE extracted. Although a relationship was observed between these two parameters in the case of MIM-based ILs, the two aromatic cores behaved differently. Next section investigates these differences.

6.2.4. Effect of the aromatic ring

Three aromatic systems were studied: pyridinium (Py), MIM and MPy. It appeared that for the butyl side chain, MPy rings resulted in better extraction, capturing 35% more DBDE than MIM. Such behaviour was expected, since charge delocalisation was more important in pyridine ring and logP values were higher. However, MIM systems extracted more DBDE than Py or MPy systems for side chain longer than six carbons, questioning the real influence of hydrophobicity. With similar sidechain length, [C6Py][Br] and [C6MPy][Br] led to very similar quantity of DBDE extracted (6.4% and 6.7% resp.). In addition, all Py and MPy based IL showed very similar amount of DBDE solvated in IL (0.31, 0.31, 0.32 and 0.34 mg.g^{-1} for [C6Py], [C4MPy], [C6MPy] and [C8MPy][Br] respectively). As a result, there was no conclusive evidence that logP exerted an influence upon the extraction efficiency for all the Py-based ILs. In addition, steric hindrance did not seem to be a factor limiting extraction, because not only did longer chain take more DBDE out, but the addition of a methyl group in position 3 of C6Py did not affect [DBDE]. Such behaviour could be related to the higher viscosity encountered with all Py-based ILs compared to their MIM-based homologues. Stronger interactions between anions and cations in the case of Py systems were responsible. As a result, the diffusion of species in these ILs was rendered harder, which was probably the reason why MPy based ILs had not only similar, but also lower efficiency.

As a conclusion, a few facts were observed regarding the effect of hydrophobicity:

- Leaching efficiency is low (<10%) because leaching presumably happens only at the surface of the particle
- Hydrophobicity has an influence on the ability of MIM-based ILs to extract DBDE, as higher logP lead to more DBDE leached

- Pyridinium-based ILs ability to leach DBDE is not related to hydrophobicity, because the viscosity possibly limit interfacial interactions

In order to improve the extraction efficiency, other external factors were changed, such as temperature of extraction and the amount of polymer used to extract DBDE in 1 g of IL. Such considerations are reported in the next section.

6.3. Influence of external factors on leaching DBDE

The experiments associated with the effect of temperature and of the amount of polymer were carried out using the procedure described in section 3.3.3.1. This section summarises the results and interpretations, and investigates the effect of these two parameters on the extraction process. The experiments were carried out using the most efficient IL for extraction, [C8MIM][Br].

6.3.1. Effect of higher temperature

Since 2 h 45 min extraction time was too short to extract all of the available DBDE from the polymer matrix, it was decided to investigate whether the rate of DBDE extraction could be increased at higher temperatures, because of the related acceleration of the kinetic of extraction according to Arrhenius law and a decrease in the viscosity of the IL under investigation. Moreover, higher temperatures might help to soften the polymer enough to allow faster diffusion. The results for the three temperatures investigated are reported in Table 6.5.

Table 6.5: Quantity of DBDE extracted in [C8MIM][Br] at different temperatures

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Because of the similar [DBDE] in the IL at the three temperatures, it was decided to compare the two dataset at 90 and 110 ºC, and at 110 and 130 ºC to determine if an increase of temperature statistically improve the extraction. Unpaired two tails t-test with 90 and 110 ºC calculated a p-value of 0.02, whereas 0.44 was returned from the test with 110 and 130 ºC. As a result, raising the temperature to 110 degree statistically increased the amount of DBDE dissolved, whereas further increase to 130 degree did not improve the extraction.

Similar unpaired two tails t-tests operated with the %DBDE extracted, more representative of the efficiency of extraction, returned a p-value of 0.36 for the comparison of 90 and 110 ºC and 0.20 between 110 and 130 ºC, so it is likely that those values are statistically similar. Variability in the % extraction did not allow identifying a difference in the extraction process. However, since the concentration of DBDE was statistically higher in the IL at 110 ºC, an improvement was definitely observed. At 130 ºC, both %DBDE and [DBDE] were statistically similar, so that further increase in temperature did not statistically improve the efficiency of the process.

These results have shown that the increase in temperature had only a limited effect on the extraction of DBDE, which agreed with the theory of surface extraction. The decrease in viscosity of [C8MIM][Br], induced by the increase in temperature, facilitated the diffusion of the solvent through the pores of the IL when raising the temperature from 90 to 110 ºC, which translated into an increase in extraction.

However, further decrease of the viscosity, obtained by increasing the temperature to 130 ºC, failed to improve the percentage of DBDE extracted because all the available surface were already reached at 110 ºC. Similarly, the increase in extraction rate linked to increase of temperature from 90 to 110 ºC could be explained by the faster kinetic after 2 h 45 min. Further increase of the temperature to 130 ºC led to no improvement, because the maximum extraction was already reached at 110 ºC after 2 h 45 min, although the faster kinetic might have helped to reach it faster. As a result, and despite the increase of the mean extracted DBDE from 9.8 to 10.5% when increasing the temperature to 130 ºC, 110 ºC was found to be the best temperature for the leaching of DBDE from HIPS in ILs.

6.3.2. DBDE leached with various polymer ratio

The last set of experiment aimed at investigating the effect of the solvent/polymer ratio in order to identify if solubility of the DBDE was not an issue in the real extraction experiment, as the initial solubility tests hinted. Results of the tests (Table 6.6) indicated that increasing the quantity of HIPS per gram of polymer led to an increase in the [DBDE] dissolved in the IL. However, the difference in extraction efficiency was very low (Table 6.6).

Table 6.6: DBDE extracted in [C8MIM][Br] at different polymer ratios

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High %RSD observed at the IL / HIPS ratio of 5 was possibly due to the difficulty to abstract the sample. The volume of polymer in the IL was too high to allow a clear separation of the solids necessary to pipette clean IL. As a result, traces of polymer could have been present in the final sample and affect the measurement. This fact was confirmed by the kinetic profile which showed high variation between measures, so it was decided to consider the IL / HIPS ratio of 5 as an outlier.

The idea of the leaching only happening in the surface was also supported by the fact that the quantity of DBDE leached in the IL increase with the amount of polymer in contact with the IL, while the percentage of DBDE extracted remained the same. Such a consideration required that the amount of DBDE leached should be directly proportional to the quantity of HIPS introduced in the IL, since the same layer of polymer is reached by the solvent. Regression operated using the HIPS / IL ratio vs. the % DBDE and [DBDE] was performed (Figure 6.8).

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Figure 6.8: Influence of the percentage of HIPS in contact with [C8MIM][Br] on the amount of DBDE extracted

Data confirmed this assumption, because the linear regression of [DBDE] led to slope of 4.3 with a R^2 of 0.99. The outlier at IL / HIPS of 5 (corresponding to HIPS / IL of 20%) was ignored in the treatment.

As a conclusion, the key outcomes of the experiments carried out to test the influence of external factors are:

- The efficiency of extraction could be improved if the temperature is raised to 110 ºC, but there was no benefit for increasing the leaching temperature further.
- The IL extracted the same percentage of DBDE from different quantities of HIPS. However, the technique used to quantify the DBDE was not applicable with IL / HIPS ratio of 5 or less.
- These two facts were in accordance with the surface mechanism of extraction

6.4. Implications for the development of a DBDE recycling process

Leaching of DBDE from the HIPS matrix is just one step in the complete recycling process (Figure 6.9). The other essential step is the recovery of the DBDE from the IL, which can be done by solvent precipitation. Such step was also investigated as a part of this project, to investigate the potential of ILs in the full recycling process.

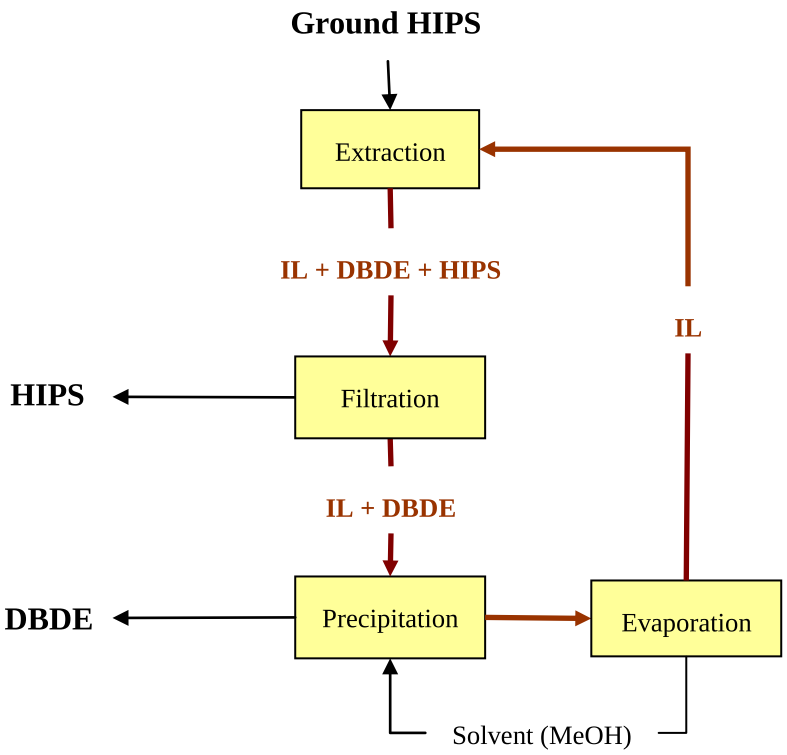

Figure 6.9: Flow chart of the recycling process

6.4.1. Recovery of DBDE from the IL

To test the ability of the IL for recovery, DBDE was precipitated from the IL using methanol MeOH as a precipitation solvent. MeOH was chosen, because it has medium boiling point (64.7 ºC), and dissolves the IL but not the DBDE. The precipitate was analysed by IR to detect the presence of IL, while the filtrate was analysed by HPLC. No trace of [C8MPy][Br], [C6MPy][Br] or [C4MPy][Br] were observed in the IR spectra (Figure 6.10) of the precipitate, showing that the DBDE precipitated was free of IL. In addition, HPLC analysis of the filtrate did not detect DBDE, showing that all the BFR precipitated.

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Figure 6.10: IR spectra of DBDE precipitated from pyridinium ILs

A trial recycling experiment was then set up, using a simple distillation system. The DBDE was precipitated upon addition of MeOH. The filtrate was then distilled to remove MeOH from the IL. The analysis of the IL by HPLC revealed no trace of DBDE, although some methanol remained in the IL (weighing the recycled IL revealed a weight increase of 5% compared to the initial mass of IL). As a result, implementation of the recovery of BFR from IL was possible and the IL could find application in the recycling process.

6.4.2. Comparison of the leaching by IL with other alternatives

The main limitation was the low extraction capacity of IL, since less than 10% of DBDE initially present in the polymer material was removed. This value was low, especially in comparison with other alternatives such as Creasolv process (Schlummer et al., 2006b) which afforded the elimination of 90% of the DBDE and 70% of the total bromine present in the input HIPS. Lateef et al., (2008) used an ionic liquid, [C6Py][Br], to extract DBDE from HIPS and found that this ionic liquid has the ability to extract 20% of DBDE from an industrial waste sample of HIPS containing 10% in weight of DBDE. The application of the same ionic liquid, [C6Py][Br], in this work extracted only 6.5% of DBDE. The difference in the extraction efficiency could be due to the difference in the initial content of DBDE present in the polymer material and also on the type of HIPS, so the efficiency of the BFR recovery can be considered similar to this work.

Other options are also available to improve the extraction of DBDE, such as the use of an organic solvent to dissolve the polymer. For instance, Lateef et al. (2008) used ethyl acetate to dissolve HIPS and performed a liquid/liquid extraction of DBDE and Sb_2O_3 in IL. The treatment afforded high recoveries of DBDE and Sb_2O_3 in the ionic phase, but the use of organic solvent is still necessary, and loss of IL in the dissolution solvent could also be an issue for large scale application. Following a similar procedure, it could be possible to form a gel with HIPS, which could solve the problem of the diffusion of the additives inside the polymeric matrix, and enhance partition up to a point where all DBDE was transferred in the IL phase.

As a conclusion, removal of DBDE from HIPS using IL as a solvent is certainly possible and it is surely a matter of time before a pilot treatment can be developed. The real issue concerns the suitability of such a method for real waste treatment, as other commercial alternative exist in the market already, with treatments such as the biphasic liquid “sink and float” technology (Schlummer et al., 2006b). Real waste is composed of a mixture of polymer from different structure, and with different additives. Recycling these involves separating the different polymers and removing additives which may affect the resistance of the recycled material. In the prospect of a multistep separation, ILs could be part of one specific process where separation of polymers and extraction of additives occur simultaneously, like in the creasolv process (Schlumer et al., 2006b). Alternatively, removal of BFR could be enforced after segregation of polymers, in a hypothetical BFR rich fraction separated by gravity. Consequently, leaching of BFR using ILs represents a potential as a new recycling technology, and although this piece of research answered some of the questions about their behaviour as leaching solvent for BFR, many other parameters need to be assessed.

6.4.3. Recommendations

Further research work, based on these results, could be undertaken to assess more in detail the influence of other parameters. For instance, the leaching of DBDE from other types of plastic or ILs containing hydrophobic anions, such as PF_6^- or BF_4^-. Such investigation would allow the gathering of more information to design ILs that display a specific set of interactions.

Through the interpretation of the results, it was deduced that the extraction was limited to the surface, which was the main barrier to overcome and to design an applicable leaching treatment involving ILs. The methodology used in this work could be modified to treat finer particle of polymer, ensuring that additional hazards associated with handling fine particles would be addressed. Separation of the IL and solid fraction could also pose a problem because it was experimentally observed that the IL would quickly block the pores from a cellulose filter paper such as qualitative filter paper standard grade Whatman N^{o}1 (11µm pores) and Whatman N^{o}3 (6 µm pores). A filter with smaller pores being necessary to retain the fine polymeric fraction, a solution has to be found in order to render the IL extract more fluid, by using a co-solvent for example.

6.5. Conclusion

Although the extraction of DBDE was low, the results obtained during these experiments have highlighted the need to select an appropriate IL based on the structure of its cation. It also demonstrated the potential of these ILs in the field of extraction, and opened the way forward to improve recovery systems based on the design of task-specific solvents technology, represented by the ILs.

The key points developed in this chapter are summarised below:

- Hydrophobicity of MIM-based cations affected the extraction of DBDE, higher hydrophobicity leading to higher extraction
- MPy-based ILs did not show a dependence on hydrophobicity, which may have been due to the higher viscosity of such ILs, which limited the diffusion
- At higher hydrophobicity, MIM-based ILs were more efficient, so the best IL identified for leaching of DBDE was [C8MIM][Br]
- Extraction only happened at the surface of the polymer grains, which explained the low leaching efficiency observed
- In the temperature range investigated (90 to 130 °C), the effect of temperature was limited, but an optimum temperature of 110 °C was demonstrated

Because of the limitation of the extraction process to a surface layer, it cannot be applied to real size removal of DBDE from WEEE. The main limitation was the very slow diffusion of the BFR from the interior of the polymer grain to the surface sites where extraction happened. As a consequence, the process extracted up to 1.24 mg in 2 g of IL, while the polymer theoretically contained 35 mg of DBDE. Although it was demonstrated that the ILs could dissolve higher amounts of DBDE by processing a larger volume of HIPS in the same volume of IL, the % DBDE extracted remained the same, because only DBDE from the surface would be removed. However, the outcome of this work was overall positive, and highlighted the possibility to improve the recycling process. Indeed, the recovery of DBDE from the IL was proved to be simple, and the better understanding of the chemistry behind leaching could lead to the development of new and more efficient ILs.

Finally, there are other barriers to the application of IL in separation science, the first of which being toxicity. Imidazolium based ILs are known to be toxic to aquatic life, as described in Section 2.3.3, especially when the side chain is longer. Unfortunately, my results showed that longer chains are more efficient for the extraction of DBDE from polymer. The development of biodegradable ILs from renewable source is of great potential to overcome these issues, and the knowledge acquired in this work could certainly be applied to their design.

As a conclusion, the objectives set up at the beginning of the chapter were met, because it was proved that ILs can leached DBDE from the polymer, although it is in small quantity, and that hydrophobicity and the type of aromatic ring were key parameters controlling the ability of an IL as a leaching solvent. ILs are under intensive investigation, and there is no doubts that more documentation about their properties, better understanding of their interactions, development of new biodegradable ILs and also about reducing the cost of manufacture will be available in the future to improve DBDE extraction. By the time such research work will be carried out, the industry is more likely to have already adopted an alternative separation method based on more traditional organic solvents. Research work on IL must continue, because the science of IL field is recent, and shows great potential in future applications.

7 Chapter 7: Conclusions

The waste management strategies have changed over the past few decades and now the main focus is to reduce the amount of hazardous waste by incorporating the 3 R's (reuse, recovery and recycling) initiatives. The implementation of such strategy for the management of waste electrical and electronic equipment (WEEE) creates technical problems, which have already been highlighted in the introduction chapter. The main aim of this research work was to develop technologies to recycle copper and DBDE from WEEE. The focus was to replace the traditional leaching media with the new and emerging solvents called room temperature ionic liquids (RTILs). This project has led to the development of the following eight major achievements:

1. A MW-assisted method was successfully used to synthesise a total of 18 methylimidazolium (MIM) and methylpyridinium (MPy) based ILs. All these ILs were obtained in high yields (>88%) and in high purity;
2. All ILs were successfully characterised by IR spectroscopy, mass spectrometry and NMR;
3. The hydrophobicity of the cations has been measured with HPLC, and successfully correlated with logP predicted by an on-line package (Molinspiration);
4. Copper oxide was successfully dissolved in IL, [CNC2MIM][Br] dissolving up to 74.4 mg of copper per g of IL;
5. Two parameters were found responsible for high solubility of the oxide in the IL, lower hydrophobicity and higher polarity of the functional group attached to the terminal position of the sidechain;

6. Linear MIM and MPy-based ILs extracted DBDE from a HIPS matrix, although a maximum of 10% DBDE was removed;
7. The extraction of DBDE depended on hydrophobicity and the nature of the cation ring, as MPy-based ILs showed no difference in extraction when hydrophobicity varied presumably because of higher viscosity which hampered diffusion of species in the IL;
8. The process only extracted DBDE from the outer surface of the polymer matrix.

All the objectives set out in the introduction chapter have been achieved, but the applications of room temperature ionic liquids (RTILs) to dissolve CuO and to extract DBDE from HIPS have highlighted the importance of the following two points:

1. Modifying the structures of ILs has an effect on their abilities to either dissolve copper oxide or extract DBDE. This effect was quantified using parameters, such as logP and the field effect coefficient F, related to the inductive effect of the functional group. On one hand, the dissolution of CuO is greatly influenced by the electronic configuration of the cation. More particularly, the field and inductive effect of the functional group played an important role in redistributing the electronic density within the cation. As a result, short substituted IL exhibited better ability to dissolve copper oxide. On the other hand, hydrophobicity influenced the amount of DBDE extracted from HIPS, because more hydrophobic ILs provided more interactions, and thus better contact at the interface with the hydrophobic polymer.

2. The range of ILs tested cannot be applied for recycling of copper or DBDE from WEEE, however, the results have highlighted their potential applications in the development of materials recovery from different types of secondary waste

arisings. The limitations associated with the solubility of copper metal from WEEE can be overcome by changing the structure of the IL, for example, incorporating acidic anions or adding a functional capable of oxidising copper metal. The addition of oxygen during the solubility process can also be investigated in order to enhance the dissolution of copper metal. However, such considerations are out of the scope of this thesis. The range of IL tested for DBDE extraction cannot be used because of the low percentage extraction <10%. The extraction of DBDE from HIPS depends on the diffusion process and the extraction was limited to the surface so DBDE in the bulk of the polymer could not be reached. In this case, opportunities also exist to overcome this barrier, for instance by forming a gel with the polymer or by reducing the size of the polymer grains.

Aquatic toxicity is another aspect of the ILs that could limit their applications. Since short chain imidazolium are less toxic than long chain, [CNC2MIM][Br], which combine a side chain of 2 carbons, a cyanide at the terminal position, and a 3-methylimidazolium ring was found to the best solvent and dissolved more CuO than any other IL investigated in this work. However, [C8MIM][Br], the most efficient IL for extraction of DBDE, possess a long side chain (8 carbons) and is, therefore, more toxic. As a result, the extraction process should be optimised in priority, and a less toxic IL can be designed afterwards, using the knowledge acquired in this thesis. Weighing all the factors involved with judging the ILs prepared and tested in this work, they still present a strong potential as an alternative and targeted solvents for applications in extraction or leaching processes.

There is no doubt that new ILs will be discovered and developed in the future, and they will be applied in many different applications. The relationship between their structure and their behaviour is studied intensively, and in addition to bring a better insight of the chemical processes associated with them, this will lead to a maximum use of the versatility they possess. This work has paved the way of developing task specific ionic liquids (TSILs) for specific materials from both primary and secondary sources.

As a result, in a purely technical point of view, the outcome of this work, and the potential application of ILs for materials recovery is very interesting. However, solving a problem by improving its technical aspect, such as improving recycling treatments, is not the only option, and even sometimes not the best option. The particularity of WEEE is that they are directly linked to the way of life of modern western societies of consumption. Electronic equipments, which were once seen as a luxury and an investment for a lifetime, are now viewed as consumable or fashion accessories (such as mobile phones) which have a very short lifetime. Such behaviour is responsible for the increasing amount of equipment discarded each year, and increase the pressure put on collection and treatment facilities. Recycling is not the ideal solution for waste treatment, as the WEEE directive states, and real emphasis should be to reduce the amount of waste and eventually reuse the material discarded. Many manufacturers are aware of that fact and already prepared novel design that include the management of their end-of- life, which is very encouraging for the future.

However, reducing the consumption of electronic goods would seriously impair the economy of the sector, which is what governments try to avoid. As a result, the most logical or efficient solution to the problem of waste management, reducing the production and consumption, is incompatible with the actual economical situation. A change in the way of consuming is always possible, but would require not only to fundamentally changing the behaviour of the public, but also would require finding another driver for the economy. This is very unlikely to happen in the future, despite more and more awareness on waste management issues.

As a conclusion, recycling is essential and a better understanding of the potential of new technologies, which has been achieved in this thesis, is necessary, not only to limit human impact on the environment, but also to sustain an economy based on consumption and to preserve the modern way of life.

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Annex A: Detailed protocols of synthesis and characterisation

This annex aims at presenting the detailed synthesis of the different ILs, and to summarise their characterisation results. The protocols are very similar for all ILs, so only the crucial information will be repeated for each synthesis. NMR results are presented in a tabular form for more clarity. The annex is divided into two sections; one for MIM based ILs and one for MPy-based ILs.

A.1 Imidazolium-based ILs

1-butyl-3-methyl imidazolium bromide [C4MIM][Br]

5.62 g of 1-methylimidazole (68.5 mmol) was added to 10.32 g of 1-butane (75.3 mmol) in a 100 ml round bottom flask and mixed thoroughly. The reaction mixture was then heated in the MW by successive irradiation periods of 20 s to 30 s separated by 10 s mixing for every minute of irradiation. Irradiation was stopped when only one clear phase could be observed. The summary of the irradiation pattern can be found in Chapter 4. The mixture was washed 4 times with 20 ml of diethylether and dried 2 h under vacuum (0.02 mmHg) to afford 13.75 g (yield 92%) of 1-hexyl-3-methylimidazolium bromide (M^+ = 139.3 amu).

IR peaks (cm^{-1}): 3136-2869 (aromatic and aliphatic C-H stretching), 1568 (C=C stretching), 1462 (CH_2 bending), 1170 (C-N stretching)

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1-hexyl-3-methyl imidazolium bromide [C6MIM][Br]

Same protocol as [C4MIM][Br] except that 4.98 g of 1-methylimidazole (60.7 mmol) was added to 11.02 g of 1-bromohexane (66.8 mmol). The reaction afforded 14.23 g (yield 95%) of 1-hexyl-3-methylimidazolium bromide (M^+ = 167.3 amu).

IR: 3137-2860 (aromatic and aliphatic C-H stretching), 1571 (C=C stretching), 1466 (CH_2 bending), 1170 (C-N stretching)

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1-octyl-3-methyl imidazolium bromide [C8MIM][Br]

Same protocol as [C4MIM][Br] except that 4.48 g of 1-methylimidazole (54.5 mmol) was added to 11.58 g of 1-bromooctane (59.9 mmol).The reaction afforded 14.54 g (yield 97%) of 1-octyl-3-methyl imidazolium bromide (M^+ = 195.4 amu).

IR: 3137-2860 (aromatic and aliphatic C-H stretching), 1571 (C=C stretching), 1466 (CH_2 bending), 1170 (C-N stretching)

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1-(2-cyanoethyl)-3-methylimidazolium bromide [CNC2MIM][Br]

Same protocol as [C4MIM][Br] except that 5.70 g of 1-methylimidazole (69.4 mmol) was added to 10.23 g of 3-bromopropionitrile (76.4 mmol). The reaction afforded 13.36 g (yield 89%) of 1-(2-cyanoethyl)-3-methylimidazolium bromide (M^+ = 136.3 amu).

IR: 3137-2860 (aromatic and aliphatic C-H stretching), 2252 (C≡N stretching), 1580, 1550 (C=C stretching), 1444 (CH_2 bending), 1170 (C-N stretching)

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1-(4-cyanobutyl)-3-methylimidazolium bromide [CNC4MIM][Br]

Same protocol as [C4MIM][Br] except that 5.05 g of 1-methylimidazole (61.4 mmol) was added to 10.95 g of 5-bromopentanenitrile (67.6 mmol) The reaction afforded 13.51 g (yield 90%) of 1-(4-cyanobutyl)-3-methylimidazolium bromide (M^+ = 150.1 amu).

IR: 3140-2868 (aromatic and aliphatic C-H stretching), 2244 (C≡N stretching), 1574 (C=C stretching), 1456 (CH_2 bending), 1336 (CH3 bending)

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1-(6-cyanohexyl)-3-methylimidazolium bromide [CNC6MIM][Br]

Same protocol as [C4MIM][Br] except that 4.53 g of 1-methylimidazole (55.1 mmol) was added to 11.52 g of 7-bromoheptanenitrile (60.6 mmol). The reaction afforded 12.07 g (yield 94%) of 1-(6-cyanohexyl)-3-methylimidazolium bromide (M^+ = 192 amu).

IR: 3140-2861 (aromatic and aliphatic C-H stretching), 2242 (C≡N stretching), 1571 (C=C stretching), 1456 (CH_2 bending), 1170 (C-N stretching)

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1-(2-carboxyethyl)-3-methylimidazolium bromide [COOHC2MIM][Br]

Same protocol as [C4MIM][Br] except that 5.76 g of 1-methylimidazole (70.2 mmol) was added to 10.74 g of 3-bromopropionic acid (63.8 mmol). The reaction afforded 15.01 g (yield 100%) of 1-(2-carboxyethyl)-3-methylimidazolium bromide (M^+ = 155.4 amu).

IR: 3407 (O-H stretching), 3092-2752 (aromatic and aliphatic C-H stretching), 1726 (C=O stretching), 1578 (C=C stretching), 1414 (CH_2 bending), 1170 (C-N stretching)

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1-(5-carboxypentyl)-3-methylimidazolium bromide [COOHC5MIM][Br]

Same protocol as [C4MIM][Br] except that 4.89 g of 1-methylimidazole (59.5 mmol) was added to 11.61 g of 6.bromohexanoic acid (54.1 mmol). The reaction afforded 13.49 g (yield 90%) of 1-(5-carboxypentyl)-3-methylimidazolium bromide (M^+ = 197.3 amu).

IR: 3407 (O-H stretching), 3140-2861 (aromatic and aliphatic C-H stretching), 1722 (C=O stretching), 1572 (C=C stretching), 1456 (CH_2 bending), 1170 (C-N stretching)

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1-(2-hydroxyethyl)-3-methylimidazolium bromide [OHC2MIM][Br]

Same protocol as [C4MIM][Br] except that 5.95 g of 1-methylimidazole (72.4 mmol) was added to 9.96 g of 2-bromoethanol (79.7 mmol). The reaction afforded 13.04 g (yield 86%) of 1-(2-hydroxyethyl)-3-methylimidazolium bromide (M^+ = 120 amu).

IR: 3402 (O-H stretching), 3020-2870 (aromatic and aliphatic C-H stretching), 1574 (C=C stretching), 1168 (C-N stretching)

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1-(6-hydroxyhexyl)-3-methylimidazolium bromide [OHC6MIM][Br]

Same protocol as [C4MIM][Br] except that 4.68 g of 1-methylimidazole (57.0 mmol) was added to 11.35 g of 6-bromohexanol (62.7 mmol). The reaction afforded 14.22 g (yield 95%) of 1-(6-hydroxyhexyl)-3-methylimidazolium bromide (M^+ = 183.3 amu).

IR: 3367 (O-H stretching), 3140-2859 (aromatic and aliphatic C-H stretching), 1572 (C=C stretching), 1456 (CH_2 bending), 1172 (C-N stretching)

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1-(5-cyano-(5,5-dimethyl)pentyl)-3-methylimidazolium bromide

[CN$(CH_2)_2$C5MIM][Br]

Same protocol as [C4MIM][Br] except that 4.30 g of 1-methylimidazole (52.4 mmol) was added to 11.77 g of 6-bromo-2,2-methylhexanenitrile (57.6 mmol). The reaction afforded 13.63 g (yield 91%) of 1-(5-cyano-(5,5-dimethyl)pentyl)-3-methylimidazolium bromide (M^+ = 206.3 amu).

IR: 3140-2868 (aromatic and aliphatic C-H stretching), 2232 (C≡N stretching), 1571 (C=C stretching), 1456 (CH_2 bending), 1170 (C-N stretching)

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A.2 Pyridinium-based ILs

1-butyl-3-methylpyridinium bromide [C4MPy][Br]

Same protocol as [C4MIM][Br] except that 6.07 g of 3-methylpyridine (65.2 mmol) was added to 9.82 g of 1-bromobutane (71.6 mmol). The reaction afforded 13.24 g (yield 88 %) of 1-butyl-3-methylpyridinium bromide (M^+ = 150.2 amu).

IR: 3020-2872 (aromatic and aliphatic C-H stretching), 1632 (C=C stretching), 1504 (C-C skeletal vibrations), 1466 (CH_2 bending), 1384 (CH3 bending), 1154 (C-N stretching)

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1-hexyl-3-methylpyridinium bromide [C6MPy][Br]

Same protocol as [C4MIM][Br] except that 5.41 g of 3-methylpyridine (58.1 mmol) was added to 10.55 g of 1-bromohexane (63.9 mmol). The reaction afforded 14.24 g (yield 95%) of 1-hexyl-3-methylpyridinium bromide (M^+ = 178.2 amu).

IR: 3020-2872 (aromatic and aliphatic C-H stretching), 1634 (C=C stretching), 1504 (C-C skeletal vibrations), 1466 (CH_2 bending), 1380 (CH3 bending), 1154 (C-N stretching)

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1-octyl-3-methylpyridinium bromide [C8MPy][Br]

Same protocol as [C4MIM][Br] except that 4.88 g of 3-methylpyridine (52.4 mmol) was added to 11.13 g of 1-bromooctane (57.6 mmol). The reaction afforded 14.72 g (yield 98%) of 1-octyl-3-methylpyridinium bromide (M^+ = 206.6 amu).

IR: 3010-2856 (aromatic and aliphatic C-H stretching), 1634 (C=C stretching), 1504 (C-C skeletal vibrations), 1466 (CH_2 bending), 1378 (CH3 bending), 1154 (C-N stretching)

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1-(2-cyanoethyl)-3-methylpyridinium bromide [CNC2MPy][Br]

Same protocol as [C4MIM][Br] except that 6.15 g of 3-methylpyridine (66.1 mmol) was added to 9.73 g of 3-bromopropionitrile (72.7 mmol). The reaction afforded 13.65 g (yield 91%) of 1-(2-cyanoethyl)-3-methylpyridinium bromide (M^+ = 147.1 amu).

IR: 3024-2646 (aromatic and aliphatic C-H stretching), 2250 (C≡N stretching), 1630 (C=C stretching), 1554 (C-C skeletal vibrations), 1474 (CH_2 bending), 1258 (CH3 bending), 1154 (C-N stretching)

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1-(4-cyanobutyl)-3-methylpyridinium bromide [CNC4MPy][Br]

Same protocol as [C4MIM][Br] except that 5.47 g of 3-methylpyridine (58.8 mmol) was added to 10.48 g of 5-bromopentanenitrile (64.7 mmol). The reaction afforded 13.07 g (yield 87%) of 1-(4-cyanobutyl)-3-methylpyridinium bromide (M^+ = 175.2 amu).

IR: 3018-2872 (aromatic and aliphatic C-H stretching), 2245 (C≡N stretching), 1634 (C=C stretching), 1554 (C-C skeletal vibrations), 1484 (CH_2 bending), 1250 (CH3 bending), 1154 (C-N stretching)

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1-(6-cyanohexyl)-3-methylpyridinium bromide [CNC6MPy][Br]

Same protocol as [C4MIM][Br] except that 4.93 g of 3-methylpyridine (53.0 mmol) was added to 11.07 g of 7-bromoheptanenitrile (58.3 mmol). The reaction afforded 13.77 g (yield 92%) of 1-(6-cyanohexyl)-3-methylpyridinium bromide (M^+ = 203.5 amu).

IR: 3018-2872 (aromatic and aliphatic C-H stretching), 2245 (C≡N stretching), 1634 (C=C stretching), 1554 (C-C skeletal vibrations), 1484 (CH_2 bending), 1250 (CH3 bending), 1154 (C-N stretching)

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1-hexylpyridinium bromide [C6Py][Br]

Same protocol as [C4MIM][Br] except that 7.43 g of pyridine (79.8 mmol) was added to 9.56 g of 1-bromohexane (87.7 mmol). The reaction afforded 13.23 g (yield 88%) of 1-hexylpyridinium bromide (M+ = 108.3 amu).

IR: 3020-2872 (aromatic and aliphatic C-H stretching), 1634 (C=C stretching), 1504 (C-C skeletal vibrations), 1466 (CH_2 bending), 1380 (CH3 bending), 1154 (C-N stretching)

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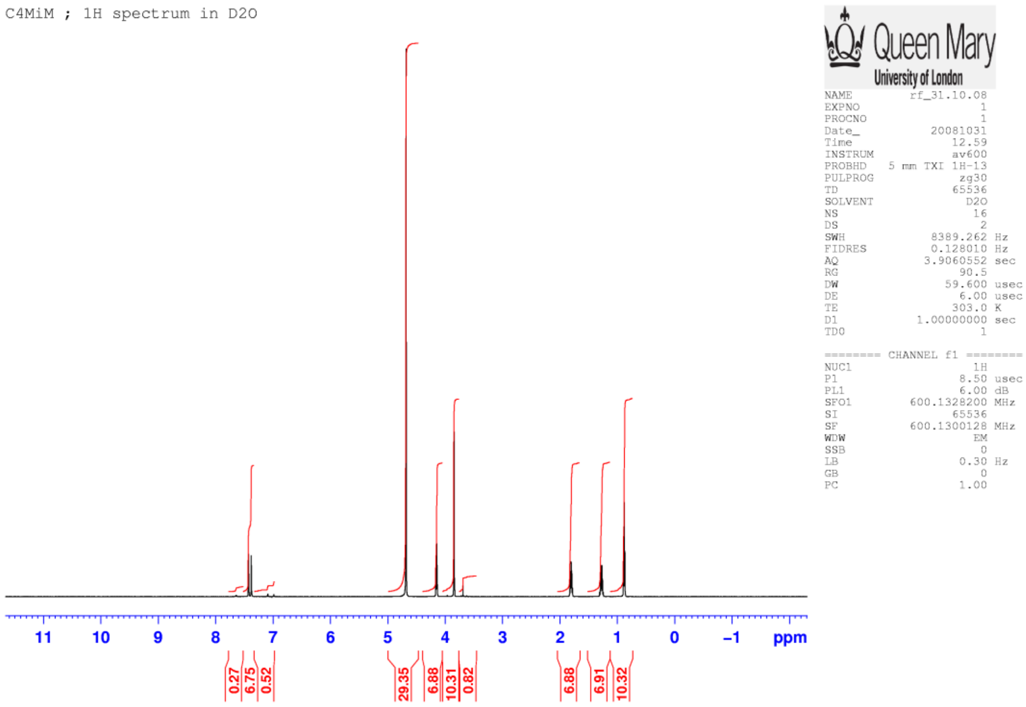
Annex B: NMR spectra of the ionic liquids

This annex regroups the NMR spectra obtained for each IL, classified by their formula.

B.1 Imidazolium-based Ils

1-butyl-3-methyl imidazolium bromide [C4MIM][Br]


C4MiM ; 1H spectrum in D2O

```
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EXPNO                   1
PROCNO                  1
Date_            20081031
Time                12.59
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PROBHD   5 mm TXI 1H-13
PULPROG              zg30
TD                  65536
SOLVENT               D2O
NS                     16
DS                      2
SWH              8389.262 Hz
FIDRES           0.128010 Hz
AQ              3.9060552 sec
RG                   90.5
DW                 59.600 usec
DE                   6.00 usec
TE                  303.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.50 usec
PL1                  6.00 dB
SFO1          600.1328200 MHz
SI                  65536
SF            600.1300128 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```
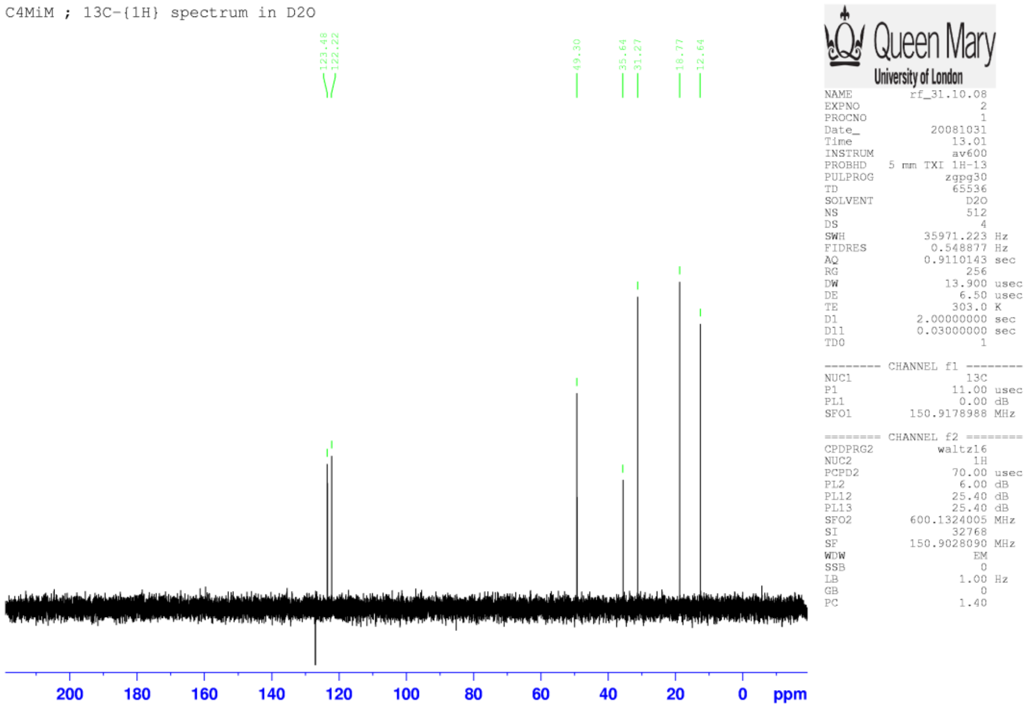
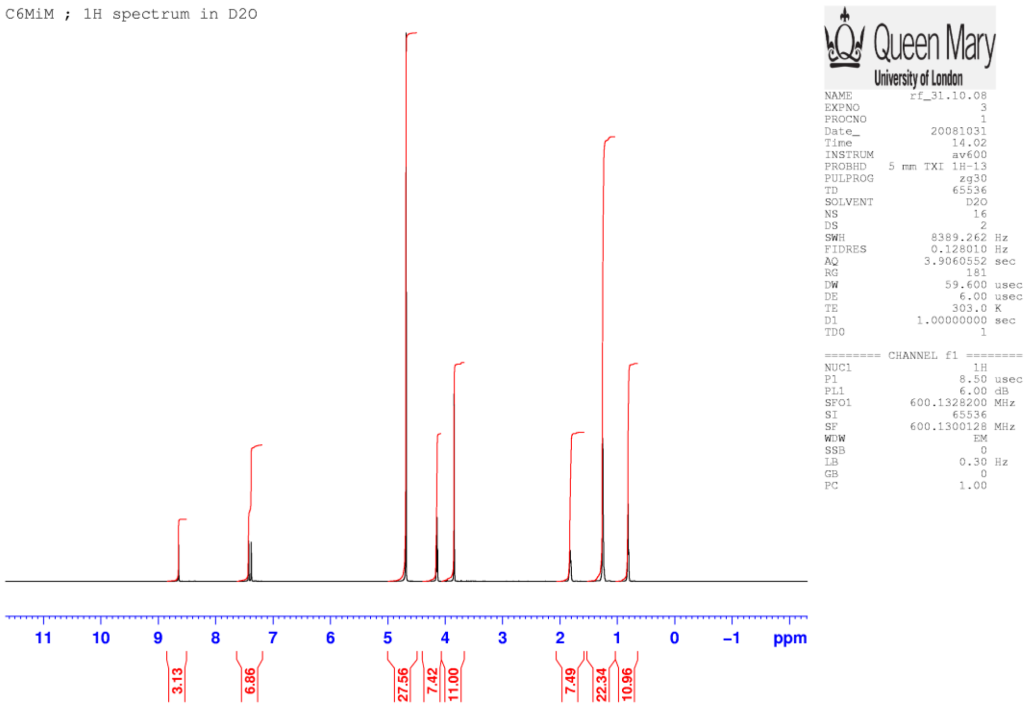
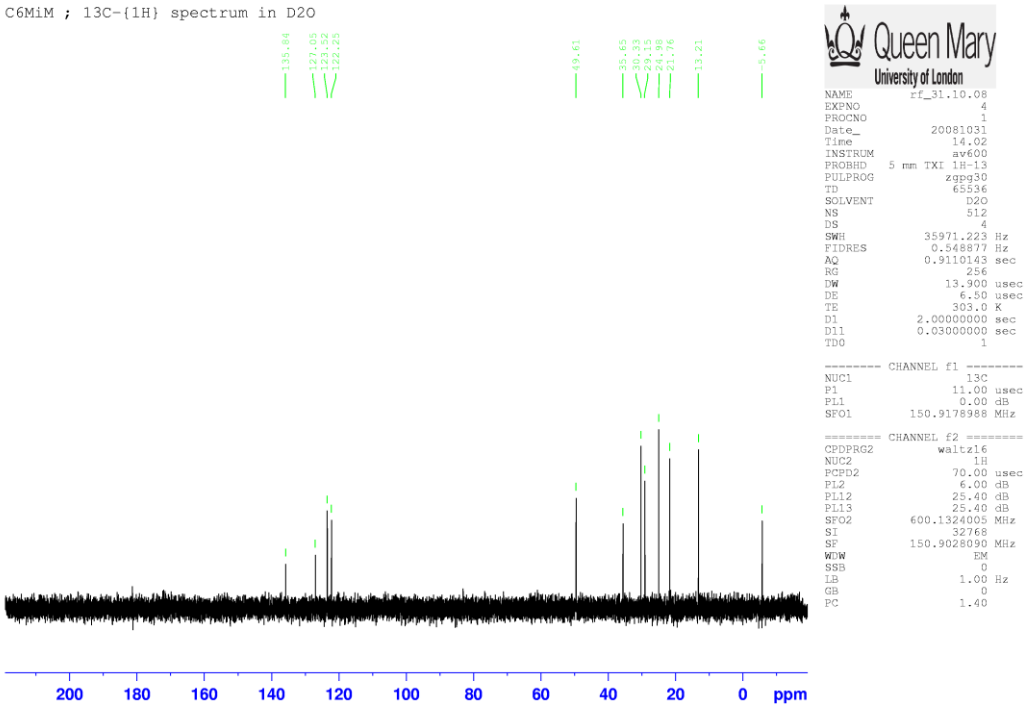


C4MiM ; 13C-{1H} spectrum in D2O

```
NAME          rf_31.10.08
EXPNO                   2
PROCNO                  1
Date_            20081031
Time                13.01
INSTRUM             av600
PROBHD   5 mm TXI 1H-13
PULPROG           zgpg30
TD                  65536
SOLVENT               D2O
NS                    512
DS                      4
SWH             35971.223 Hz
FIDRES           0.548877 Hz
AQ              0.9110143 sec
RG                    256
DW                 13.900 usec
DE                   6.50 usec
TE                  303.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  11.00 usec
PL1                  0.00 dB
SFO1          150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               70.00 usec
PL2                  6.00 dB
PL12                25.40 dB
PL13                25.40 dB
SFO2          600.1324005 MHz
SI                  32768
SF            150.9028090 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

1-hexyl-3-methyl imidazolium bromide [C6MIM][Br]

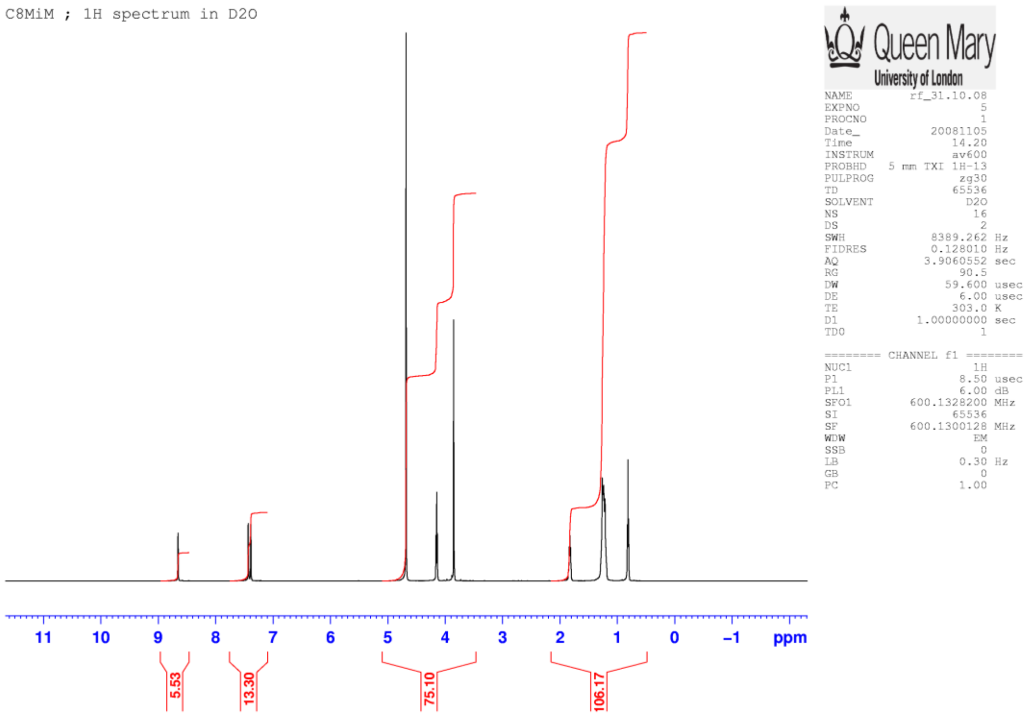


```
NAME           rf_31.10.08
EXPNO                    3
PROCNO                   1
Date_             20081031
Time                 14.02
INSTRUM              av600
PROBHD   5 mm TXI 1H-13
PULPROG               zg30
TD                   65536
SOLVENT                D2O
NS                      16
DS                       2
SWH               8389.262 Hz
FIDRES            0.128010 Hz
AQ               3.9060552 sec
RG                     181
DW                  59.600 usec
DE                    6.00 usec
TE                   303.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    8.50 usec
PL1                   6.00 dB
SFO1           600.1328200 MHz
SI                   65536
SF             600.1300128 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



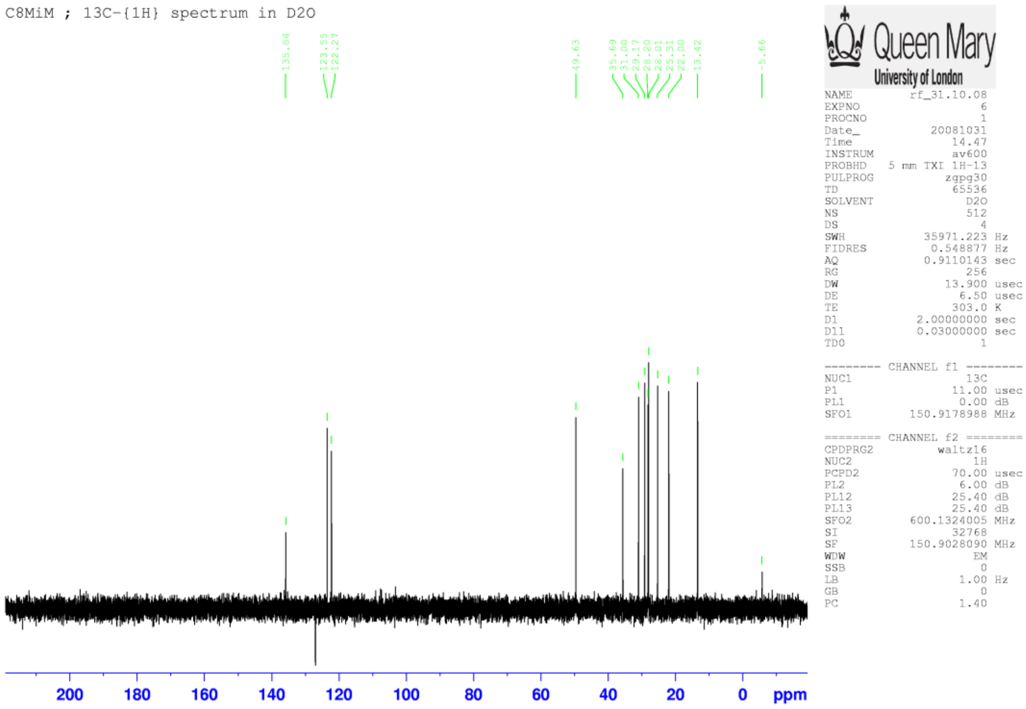
```
NAME           rf_31.10.08
EXPNO                    4
PROCNO                   1
Date_             20081031
Time                 14.02
INSTRUM              av600
PROBHD   5 mm TXI 1H-13
PULPROG             zgpg30
TD                   65536
SOLVENT                D2O
NS                     512
DS                       4
SWH              35971.223 Hz
FIDRES            0.548877 Hz
AQ               0.9110143 sec
RG                     256
DW                  13.900 usec
DE                    6.50 usec
TE                   303.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

-------- CHANNEL f1 --------
NUC1                   13C
P1                   11.00 usec
PL1                   0.00 dB
SFO1           150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                   6.00 dB
PL12                 25.40 dB
PL13                 25.40 dB
SFO2           600.1324005 MHz
SI                   32768
SF             150.9028090 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

1-octyl-3-methyl imidazolium bromide [C8MIM][Br]



C8MiM ; 1H spectrum in D2O

```
NAME          rf_31.10.08
EXPNO                   5
PROCNO                  1
Date_            20081105
Time                14.20
INSTRUM             av600
PROBHD   5 mm TXI 1H-13
PULPROG              zg30
TD                  65536
SOLVENT               D2O
NS                     16
DS                      2
SWH              8389.262 Hz
FIDRES           0.128010 Hz
AQ              3.9060552 sec
RG                   90.5
DW                 59.600 usec
DE                   6.00 usec
TE                  303.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.50 usec
PL1                  6.00 dB
SFO1          600.1328200 MHz
SI                  65536
SF            600.1300128 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

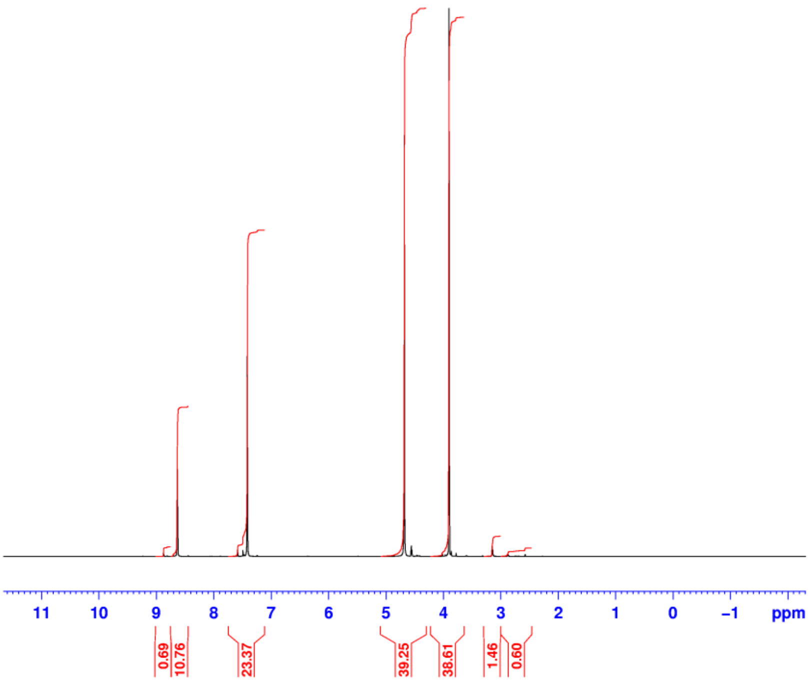


C8MiM ; 13C-{1H} spectrum in D2O

```
NAME          rf_31.10.08
EXPNO                   6
PROCNO                  1
Date_            20081031
Time                14.47
INSTRUM             av600
PROBHD   5 mm TXI 1H-13
PULPROG           zgpg30
TD                  65536
SOLVENT               D2O
NS                    512
DS                      4
SWH             35971.223 Hz
FIDRES           0.548877 Hz
AQ              0.9110143 sec
RG                    256
DW                 13.900 usec
DE                   6.50 usec
TE                  303.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

-------- CHANNEL f1 --------
NUC1                  13C
P1                  11.00 usec
PL1                  0.00 dB
SFO1          150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               70.00 usec
PL2                  6.00 dB
PL12                25.40 dB
PL13                25.40 dB
SFO2          600.1324005 MHz
SI                  32768
SF            150.9028090 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

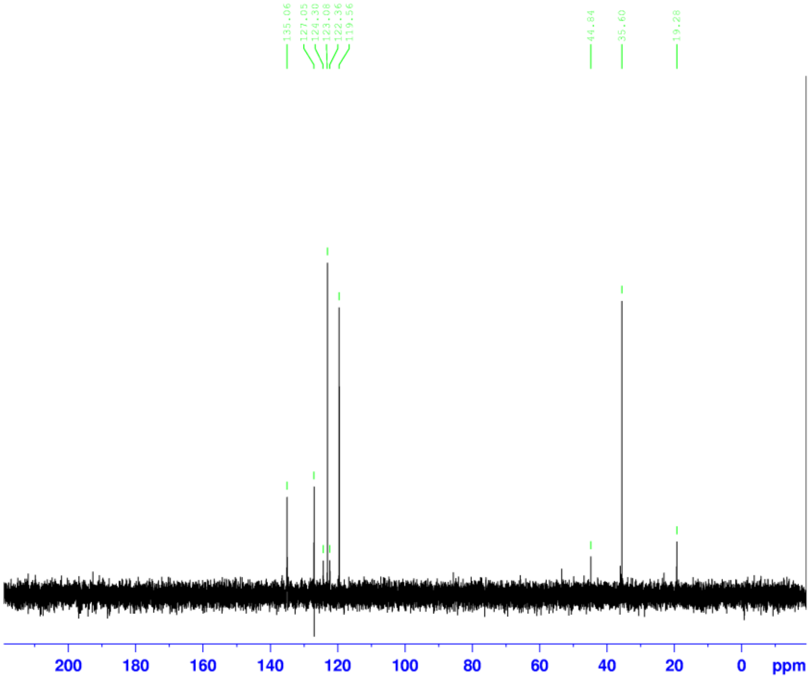
1-(2-cyanoethyl)-3-methylimidazolium bromide [CNC2MIM][Br]

CNC2MiM ; 1H spectrum in D2O



```
NAME           rf_31.10.08
EXPNO                   13
PROCNO                   1
Date_             20081031
Time                 16.59
INSTRUM              av600
PROBHD   5 mm TXI 1H-13
PULPROG               zg30
TD                   65536
SOLVENT                D2O
NS                      16
DS                       2
SWH               8389.262 Hz
FIDRES            0.128010 Hz
AQ               3.9060552 sec
RG                   161.3
DW                  59.600 usec
DE                    6.00 usec
TE                   303.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    8.50 usec
PL1                   6.00 dB
SFO1           600.1328200 MHz
SI                   65536
SF             600.1300128 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

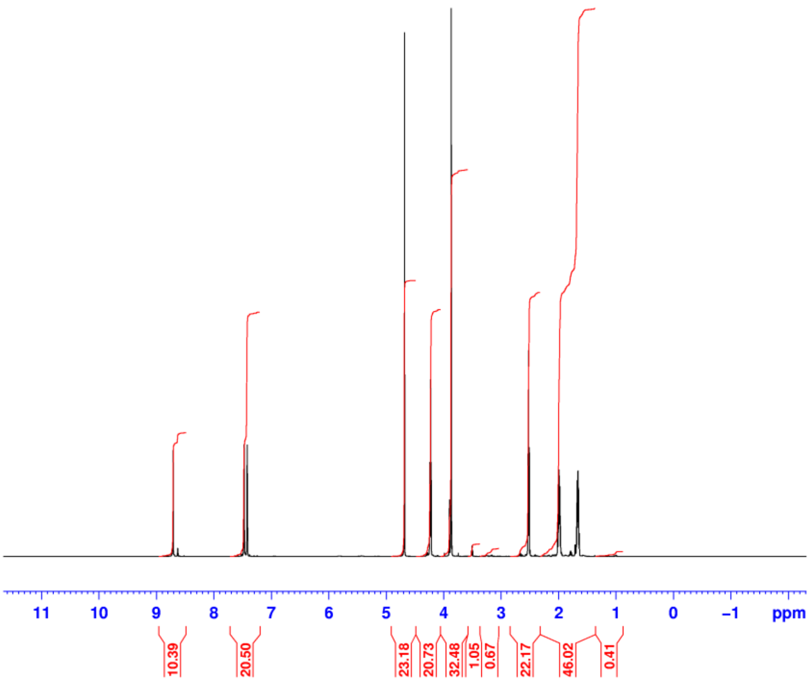
CNC2MiM ; 13C-{1H} spectrum in D2O



```
NAME           rf_31.10.08
EXPNO                   14
PROCNO                   1
Date_             20081031
Time                 17.25
INSTRUM              av600
PROBHD   5 mm TXI 1H-13
PULPROG             zgpg30
TD                   65536
SOLVENT                D2O
NS                     512
DS                       4
SWH              35971.223 Hz
FIDRES            0.548877 Hz
AQ               0.9110143 sec
RG                     362
DW                  13.900 usec
DE                    6.50 usec
TE                   303.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

-------- CHANNEL f1 --------
NUC1                   13C
P1                   11.00 usec
PL1                   0.00 dB
SFO1           150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                   6.00 dB
PL12                 25.40 dB
PL13                 25.40 dB
SFO2           600.1324005 MHz
SI                   32768
SF             150.9028090 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.00
```

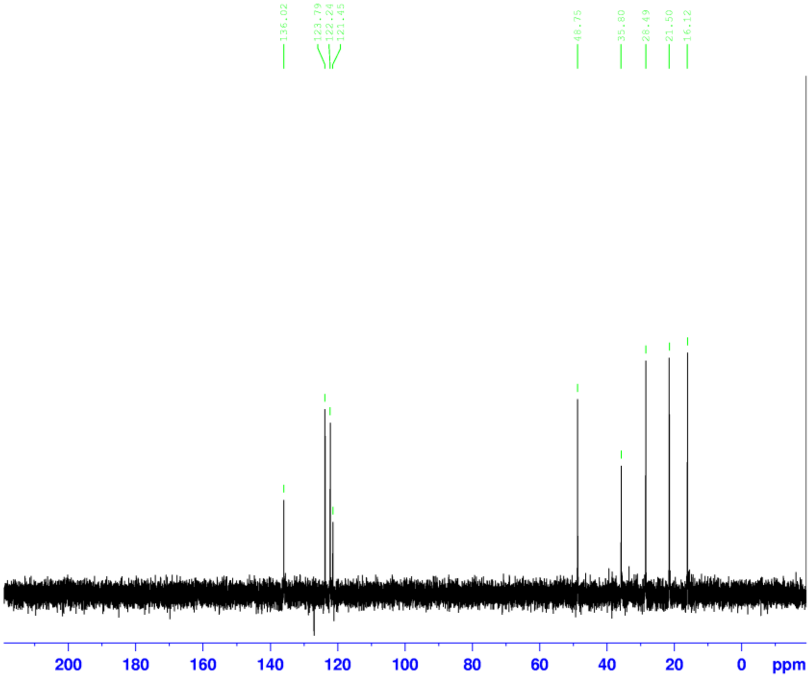
1-(4-cyanobutyl)-3-methylimidazolium bromide [CNC4MIM][Br]

CNC4MiM ; 1H spectrum in D2O



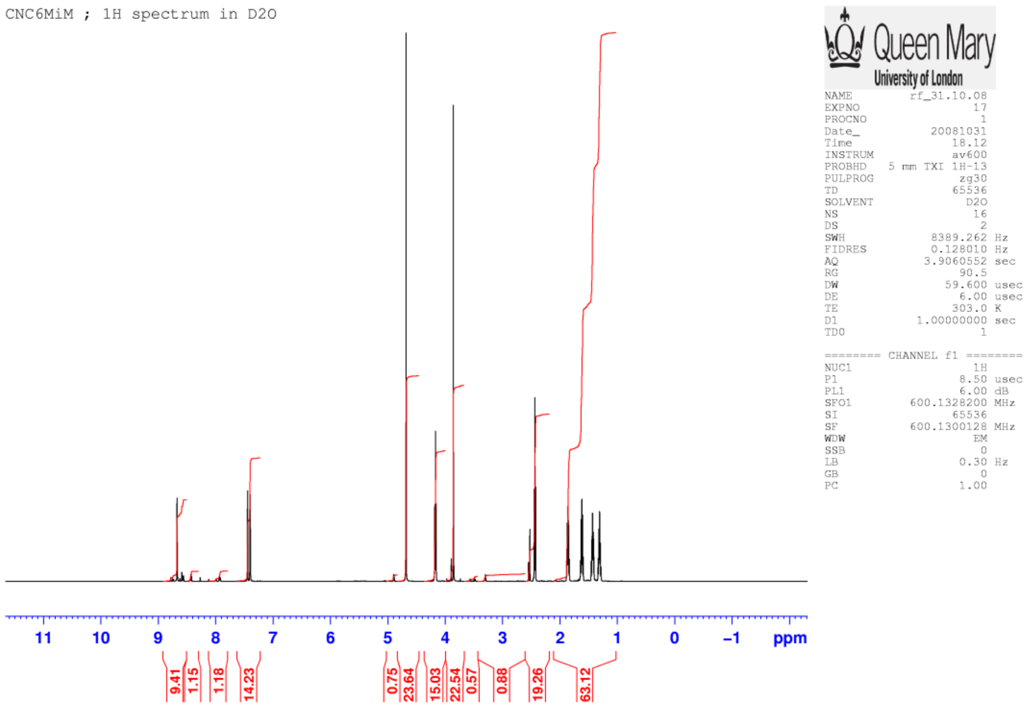
```
NAME          rf_31.10.08
EXPNO                  15
PROCNO                  1
Date_            20081104
Time                10.42
INSTRUM             av600
PROBHD   5 mm TXI 1H-13
PULPROG              zg30
TD                  65536
SOLVENT               D2O
NS                     16
DS                      2
SWH              8389.262 Hz
FIDRES           0.128010 Hz
AQ              3.9060552 sec
RG                   90.5
DW                 59.600 usec
DE                   6.00 usec
TE                  303.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.50 usec
PL1                  6.00 dB
SFO1          600.1328200 MHz
SI                  65536
SF            600.1300128 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

CNC4MiM ; 13C-{1H} spectrum in D2O

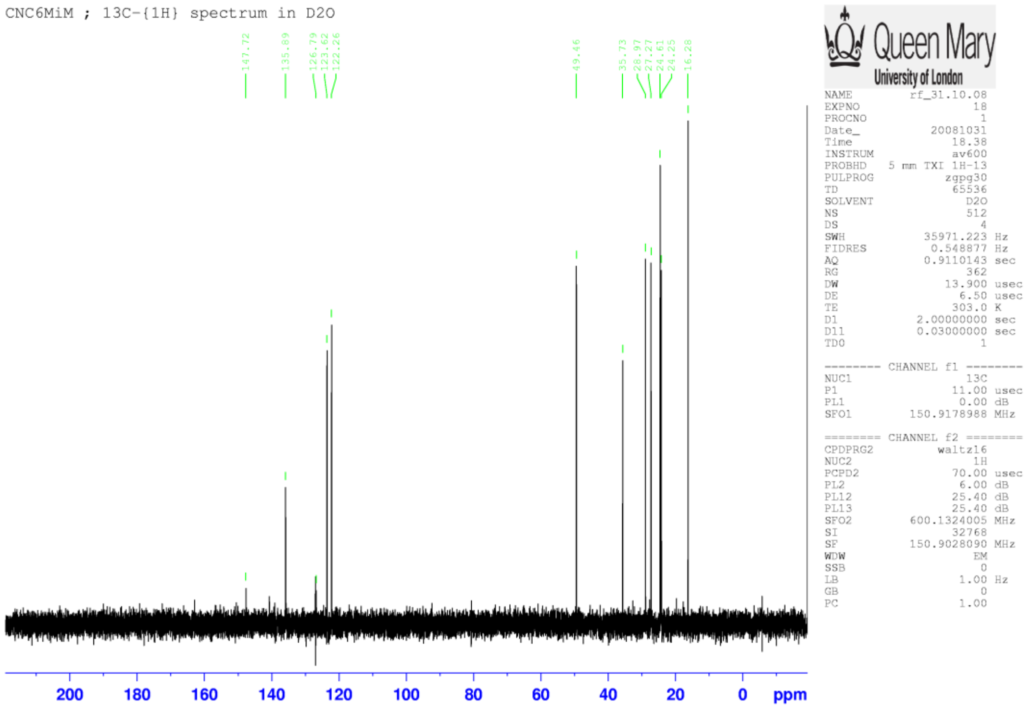


```
NAME          rf_31.10.08
EXPNO                  16
PROCNO                  1
Date_            20081031
Time                18.03
INSTRUM             av600
PROBHD   5 mm TXI 1H-13
PULPROG            zgpg30
TD                  65536
SOLVENT               D2O
NS                    512
DS                      4
SWH             35971.223 Hz
FIDRES           0.548877 Hz
AQ              0.9110143 sec
RG                    362
DW                 13.900 usec
DE                   6.50 usec
TE                  303.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

-------- CHANNEL f1 --------
NUC1                  13C
P1                  11.00 usec
PL1                  0.00 dB
SFO1          150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               70.00 usec
PL2                  6.00 dB
PL12                25.40 dB
PL13                25.40 dB
SFO2          600.1324005 MHz
SI                  32768
SF            150.9028090 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00
```

1-(6-cyanohexyl)-3-methylimidazolium bromide [CNC6MIM][Br]

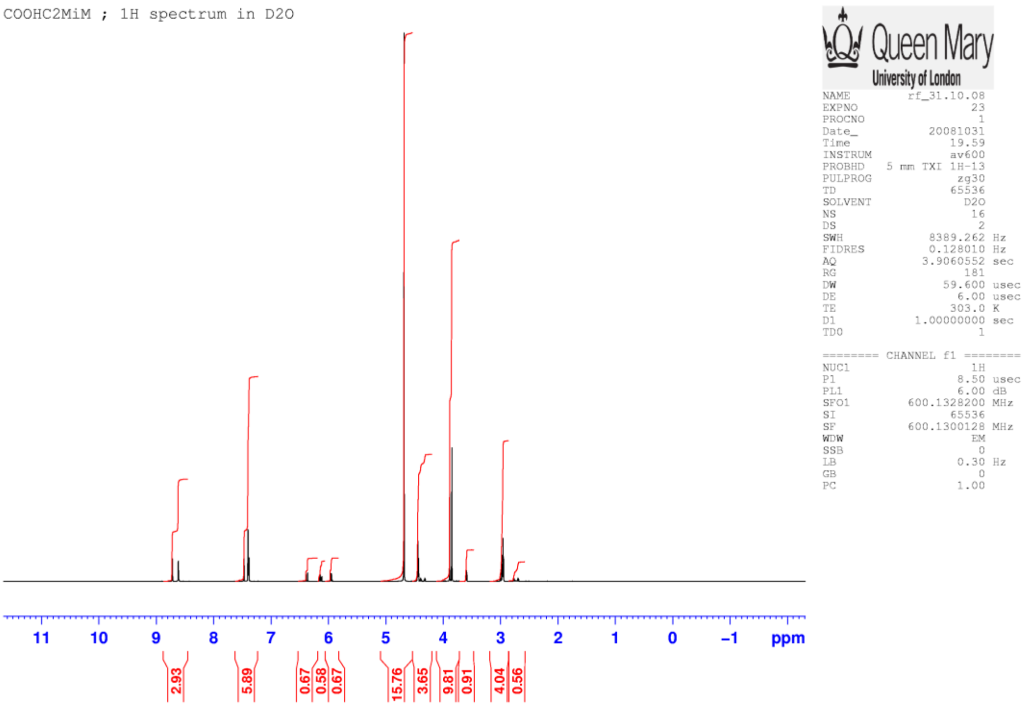


```
NAME           rf_31.10.08
EXPNO                   17
PROCNO                   1
Date_             20081031
Time                 18.12
INSTRUM              av600
PROBHD   5 mm TXI 1H-13
PULPROG               zg30
TD                   65536
SOLVENT                D2O
NS                      16
DS                       2
SWH               8389.262 Hz
FIDRES            0.128010 Hz
AQ               3.9060552 sec
RG                    90.5
DW                  59.600 usec
DE                    6.00 usec
TE                   303.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    8.50 usec
PL1                   6.00 dB
SFO1           600.1328200 MHz
SI                   65536
SF             600.1300128 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

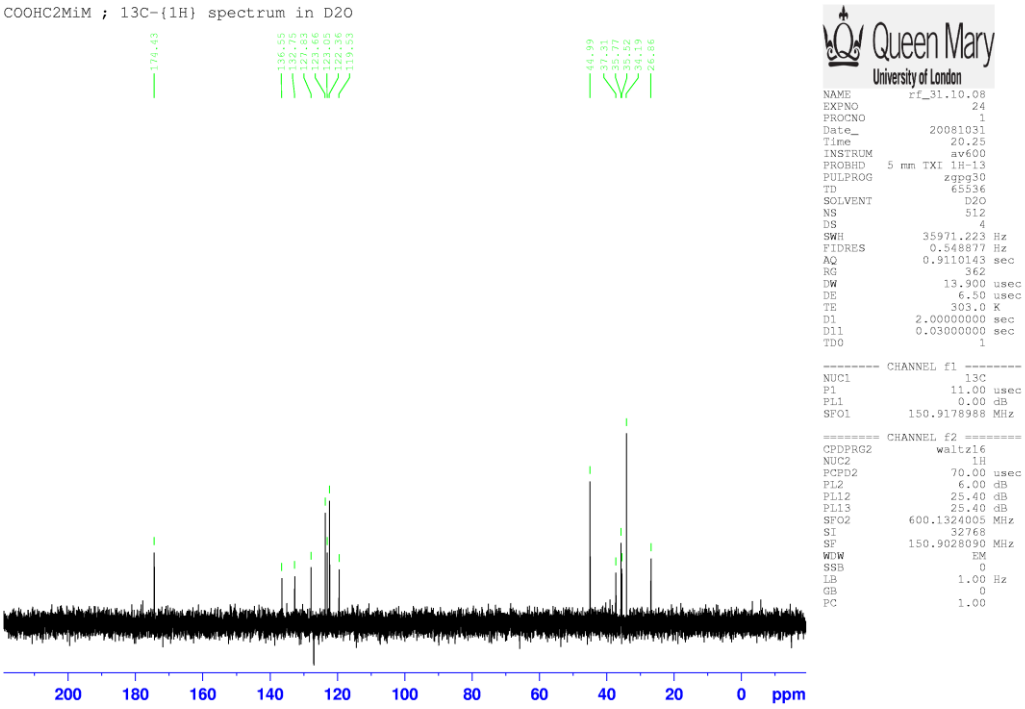


```
NAME           rf_31.10.08
EXPNO                   18
PROCNO                   1
Date_             20081031
Time                 18.38
INSTRUM              av600
PROBHD   5 mm TXI 1H-13
PULPROG             zgpg30
TD                   65536
SOLVENT                D2O
NS                     512
DS                       4
SWH              35971.223 Hz
FIDRES            0.548877 Hz
AQ               0.9110143 sec
RG                     362
DW                  13.900 usec
DE                    6.50 usec
TE                   303.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   11.00 usec
PL1                   0.00 dB
SFO1           150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                   6.00 dB
PL12                 25.40 dB
PL13                 25.40 dB
SFO2           600.1324005 MHz
SI                   32768
SF             150.9028090 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.00
```

1-(2-carboxyethyl)-3-methylimidazolium bromide [COOHC2MIM][Br]

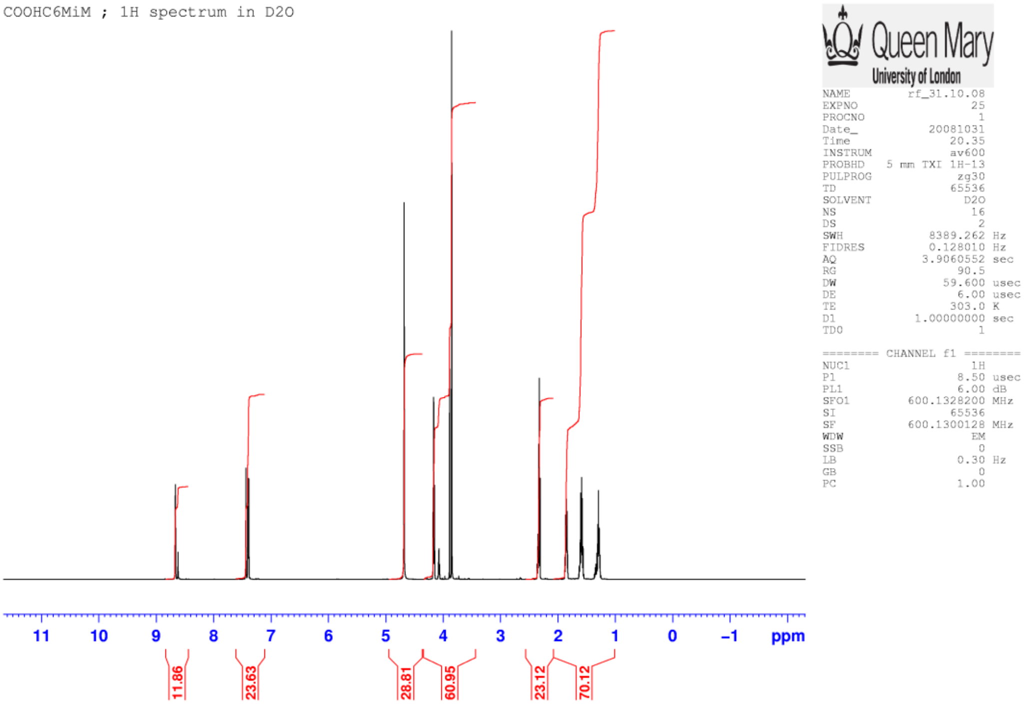


```
NAME           rf_31.10.08
EXPNO                   23
PROCNO                   1
Date_             20081031
Time                 19.59
INSTRUM              av600
PROBHD    5 mm TXI 1H-13
PULPROG               zg30
TD                   65536
SOLVENT                D2O
NS                      16
DS                       2
SWH               8389.262 Hz
FIDRES            0.128010 Hz
AQ               3.9060552 sec
RG                     181
DW                  59.600 usec
DE                    6.00 usec
TE                   303.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    8.50 usec
PL1                   6.00 dB
SFO1           600.1328200 MHz
SI                   65536
SF             600.1300128 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



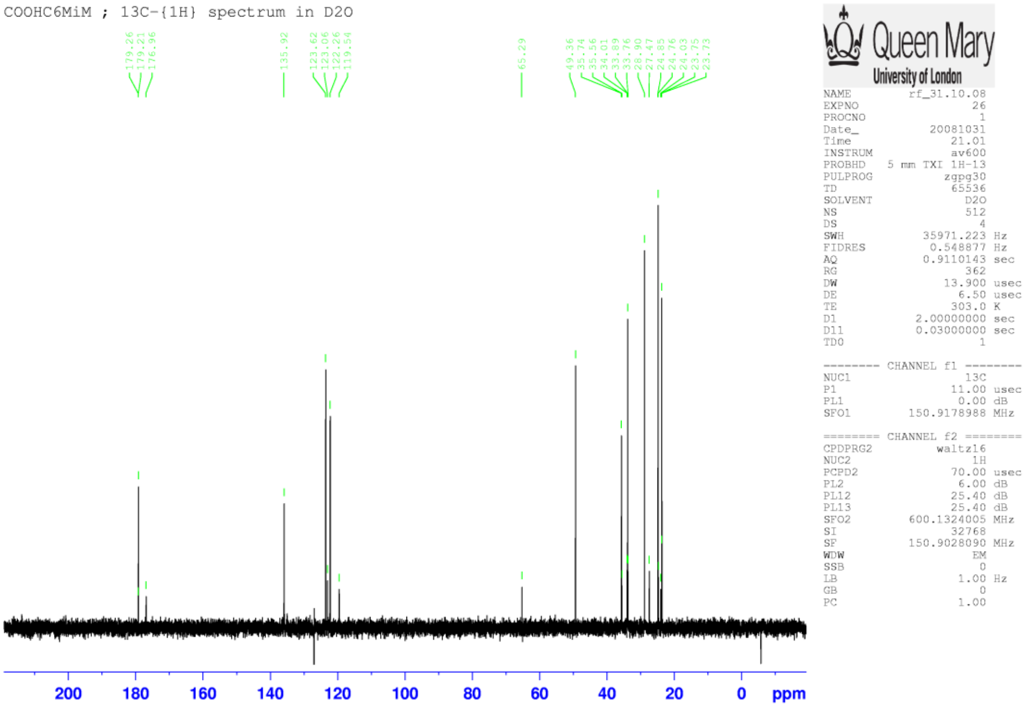
```
NAME           rf_31.10.08
EXPNO                   24
PROCNO                   1
Date_             20081031
Time                 20.25
INSTRUM              av600
PROBHD    5 mm TXI 1H-13
PULPROG             zgpg30
TD                   65536
SOLVENT                D2O
NS                     512
DS                       4
SWH              35971.223 Hz
FIDRES            0.548877 Hz
AQ               0.9110143 sec
RG                     362
DW                  13.900 usec
DE                    6.50 usec
TE                   303.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

-------- CHANNEL f1 --------
NUC1                   13C
P1                   11.00 usec
PL1                   0.00 dB
SFO1           150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                   6.00 dB
PL12                 25.40 dB
PL13                 25.40 dB
SFO2           600.1324005 MHz
SI                   32768
SF             150.9028090 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.00
```

1-(5-carboxypentyl)-3-methylimidazolium bromide [COOHC5MIM][Br]



COOHC6MiM ; 1H spectrum in D2O

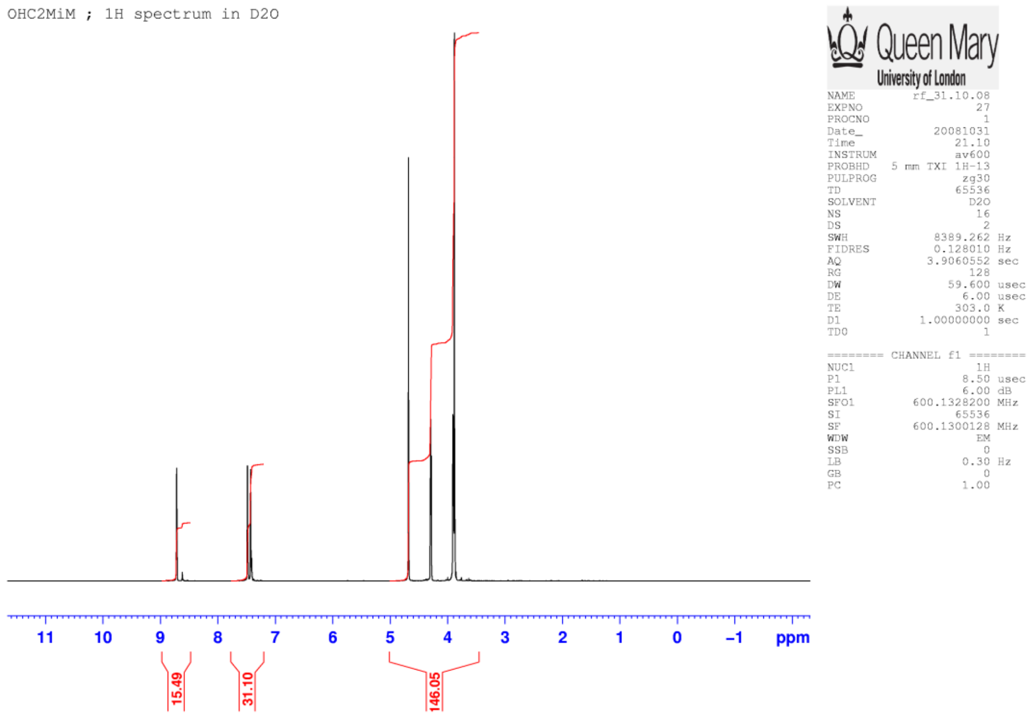
```
NAME          rf_31.10.08
EXPNO                  25
PROCNO                  1
Date_            20081031
Time                20.35
INSTRUM             av600
PROBHD   5 mm TXI 1H-13
PULPROG              zg30
TD                  65536
SOLVENT               D2O
NS                     16
DS                      2
SWH              8389.262 Hz
FIDRES           0.128010 Hz
AQ              3.9060552 sec
RG                   90.5
DW                 59.600 usec
DE                   6.00 usec
TE                  303.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.50 usec
PL1                  6.00 dB
SFO1          600.1328200 MHz
SI                  65536
SF            600.1300128 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



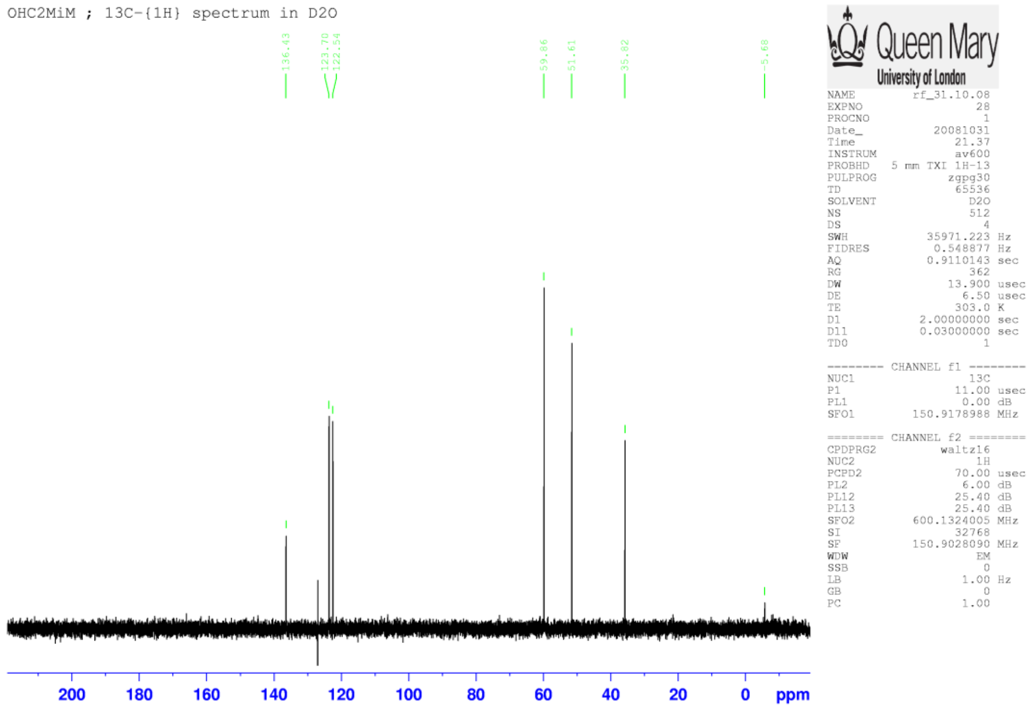
COOHC6MiM ; 13C-{1H} spectrum in D2O

```
NAME          rf_31.10.08
EXPNO                  26
PROCNO                  1
Date_            20081031
Time                21.01
INSTRUM             av600
PROBHD   5 mm TXI 1H-13
PULPROG            zgpg30
TD                  65536
SOLVENT               D2O
NS                    512
DS                      4
SWH             35971.223 Hz
FIDRES           0.548877 Hz
AQ              0.9110143 sec
RG                    362
DW                 13.900 usec
DE                   6.50 usec
TE                  303.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

-------- CHANNEL f1 --------
NUC1                  13C
P1                  11.00 usec
PL1                  0.00 dB
SFO1          150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               70.00 usec
PL2                  6.00 dB
PL12                25.40 dB
PL13                25.40 dB
SFO2          600.1324005 MHz
SI                  32768
SF            150.9028090 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00
```

1-(2-hydroxyethyl)-3-methylimidazolium bromide [OHC2MIM][Br]

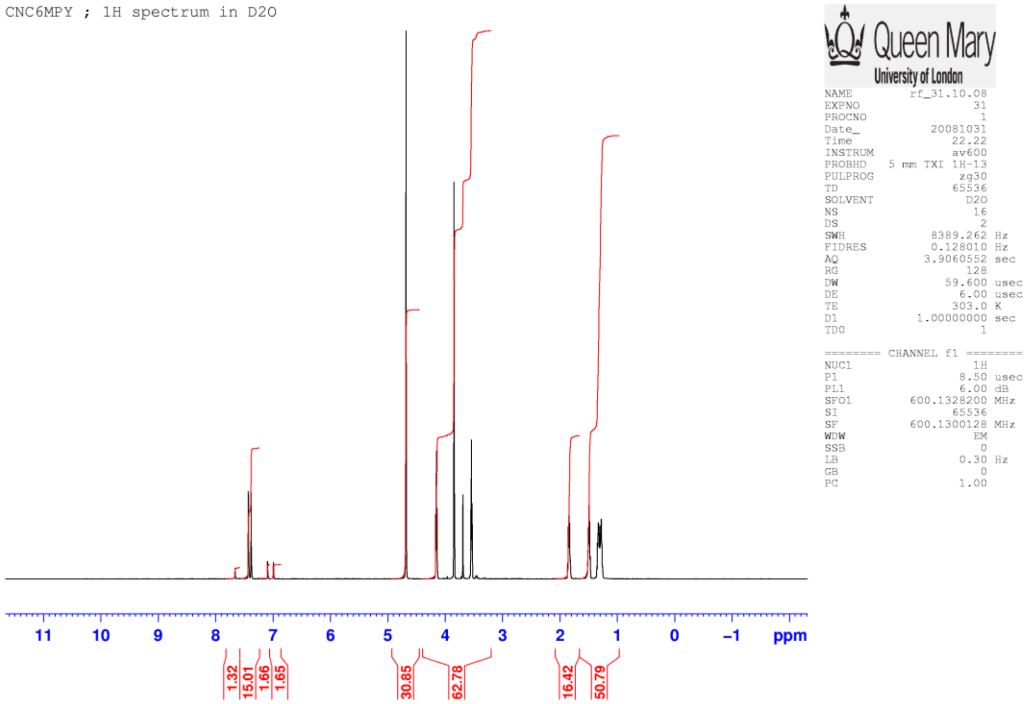


```
NAME          rf_31.10.08
EXPNO                  27
PROCNO                  1
Date_            20081031
Time                21.10
INSTRUM             av600
PROBHD   5 mm TXI 1H-13
PULPROG              zg30
TD                  65536
SOLVENT               D2O
NS                     16
DS                      2
SWH              8389.262 Hz
FIDRES           0.128010 Hz
AQ              3.9060552 sec
RG                    128
DW                 59.600 usec
DE                   6.00 usec
TE                  303.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.50 usec
PL1                  6.00 dB
SFO1          600.1328200 MHz
SI                  65536
SF            600.1300128 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

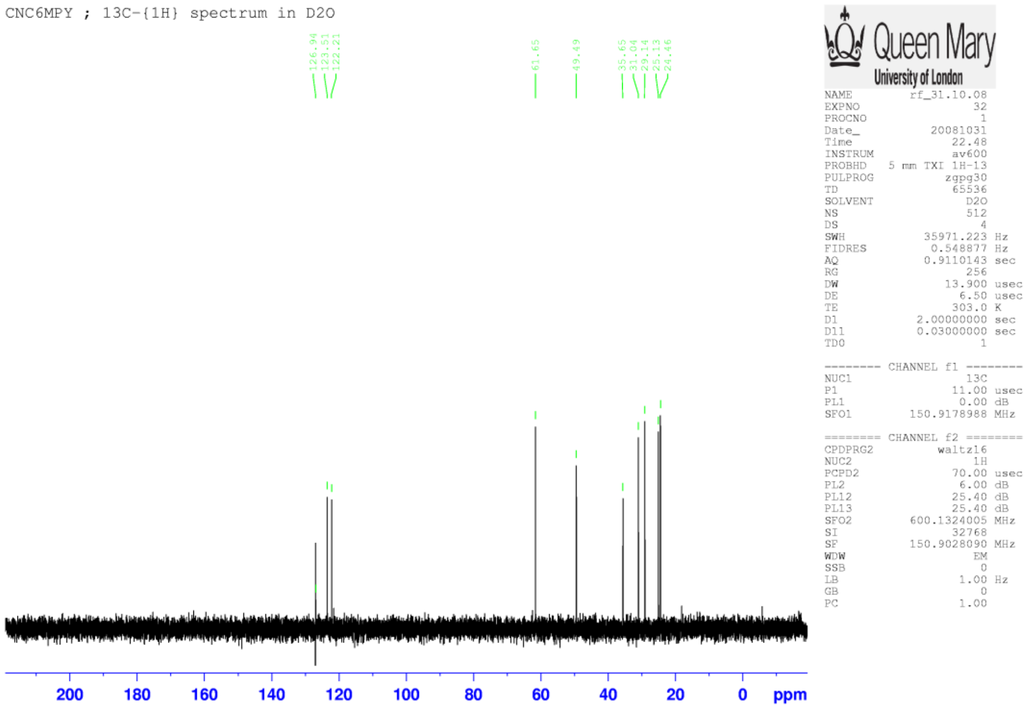


```
NAME          rf_31.10.08
EXPNO                  28
PROCNO                  1
Date_            20081031
Time                21.37
INSTRUM             av600
PROBHD   5 mm TXI 1H-13
PULPROG            zgpg30
TD                  65536
SOLVENT               D2O
NS                    512
DS                      4
SWH             35971.223 Hz
FIDRES           0.548877 Hz
AQ              0.9110143 sec
RG                    362
DW                 13.900 usec
DE                   6.50 usec
TE                  303.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

-------- CHANNEL f1 --------
NUC1                  13C
P1                  11.00 usec
PL1                  0.00 dB
SFO1          150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               70.00 usec
PL2                  6.00 dB
PL12                25.40 dB
PL13                25.40 dB
SFO2          600.1324005 MHz
SI                  32768
SF            150.9028090 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00
```

1-(6-hydroxyhexyl)-3-methylimidazolium bromide [OHC6MIM][Br]



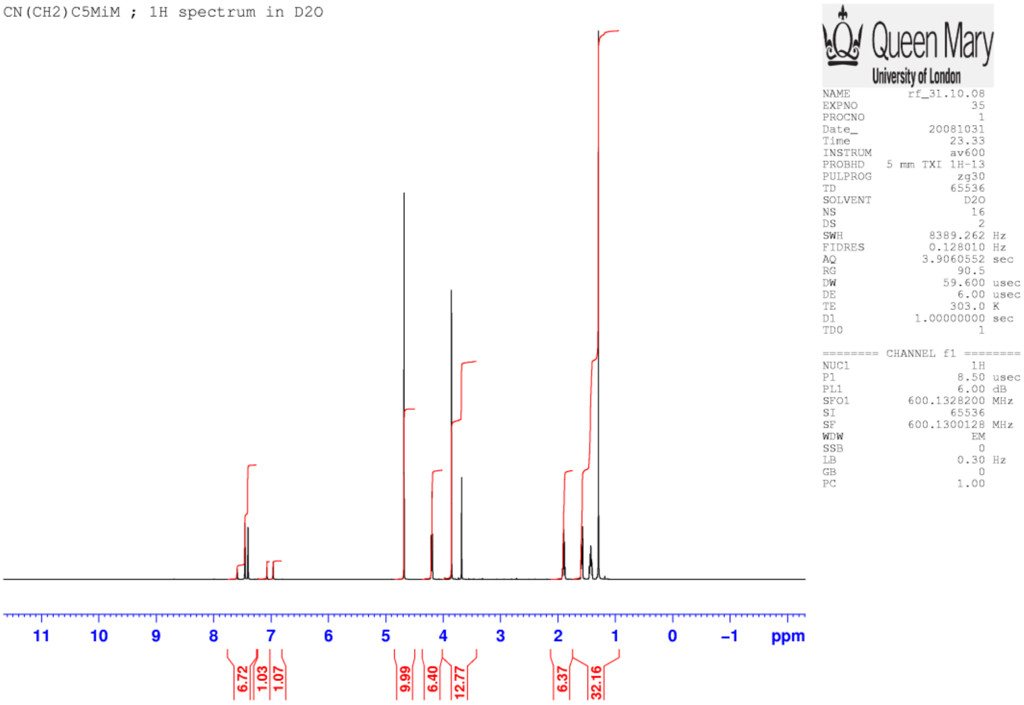
```
NAME          rf_31.10.08
EXPNO                  31
PROCNO                  1
Date_            20081031
Time                22.22
INSTRUM             av600
PROBHD   5 mm TXI 1H-13
PULPROG              zg30
TD                  65536
SOLVENT               D2O
NS                     16
DS                      2
SWH              8389.262 Hz
FIDRES           0.128010 Hz
AQ              3.9060552 sec
RG                    128
DW                 59.600 usec
DE                   6.00 usec
TE                  303.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.50 usec
PL1                  6.00 dB
SFO1          600.1328200 MHz
SI                  65536
SF            600.1300128 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

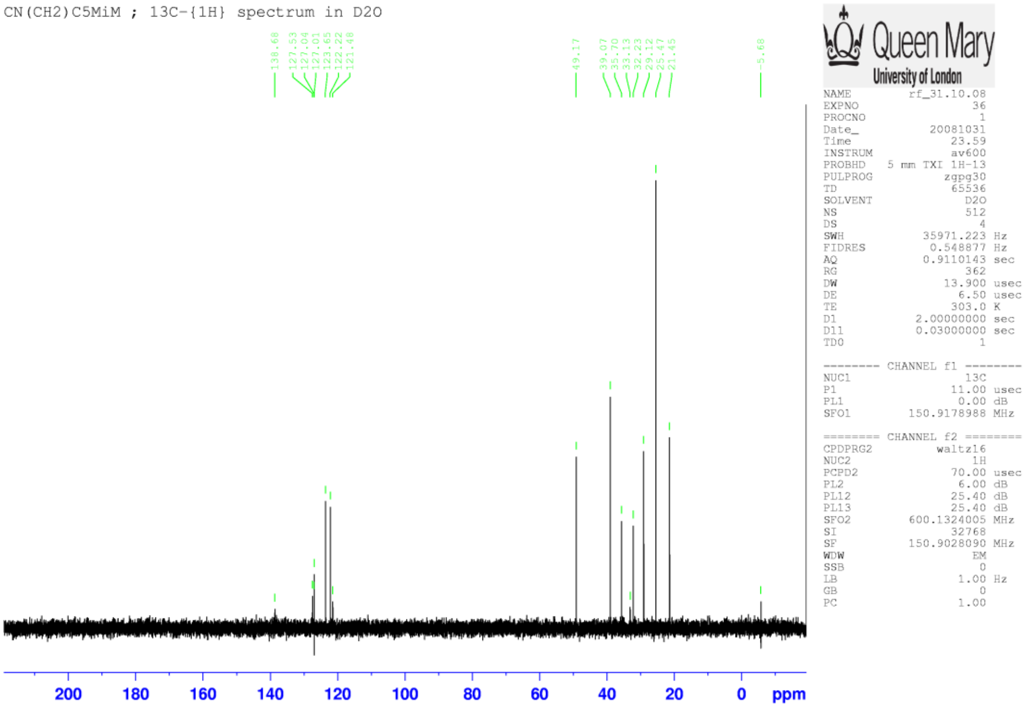


```
NAME          rf_31.10.08
EXPNO                  32
PROCNO                  1
Date_            20081031
Time                22.48
INSTRUM             av600
PROBHD   5 mm TXI 1H-13
PULPROG            zgpg30
TD                  65536
SOLVENT               D2O
NS                    512
DS                      4
SWH             35971.223 Hz
FIDRES           0.548877 Hz
AQ              0.9110143 sec
RG                    256
DW                 13.900 usec
DE                   6.50 usec
TE                  303.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

-------- CHANNEL f1 --------
NUC1                  13C
P1                  11.00 usec
PL1                  0.00 dB
SFO1          150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               70.00 usec
PL2                  6.00 dB
PL12                25.40 dB
PL13                25.40 dB
SFO2          600.1324005 MHz
SI                  32768
SF            150.9028090 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00
```

1-(5-cyano-(5,5-dimethyl)pentyl)-3-methylimidazolium bromide

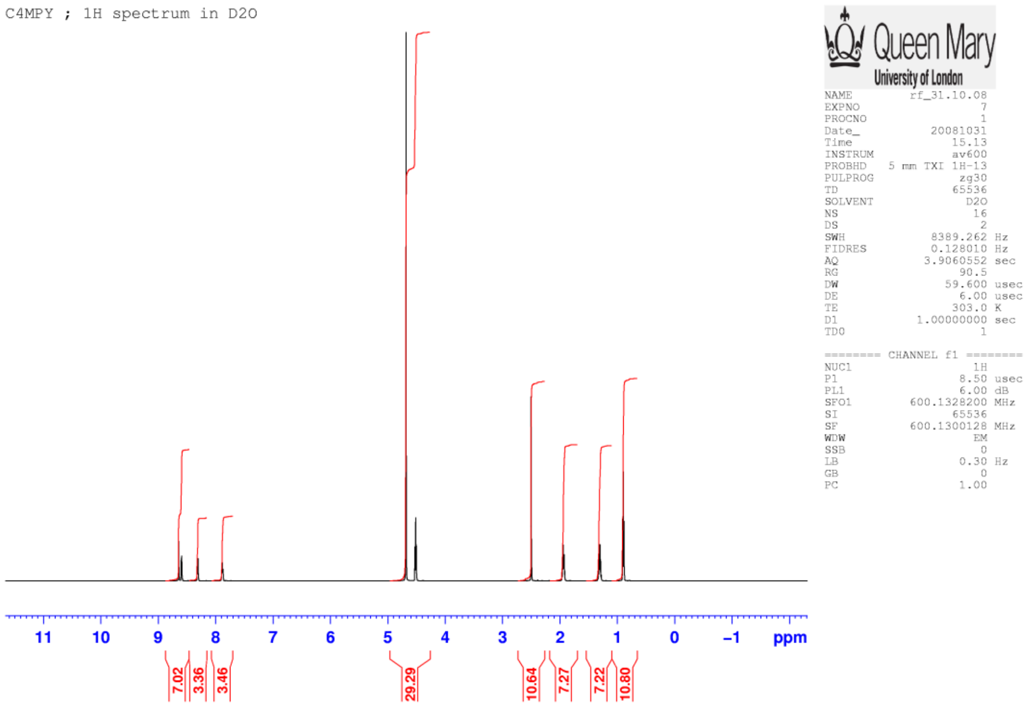
[CN(CH$_2$)$_2$C5MIM][Br]



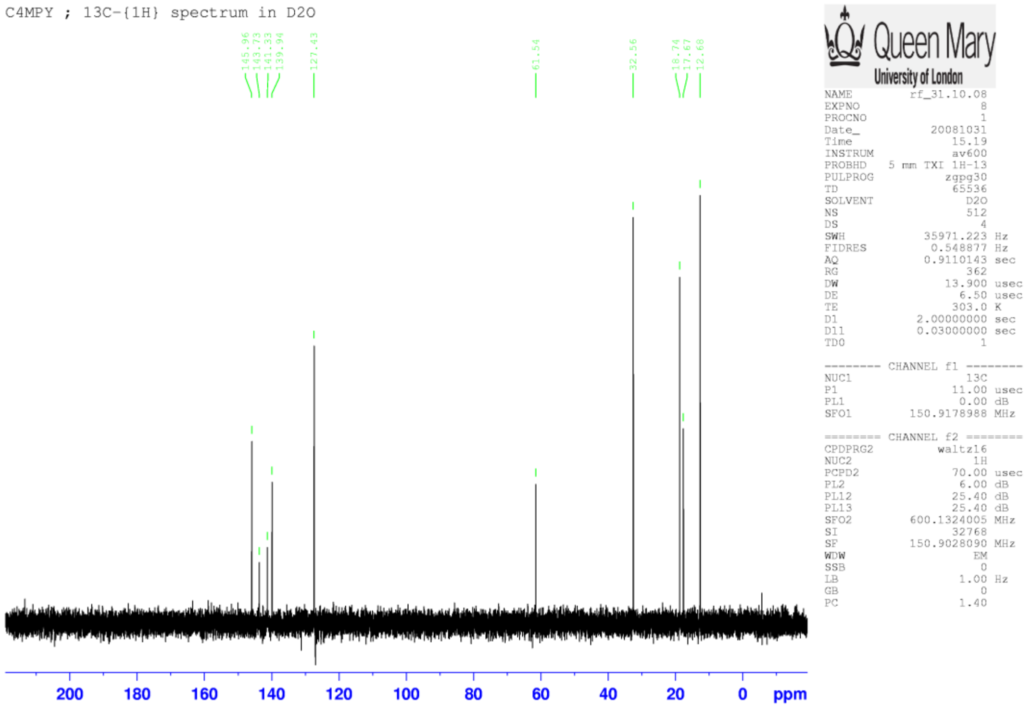


B.2 Pyridinium-based ILs

1-butyl-3-methylpyridinium bromide [C4MPy][Br]

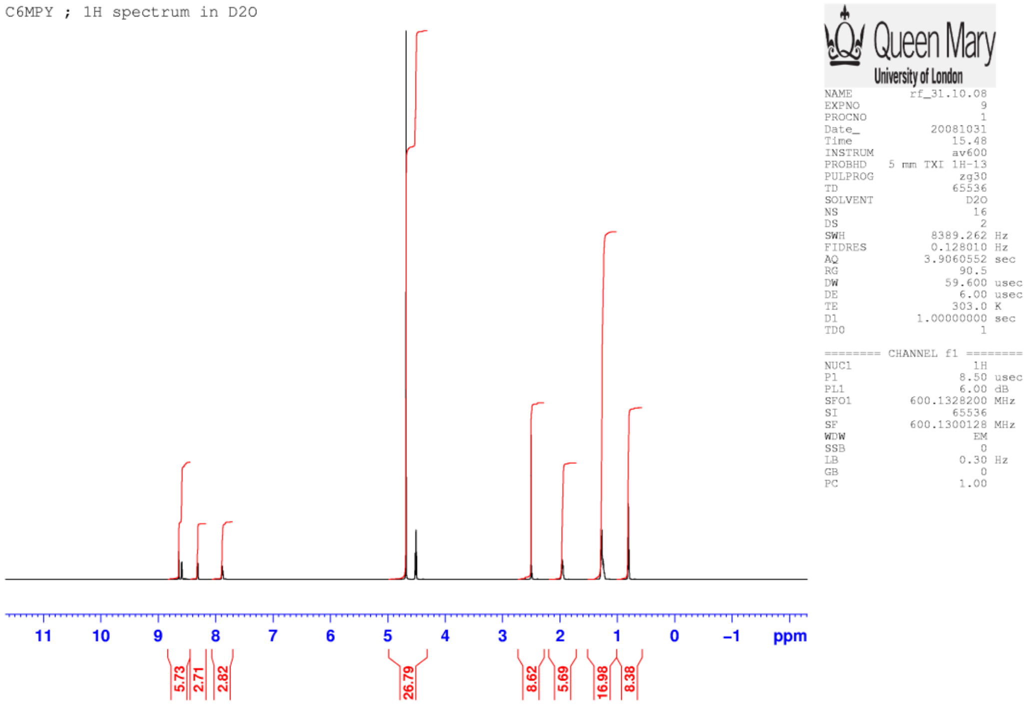


```
NAME             rf_31.10.08
EXPNO                      7
PROCNO                     1
Date_               20081031
Time                   15.13
INSTRUM                av600
PROBHD     5 mm TXI 1H-13
PULPROG                 zg30
TD                     65536
SOLVENT                  D2O
NS                        16
DS                         2
SWH                 8389.262 Hz
FIDRES              0.128010 Hz
AQ                 3.9060552 sec
RG                      90.5
DW                    59.600 usec
DE                      6.00 usec
TE                     303.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                      8.50 usec
PL1                     6.00 dB
SFO1             600.1328200 MHz
SI                     65536
SF               600.1300128 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

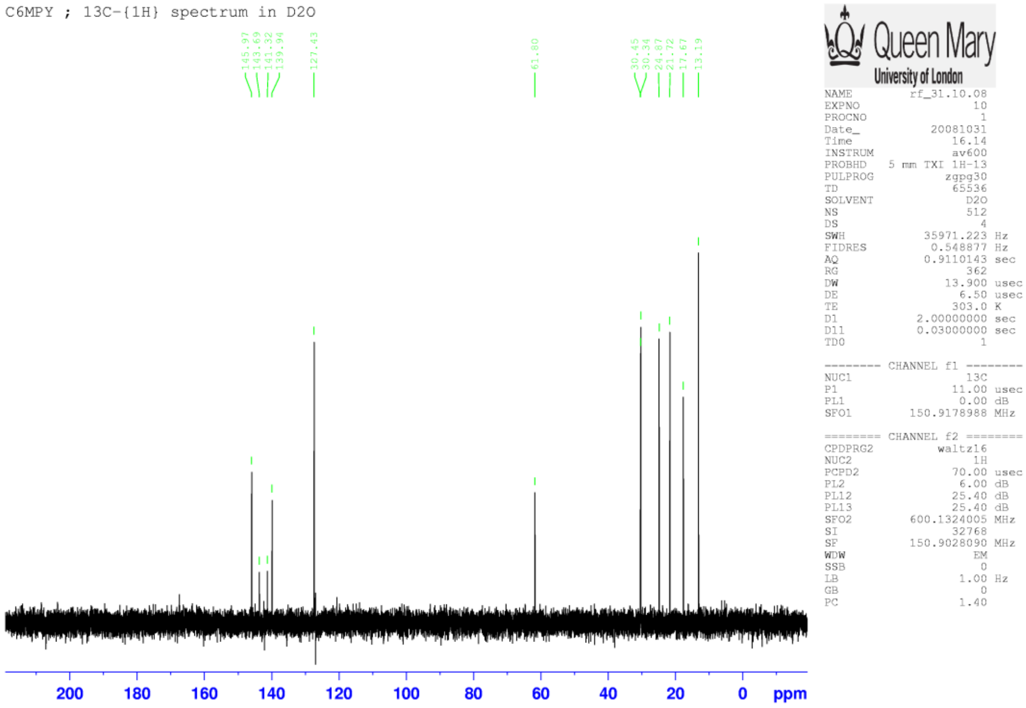


```
NAME             rf_31.10.08
EXPNO                      8
PROCNO                     1
Date_               20081031
Time                   15.19
INSTRUM                av600
PROBHD     5 mm TXI 1H-13
PULPROG               zgpg30
TD                     65536
SOLVENT                  D2O
NS                       512
DS                         4
SWH                35971.223 Hz
FIDRES              0.548877 Hz
AQ                 0.9110143 sec
RG                       362
DW                    13.900 usec
DE                      6.50 usec
TE                     303.0 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

-------- CHANNEL f1 --------
NUC1                     13C
P1                     11.00 usec
PL1                     0.00 dB
SFO1             150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                  70.00 usec
PL2                     6.00 dB
PL12                   25.40 dB
PL13                   25.40 dB
SFO2             600.1324005 MHz
SI                     32768
SF               150.9028090 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

1-hexyl-3-methylpyridinium bromide [C6MPy][Br]


C6MPY ; 1H spectrum in D2O

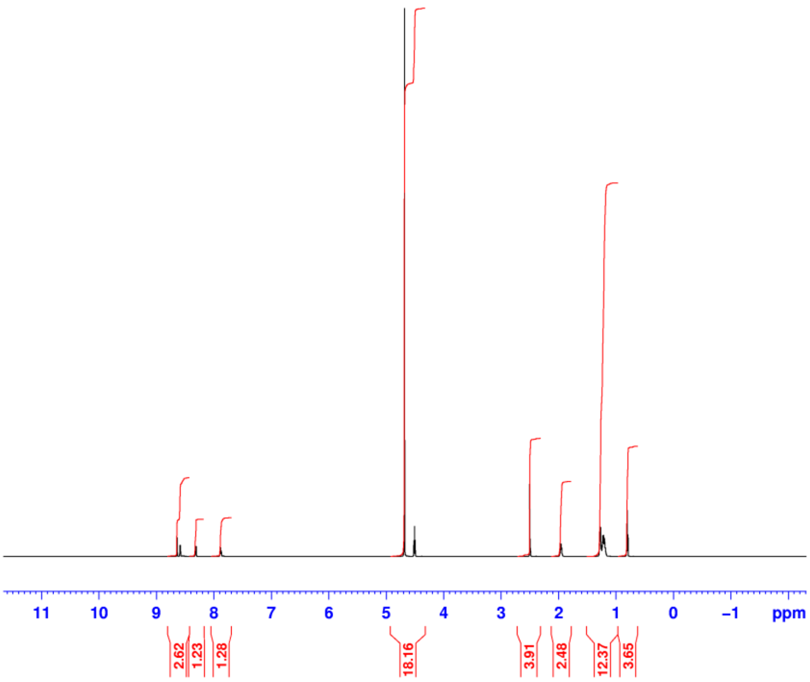
```
NAME         rf_31.10.08
EXPNO                  9
PROCNO                 1
Date_           20081031
Time               15.48
INSTRUM            av600
PROBHD   5 mm TXI 1H-13
PULPROG             zg30
TD                 65536
SOLVENT              D2O
NS                    16
DS                     2
SWH             8389.262 Hz
FIDRES          0.128010 Hz
AQ             3.9060552 sec
RG                  90.5
DW                59.600 usec
DE                  6.00 usec
TE                 303.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  8.50 usec
PL1                 6.00 dB
SFO1         600.1328200 MHz
SI                 65536
SF           600.1300128 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```


C6MPY ; 13C-{1H} spectrum in D2O

```
NAME         rf_31.10.08
EXPNO                 10
PROCNO                 1
Date_           20081031
Time               16.14
INSTRUM            av600
PROBHD   5 mm TXI 1H-13
PULPROG           zgpg30
TD                 65536
SOLVENT              D2O
NS                   512
DS                     4
SWH            35971.223 Hz
FIDRES          0.548877 Hz
AQ             0.9110143 sec
RG                   362
DW                13.900 usec
DE                  6.50 usec
TE                 303.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

-------- CHANNEL f1 --------
NUC1                 13C
P1                 11.00 usec
PL1                 0.00 dB
SFO1         150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              70.00 usec
PL2                 6.00 dB
PL12               25.40 dB
PL13               25.40 dB
SFO2         600.1324005 MHz
SI                 32768
SF           150.9028090 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

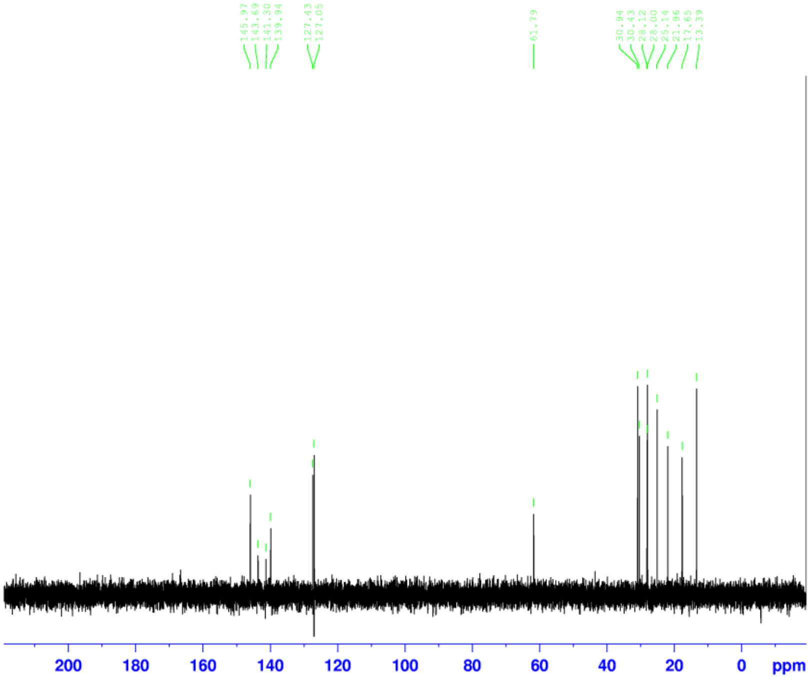
1-octyl-3-methylpyridinium bromide [C8MPy][Br]

C8MPY ; 1H spectrum in D2O



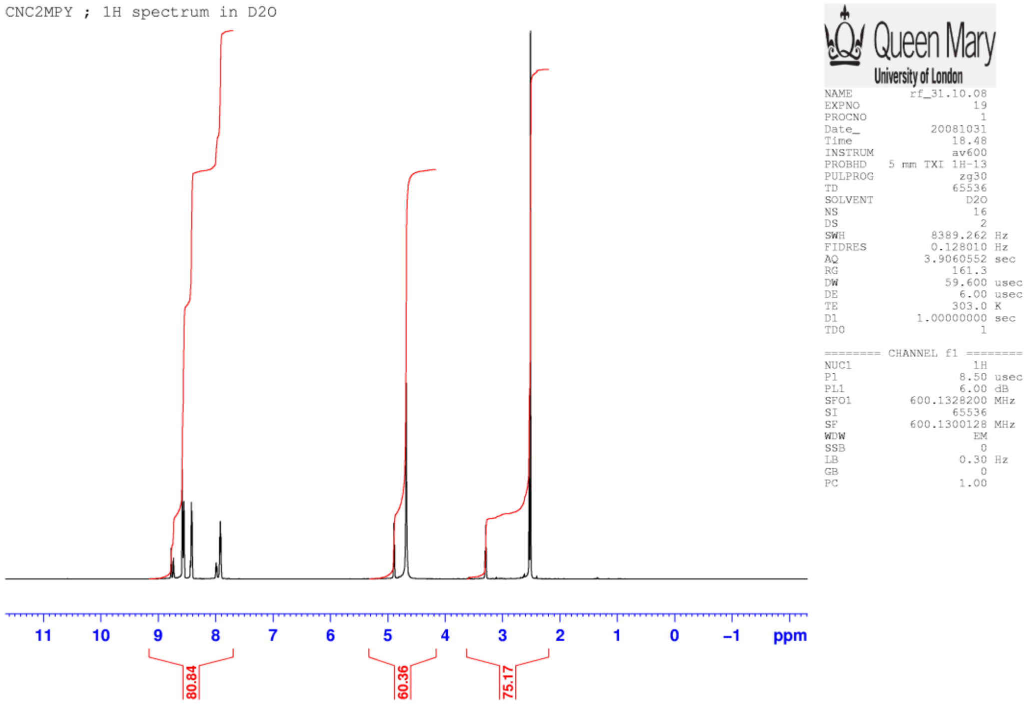
```
NAME             rf_31.10.08
EXPNO                     11
PROCNO                     1
Date_               20081031
Time                   16.24
INSTRUM                av600
PROBHD   5 mm TXI 1H-13
PULPROG                 zg30
TD                     65536
SOLVENT                  D2O
NS                        16
DS                         2
SWH                 8389.262 Hz
FIDRES              0.128010 Hz
AQ                 3.9060552 sec
RG                       128
DW                    59.600 usec
DE                      6.00 usec
TE                     303.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                      8.50 usec
PL1                     6.00 dB
SFO1             600.1328200 MHz
SI                     65536
SF               600.1300128 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

C8MPY ; 13C-{1H} spectrum in D2O

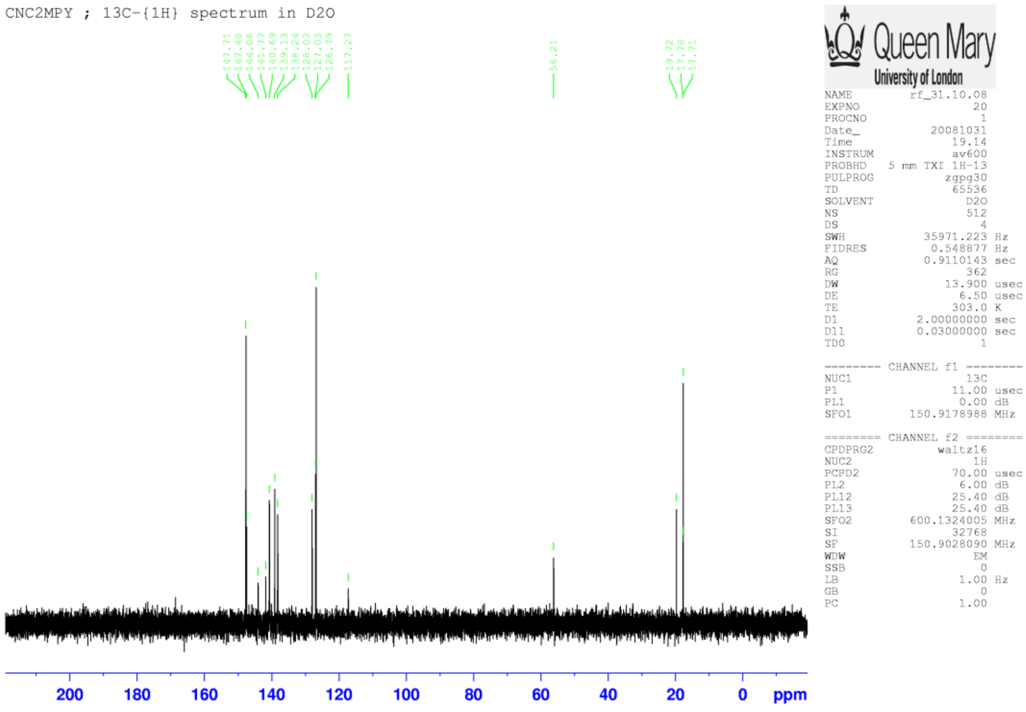


```
NAME             rf_31.10.08
EXPNO                     12
PROCNO                     1
Date_               20081031
Time                   16.50
INSTRUM                av600
PROBHD   5 mm TXI 1H-13
PULPROG               zgpg30
TD                     65536
SOLVENT                  D2O
NS                       512
DS                         4
SWH                35971.223 Hz
FIDRES              0.548877 Hz
AQ                 0.9110143 sec
RG                       362
DW                    13.900 usec
DE                      6.50 usec
TE                     303.0 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                     11.00 usec
PL1                     0.00 dB
SFO1             150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                  70.00 usec
PL2                     6.00 dB
PL12                   25.40 dB
PL13                   25.40 dB
SFO2             600.1324005 MHz
SI                     32768
SF               150.9028090 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

1-(2-cyanoethyl)-3-methylpyridinium bromide [CNC2MPy][Br]

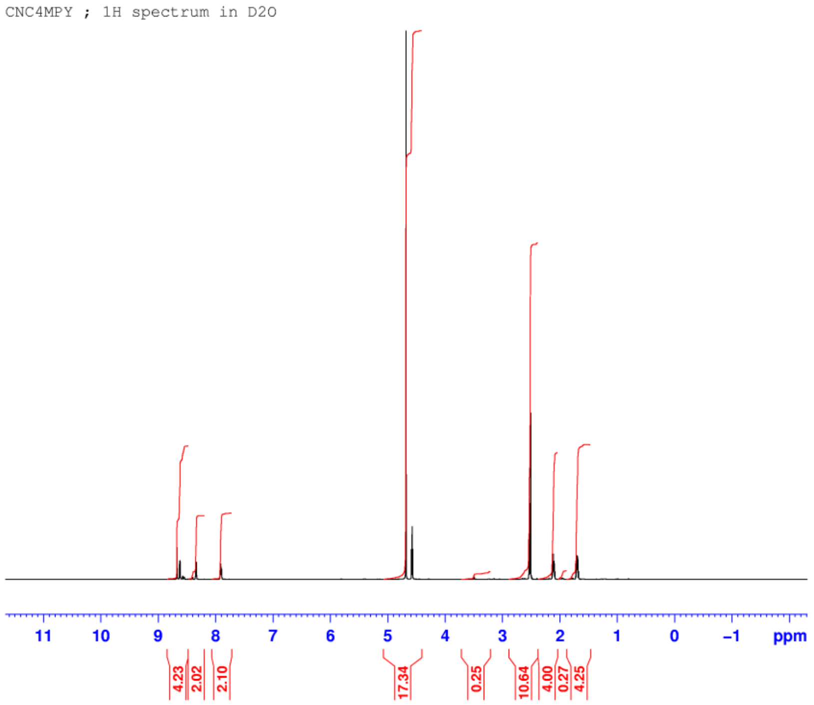


```
NAME          rf_31.10.08
EXPNO                  19
PROCNO                  1
Date_            20081031
Time                18.48
INSTRUM             av600
PROBHD   5 mm TXI 1H-13
PULPROG              zg30
TD                  65536
SOLVENT               D2O
NS                     16
DS                      2
SWH              8389.262 Hz
FIDRES           0.128010 Hz
AQ              3.9060552 sec
RG                  161.3
DW                 59.600 usec
DE                   6.00 usec
TE                  303.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.50 usec
PL1                  6.00 dB
SFO1          600.1328200 MHz
SI                  65536
SF            600.1300128 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

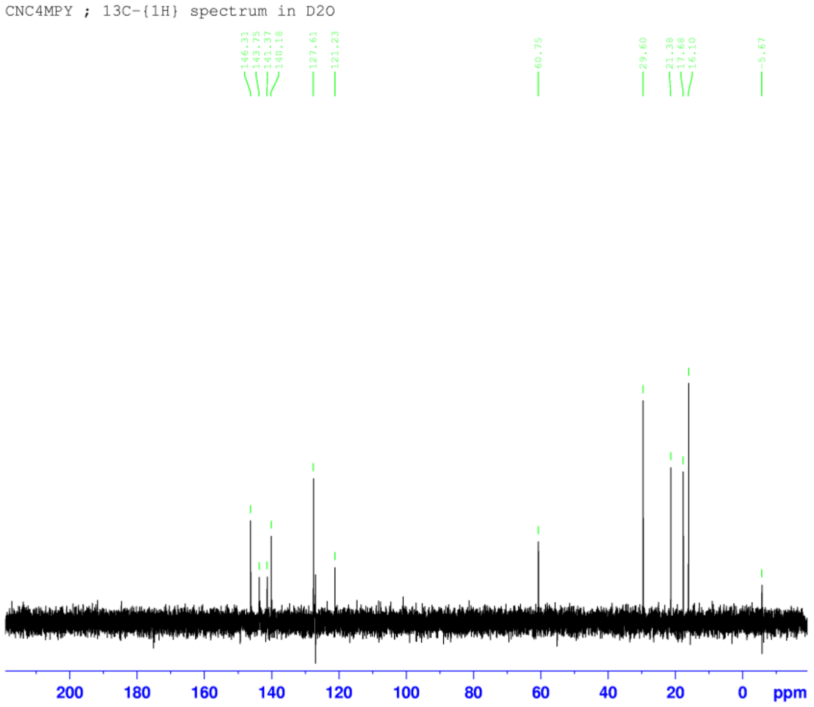


```
NAME          rf_31.10.08
EXPNO                  20
PROCNO                  1
Date_            20081031
Time                19.14
INSTRUM             av600
PROBHD   5 mm TXI 1H-13
PULPROG            zgpg30
TD                  65536
SOLVENT               D2O
NS                    512
DS                      4
SWH             35971.223 Hz
FIDRES           0.548877 Hz
AQ              0.9110143 sec
RG                    362
DW                 13.900 usec
DE                   6.50 usec
TE                  303.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

-------- CHANNEL f1 --------
NUC1                  13C
P1                  11.00 usec
PL1                  0.00 dB
SFO1          150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               70.00 usec
PL2                  6.00 dB
PL12                25.40 dB
PL13                25.40 dB
SFO2          600.1324005 MHz
SI                  32768
SF            150.9028090 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00
```

1-(4-cyanobutyl)-3-methylpyridinium bromide [CNC4MPy][Br]

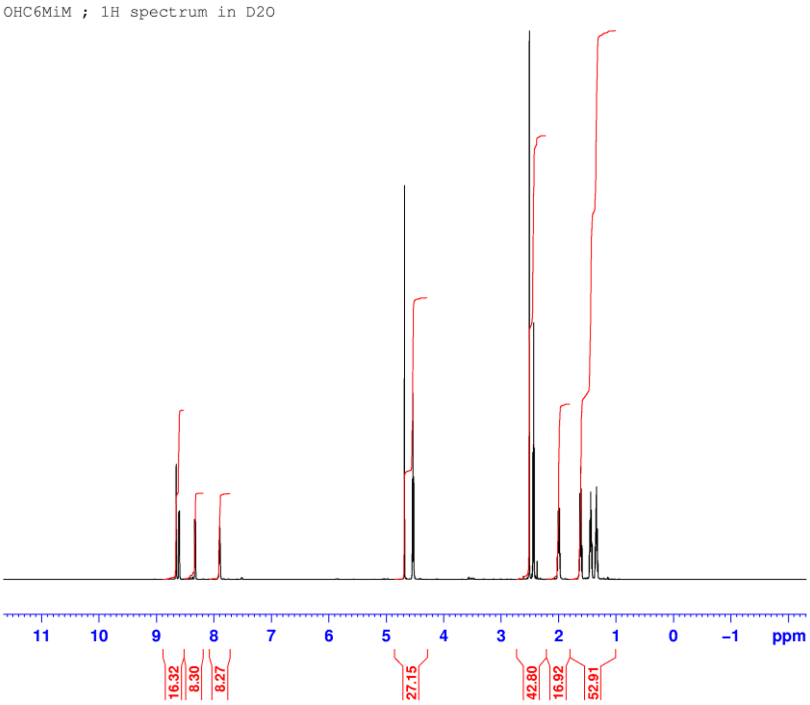

CNC4MPY ; 1H spectrum in D2O

```
NAME          rf_31.10.08
EXPNO                  21
PROCNO                  1
Date_            20081031
Time                19.24
INSTRUM             av600
PROBHD   5 mm TXI 1H-13
PULPROG              zg30
TD                  65536
SOLVENT               D2O
NS                     16
DS                      2
SWH              8389.262 Hz
FIDRES           0.128010 Hz
AQ              3.9060552 sec
RG                    181
DW                 59.600 usec
DE                   6.00 usec
TE                  303.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.50 usec
PL1                  6.00 dB
SFO1          600.1328200 MHz
SI                  65536
SF            600.1300128 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

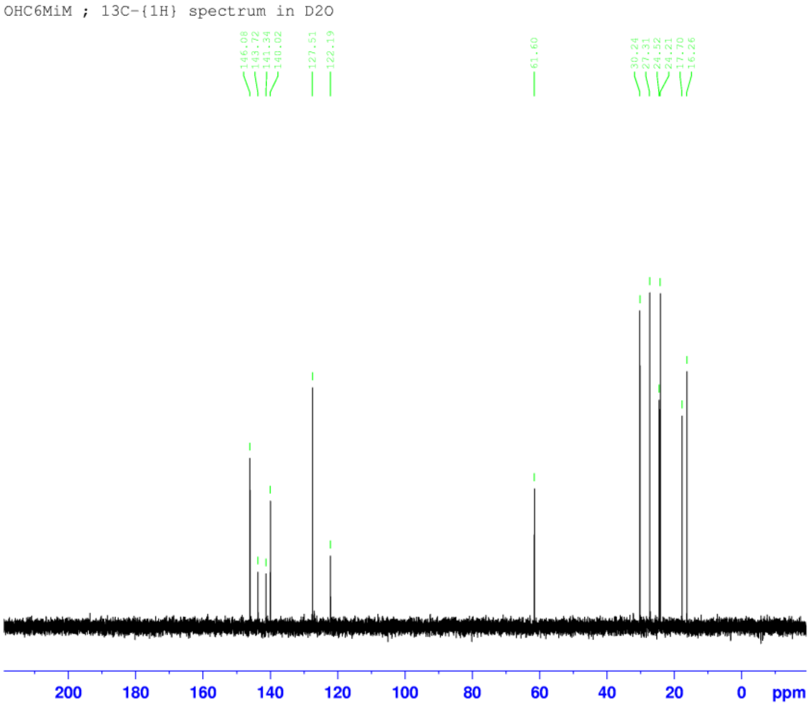

CNC4MPY ; 13C-{1H} spectrum in D2O

```
NAME          rf_31.10.08
EXPNO                  22
PROCNO                  1
Date_            20081031
Time                19.50
INSTRUM             av600
PROBHD   5 mm TXI 1H-13
PULPROG            zgpg30
TD                  65536
SOLVENT               D2O
NS                    512
DS                      4
SWH             35971.223 Hz
FIDRES           0.548877 Hz
AQ              0.9110143 sec
RG                    362
DW                 13.900 usec
DE                   6.50 usec
TE                  303.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

-------- CHANNEL f1 --------
NUC1                  13C
P1                  11.00 usec
PL1                  0.00 dB
SFO1          150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               70.00 usec
PL2                  6.00 dB
PL12                25.40 dB
PL13                25.40 dB
SFO2          600.1324005 MHz
SI                  32768
SF            150.9028090 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00
```

1-(6-cyanohexyl)-3-methylpyridinium bromide [CNC6MPy][Br]

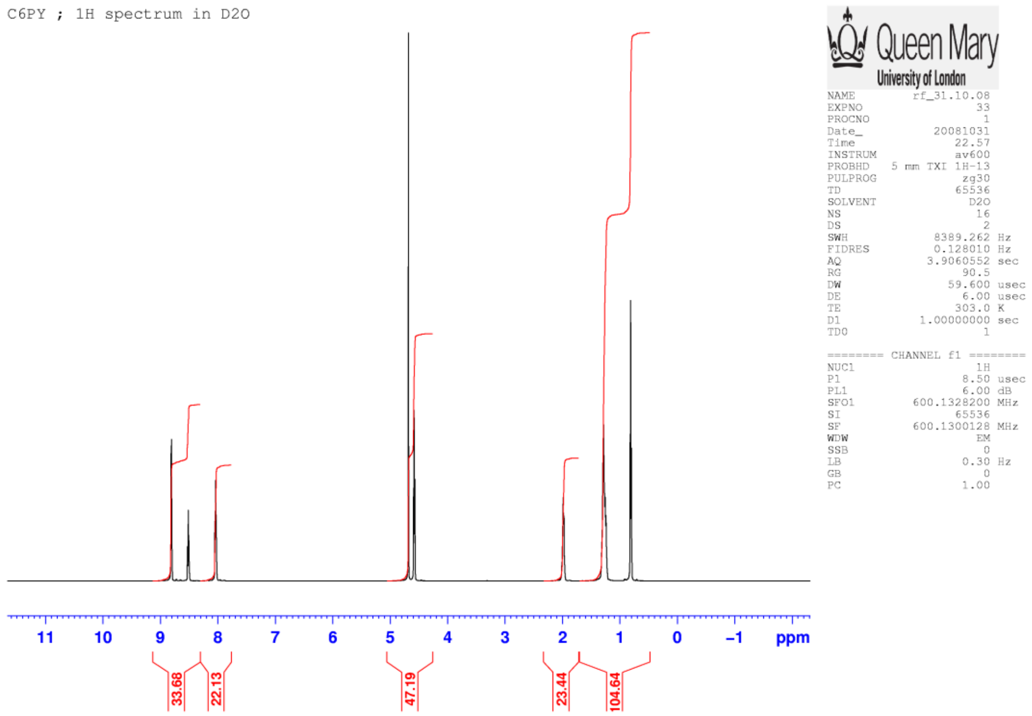


```
Queen Mary
University of London
NAME           rf_31.10.08
EXPNO                   29
PROCNO                   1
Date_             20081031
Time                 21.46
INSTRUM              av600
PROBHD    5 mm TXI 1H-13
PULPROG               zg30
TD                   65536
SOLVENT                D2O
NS                      16
DS                       2
SWH               8389.262 Hz
FIDRES            0.128010 Hz
AQ               3.9060552 sec
RG                    90.5
DW                  59.600 usec
DE                    6.00 usec
TE                   303.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    8.50 usec
PL1                   6.00 dB
SFO1           600.1328200 MHz
SI                   65536
SF             600.1300128 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

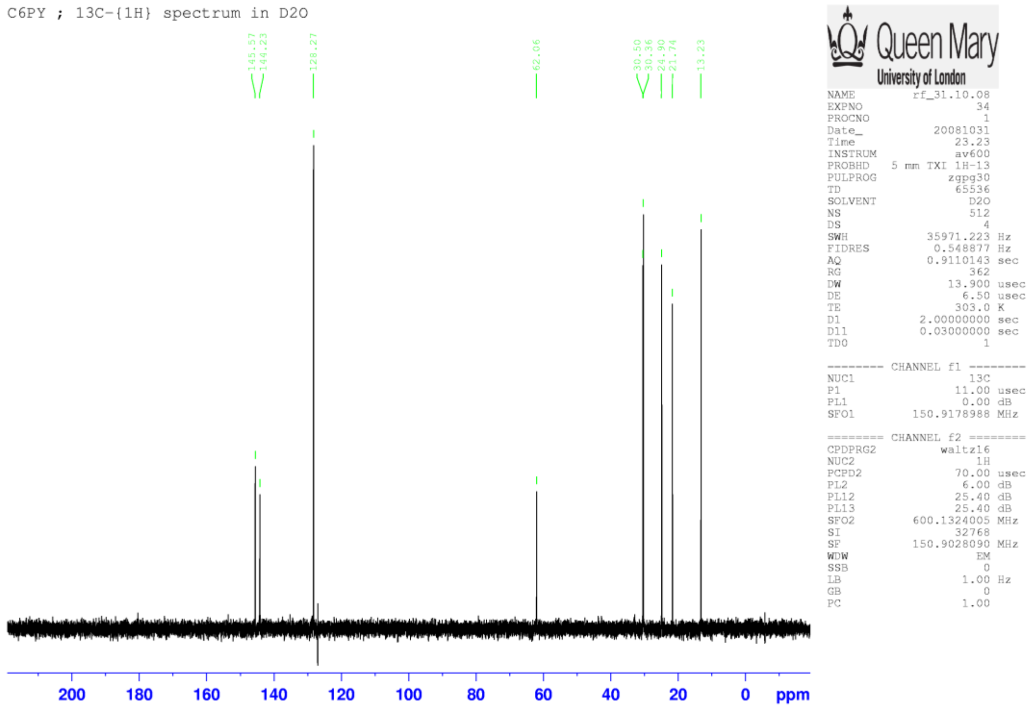


```
Queen Mary
University of London
NAME           rf_31.10.08
EXPNO                   30
PROCNO                   1
Date_             20081031
Time                 22.12
INSTRUM              av600
PROBHD    5 mm TXI 1H-13
PULPROG             zgpg30
TD                   65536
SOLVENT                D2O
NS                     512
DS                       4
SWH              35971.223 Hz
FIDRES            0.548877 Hz
AQ               0.9110143 sec
RG                     362
DW                  13.900 usec
DE                    6.50 usec
TE                   303.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

-------- CHANNEL f1 --------
NUC1                   13C
P1                   11.00 usec
PL1                   0.00 dB
SFO1           150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                   6.00 dB
PL12                 25.40 dB
PL13                 25.40 dB
SFO2           600.1324005 MHz
SI                   32768
SF             150.9028090 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.00
```

1-hexylpyridinium bromide [C6Py][Br]



```
NAME          rf_31.10.08
EXPNO                  33
PROCNO                  1
Date_            20081031
Time                22.57
INSTRUM             av600
PROBHD   5 mm TXI 1H-13
PULPROG              zg30
TD                  65536
SOLVENT               D2O
NS                     16
DS                      2
SWH              8389.262 Hz
FIDRES           0.128010 Hz
AQ              3.9060552 sec
RG                   90.5
DW                 59.600 usec
DE                   6.00 usec
TE                  303.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.50 usec
PL1                  6.00 dB
SFO1          600.1328200 MHz
SI                  65536
SF            600.1300128 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

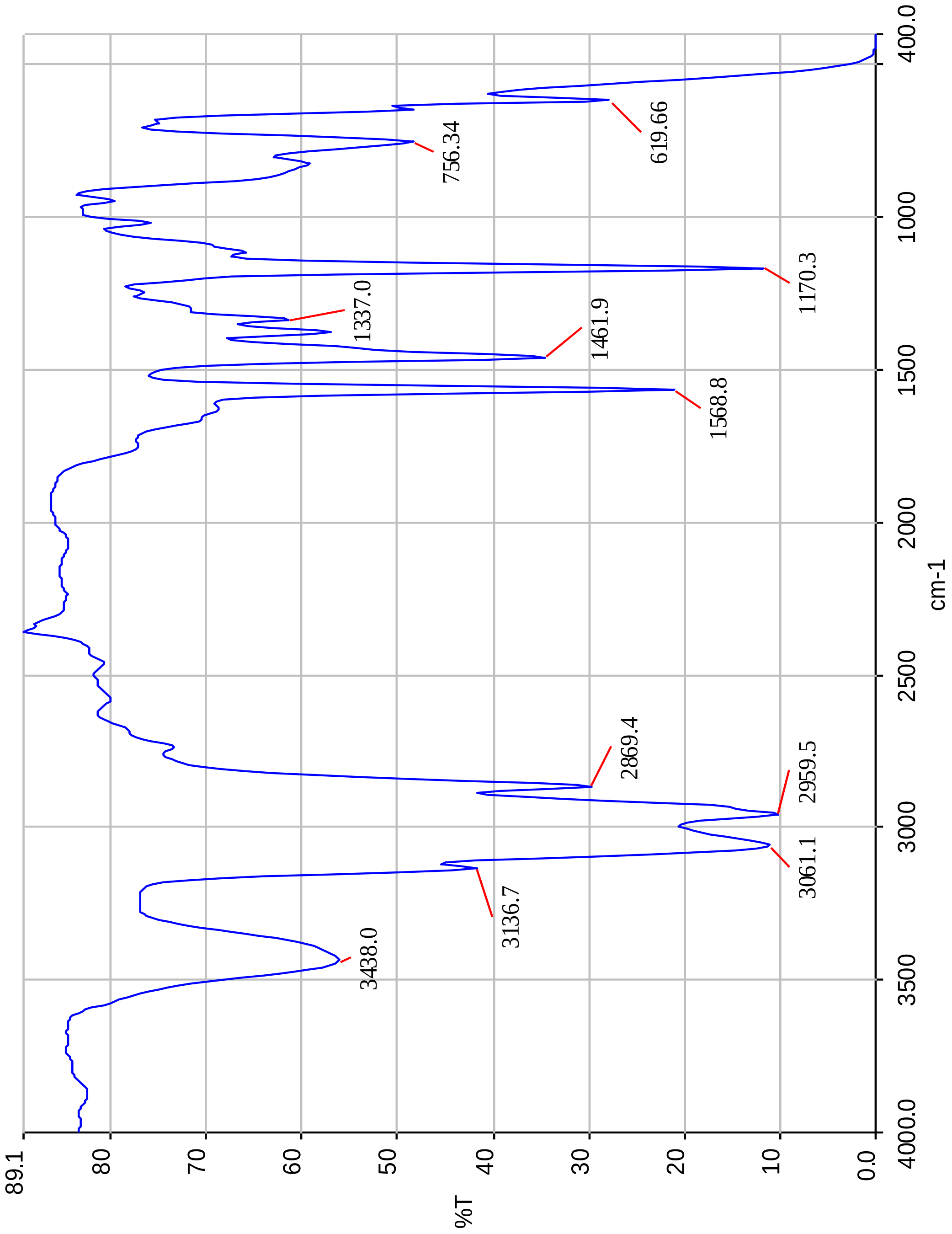


```
NAME          rf_31.10.08
EXPNO                  34
PROCNO                  1
Date_            20081031
Time                23.23
INSTRUM             av600
PROBHD   5 mm TXI 1H-13
PULPROG            zgpg30
TD                  65536
SOLVENT               D2O
NS                    512
DS                      4
SWH             35971.223 Hz
FIDRES           0.548877 Hz
AQ              0.9110143 sec
RG                    362
DW                 13.900 usec
DE                   6.50 usec
TE                  303.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  11.00 usec
PL1                  0.00 dB
SFO1          150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               70.00 usec
PL2                  6.00 dB
PL12                25.40 dB
PL13                25.40 dB
SFO2          600.1324005 MHz
SI                  32768
SF            150.9028090 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00
```

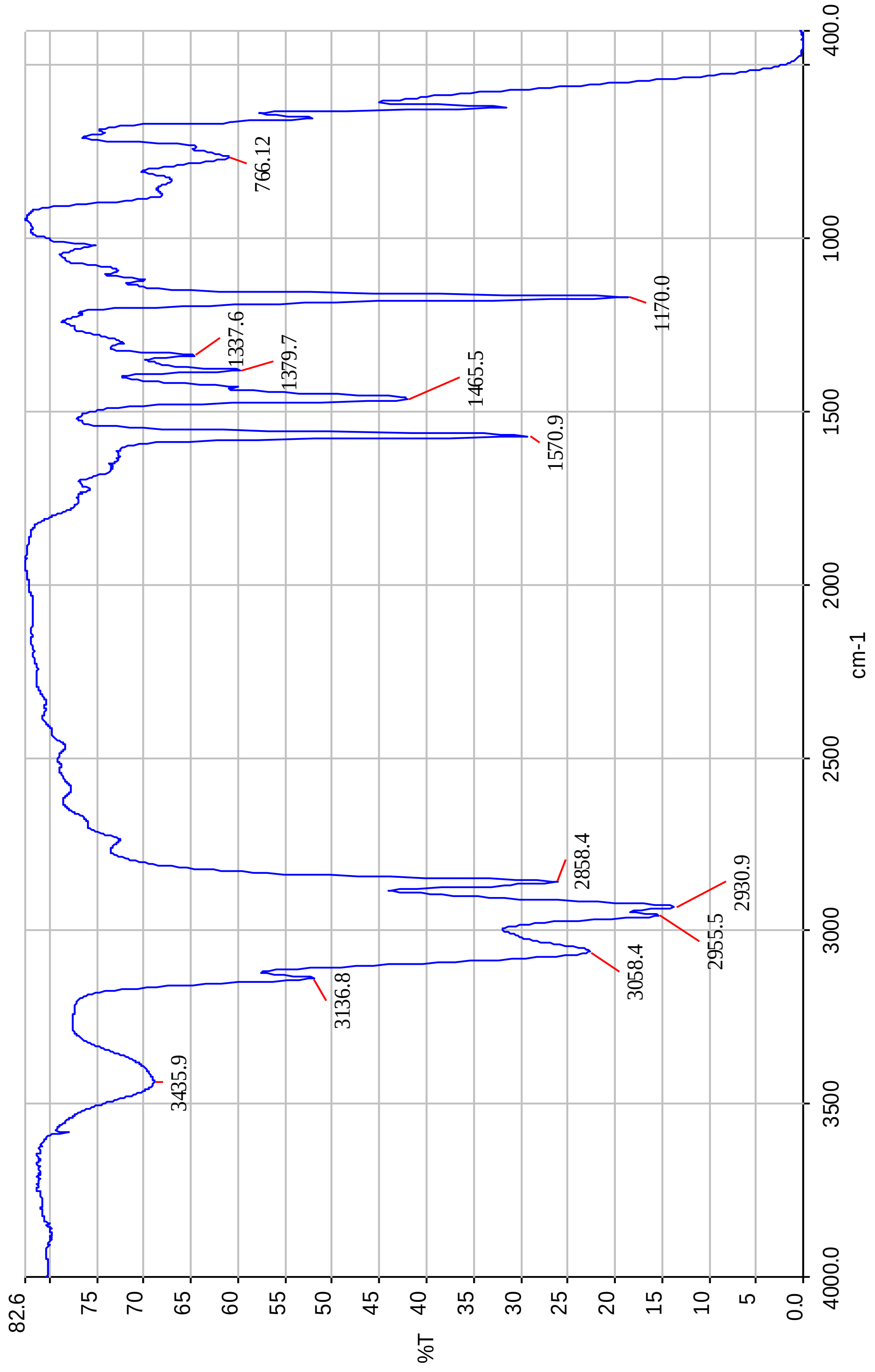
Annex C: Infrared spectra of the ionic liquids

C.1 Imidazolium-based ILs

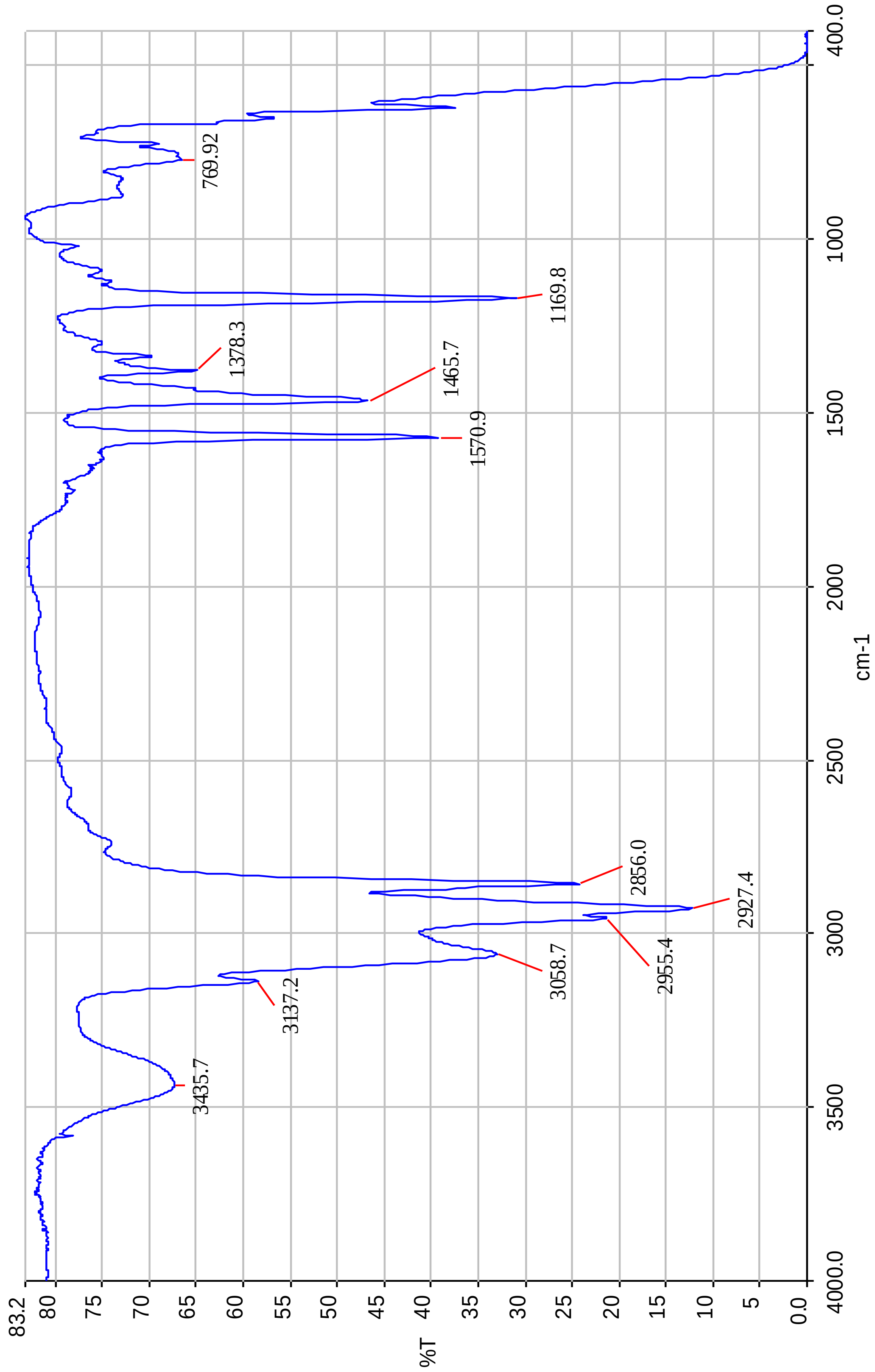
1-butyl-3-methyl imidazolium bromide [C4MIM][Br]



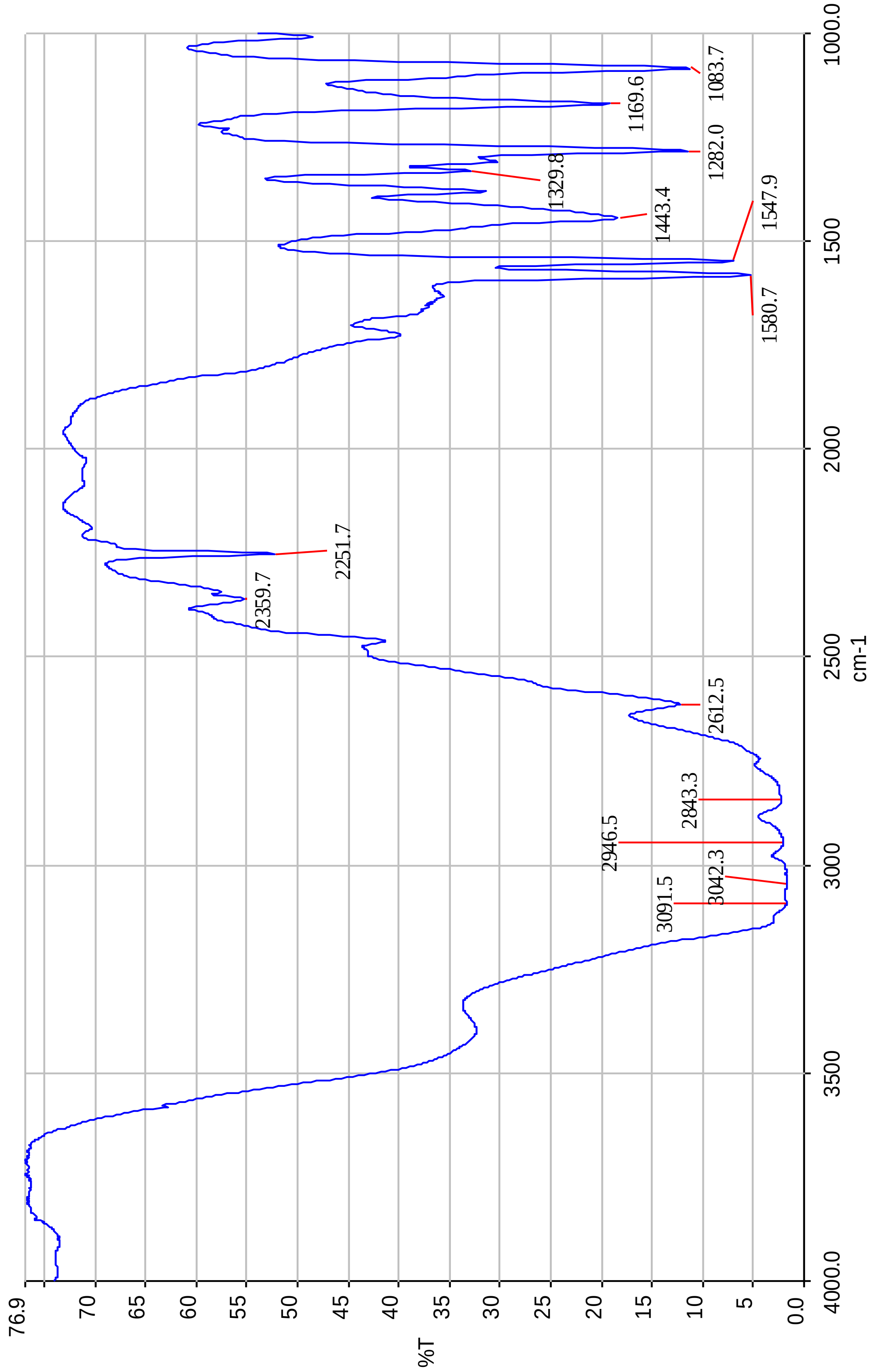
1-hexyl-3-methyl imidazolium bromide [C6MIM][Br]



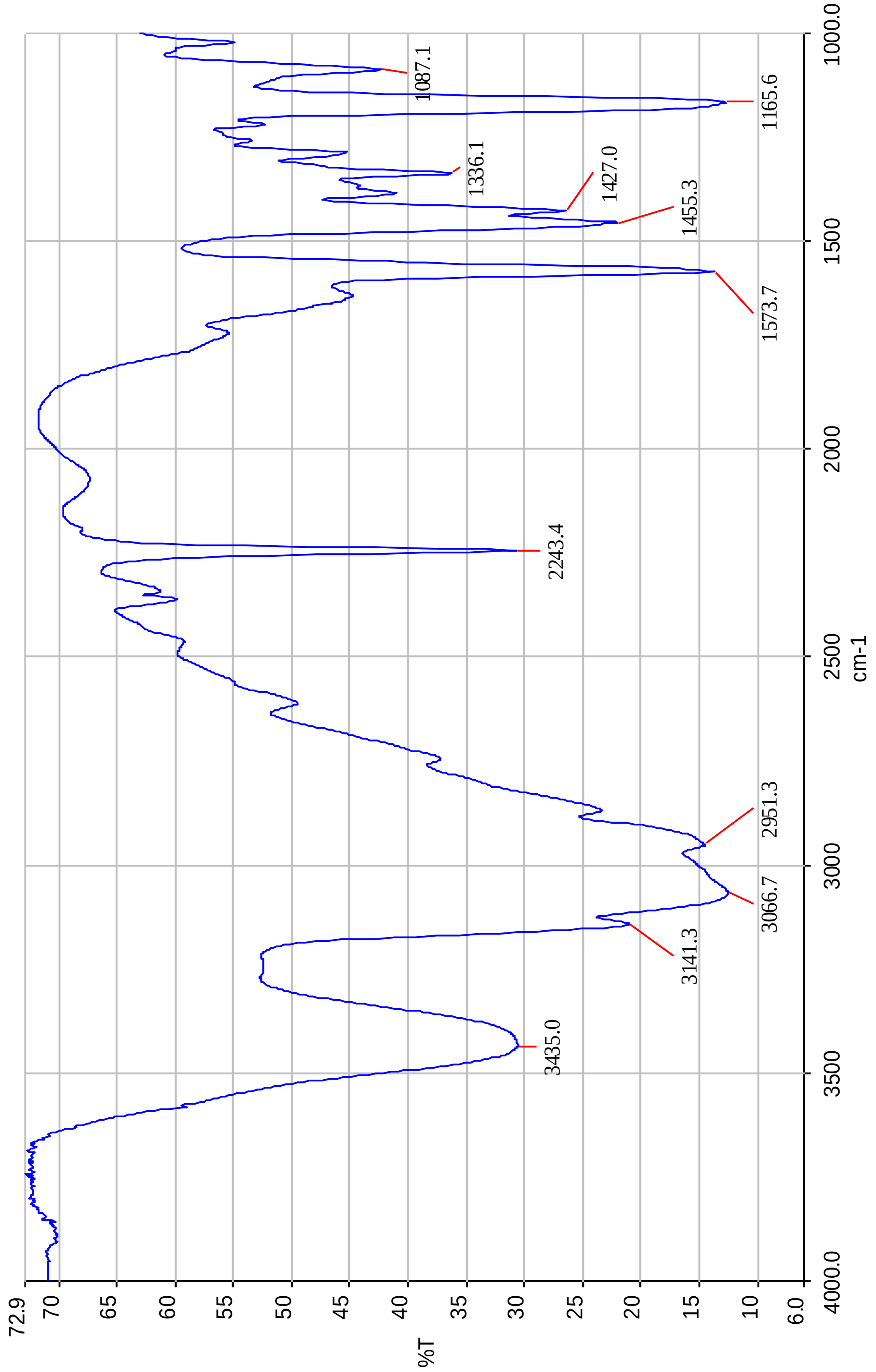
1-octyl-3-methyl imidazolium bromide [C8MIM][Br]



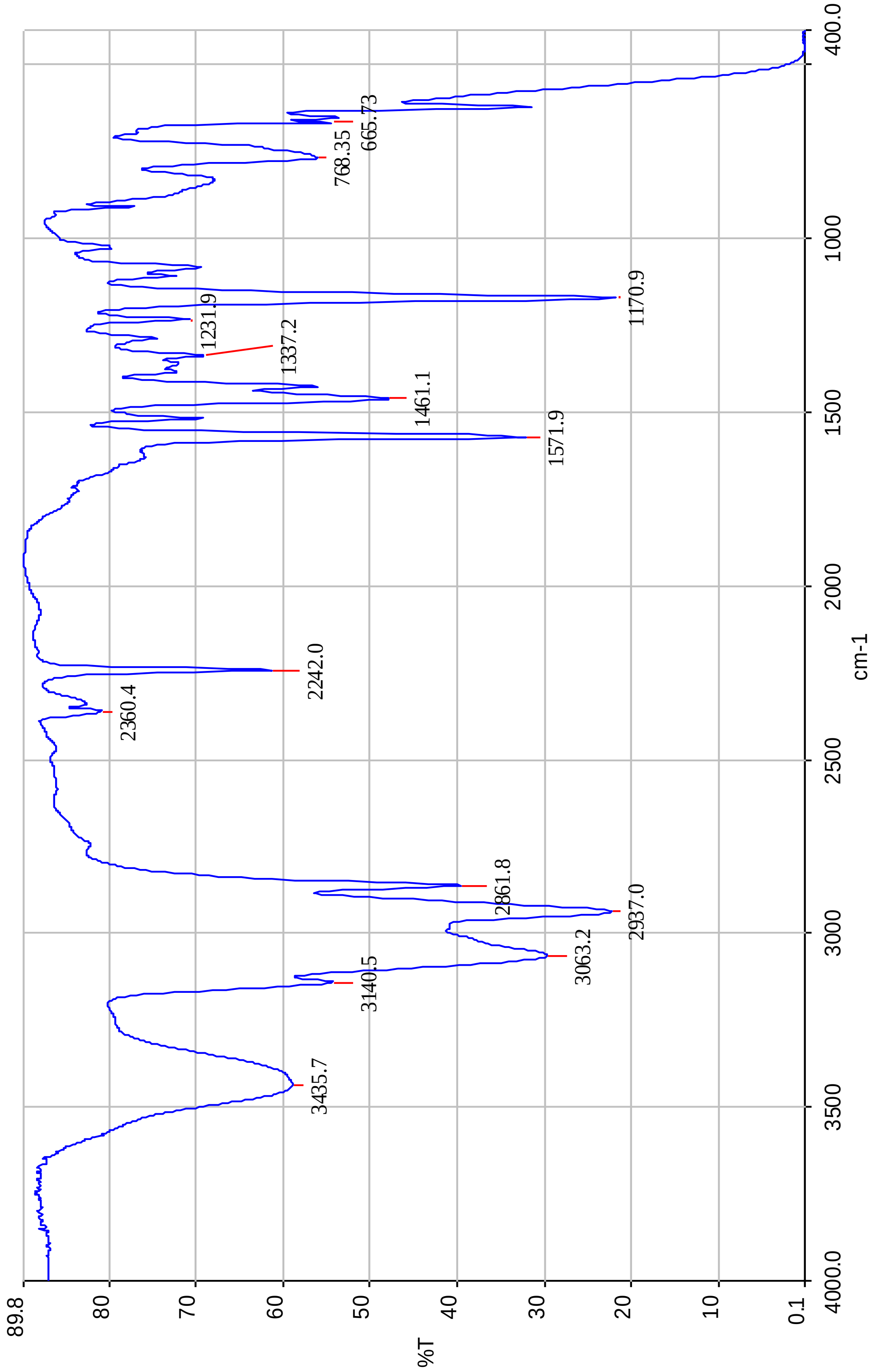
1-(2-cyanoethyl)-3-methylimidazolium bromide [CNC2MIM][Br]



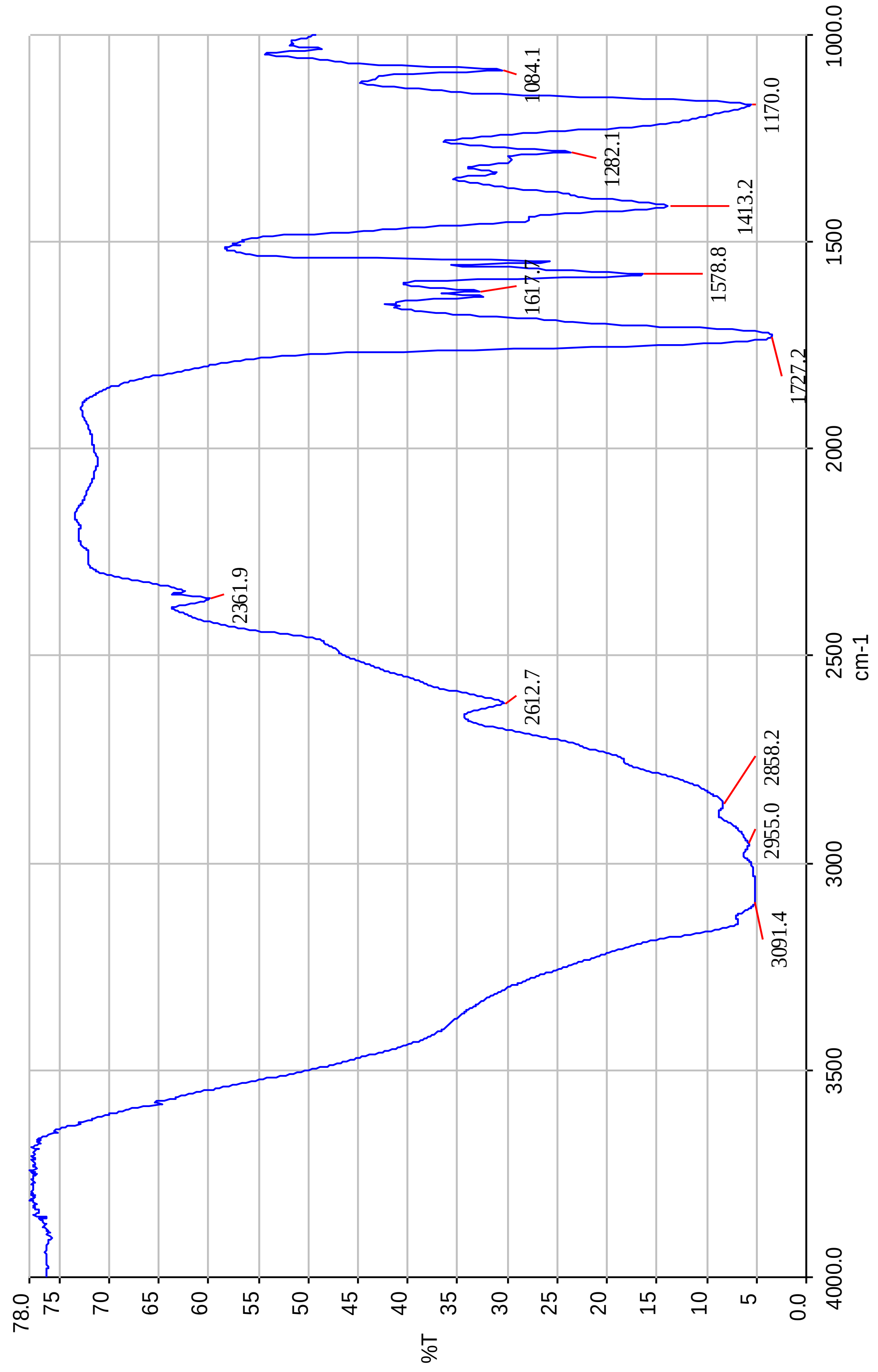
1-(4-cyanobutyl)-3-methylimidazolium bromide [CNC4MIM][Br]



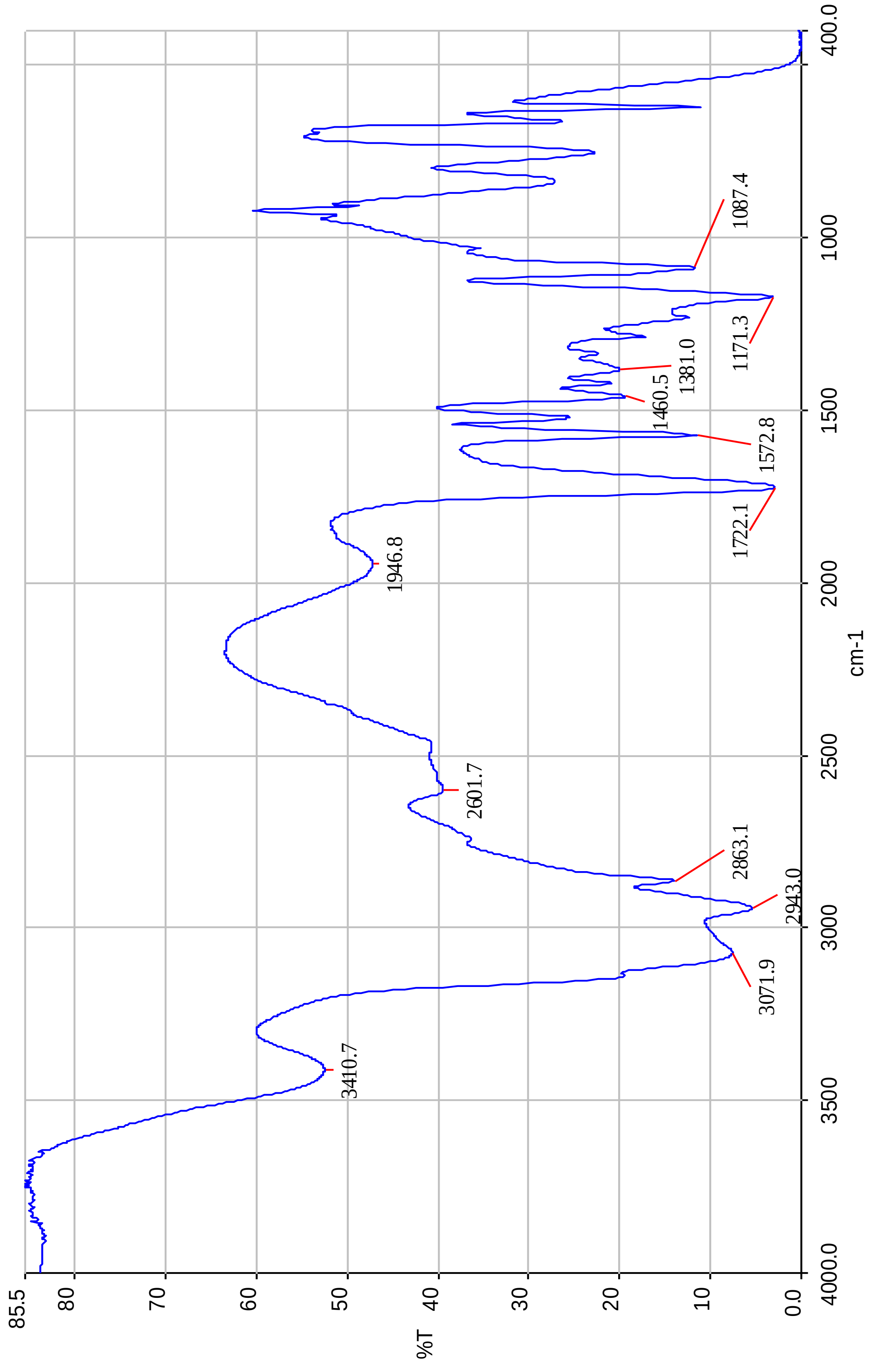
1-(6-cyanohexyl)-3-methylimidazolium bromide [CNC6MIM][Br]



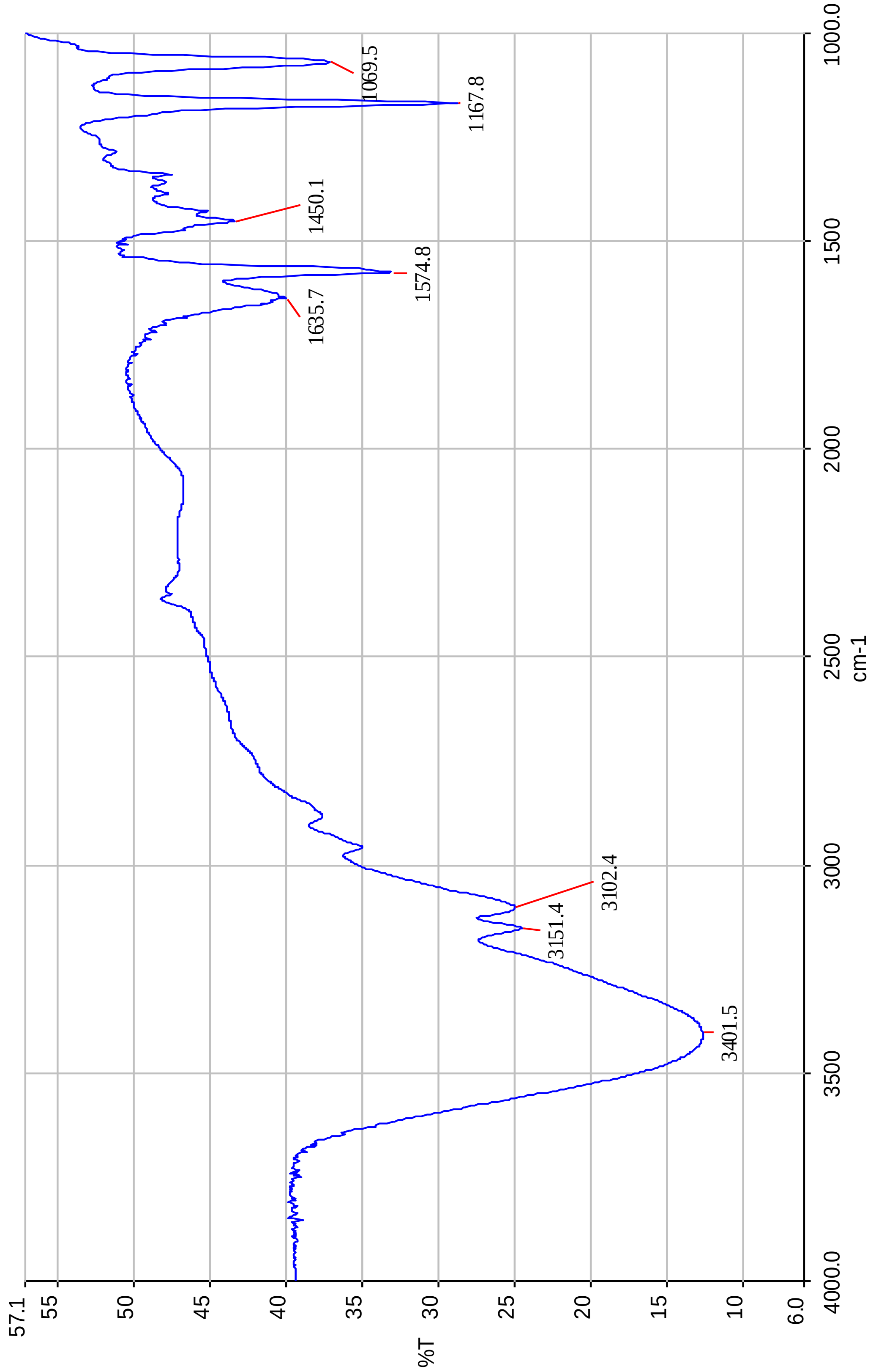
1-(2-carboxyethyl)-3-methylimidazolium bromide [COOHC2MIM][Br]



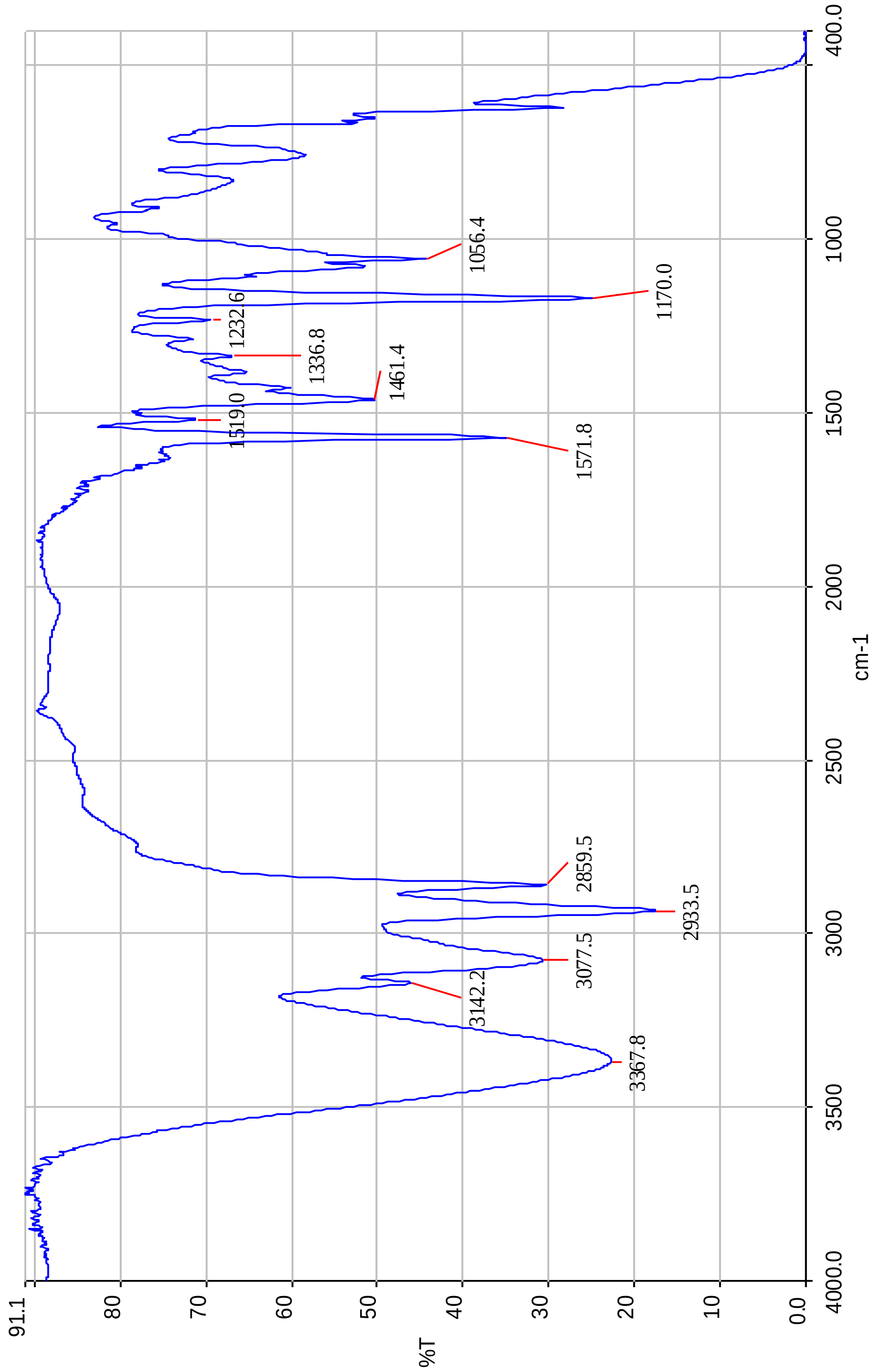
1-(5-carboxypentyl)-3-methylimidazolium bromide [COOHC5MIM][Br]



1-(2-hydroxyethyl)-3-methylimidazolium bromide [OHC2MIM][Br]

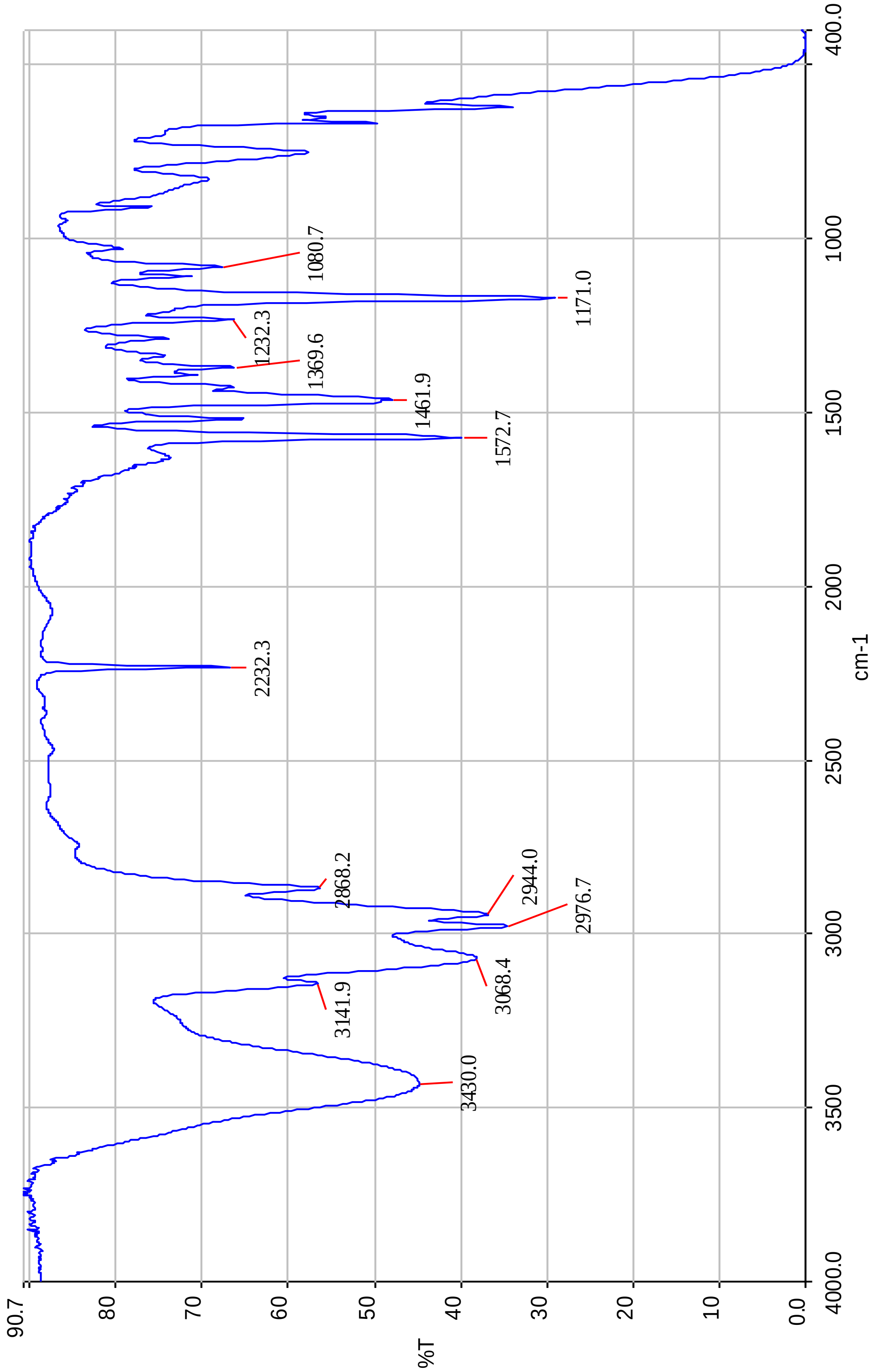


1-(6-hydroxyhexyl)-3-methylimidazolium bromide [OHC6MIM][Br]



1-(5-cyano-(5,5-dimethyl)pentyl)-3-methylimidazolium bromide

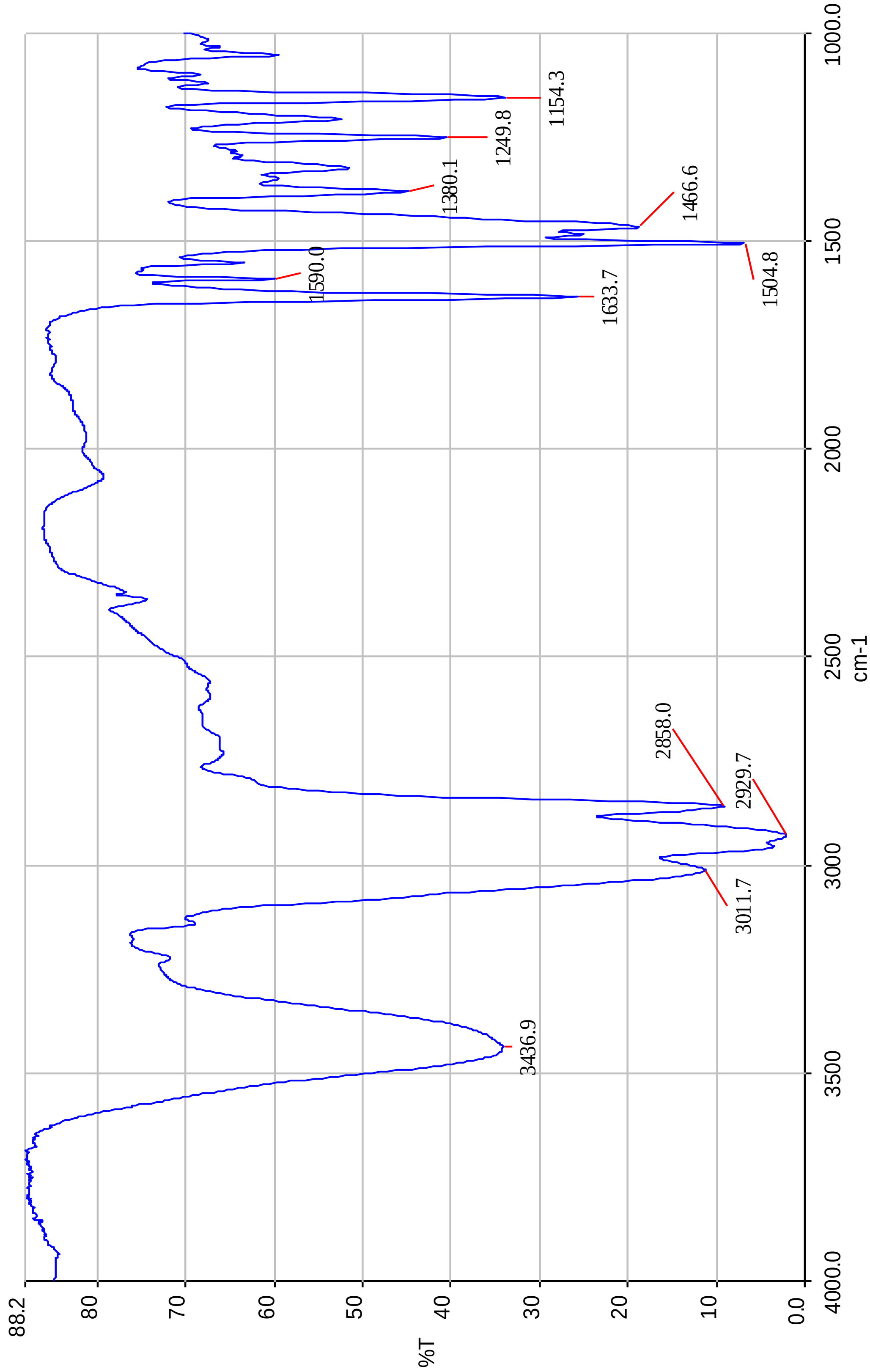
[CN(CH$_2$)$_2$C5MIM][Br]



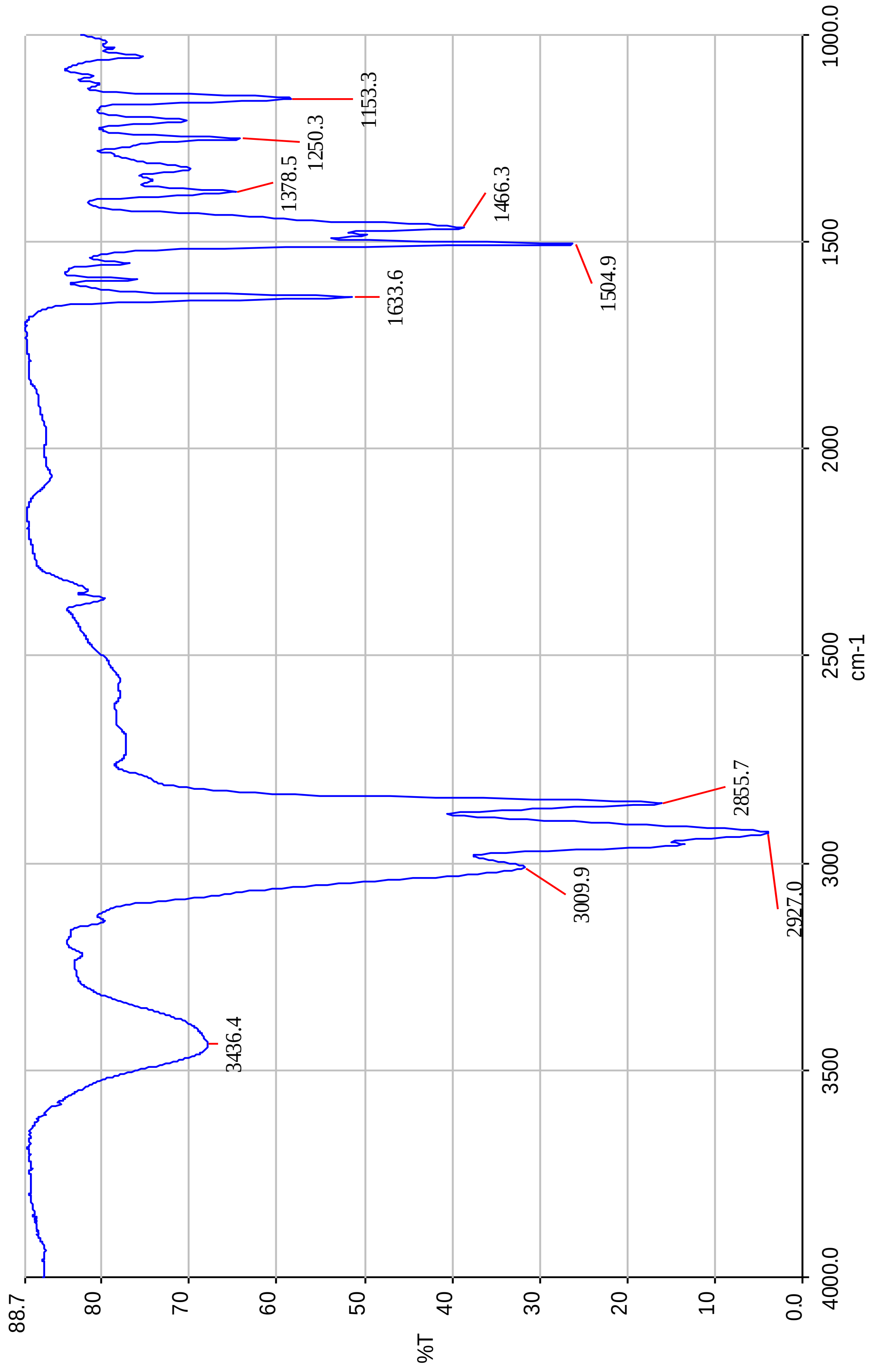
C.2 Pyridinium-based ILs

1-butyl-3-methylpyridinium bromide [C4MPy][Br]

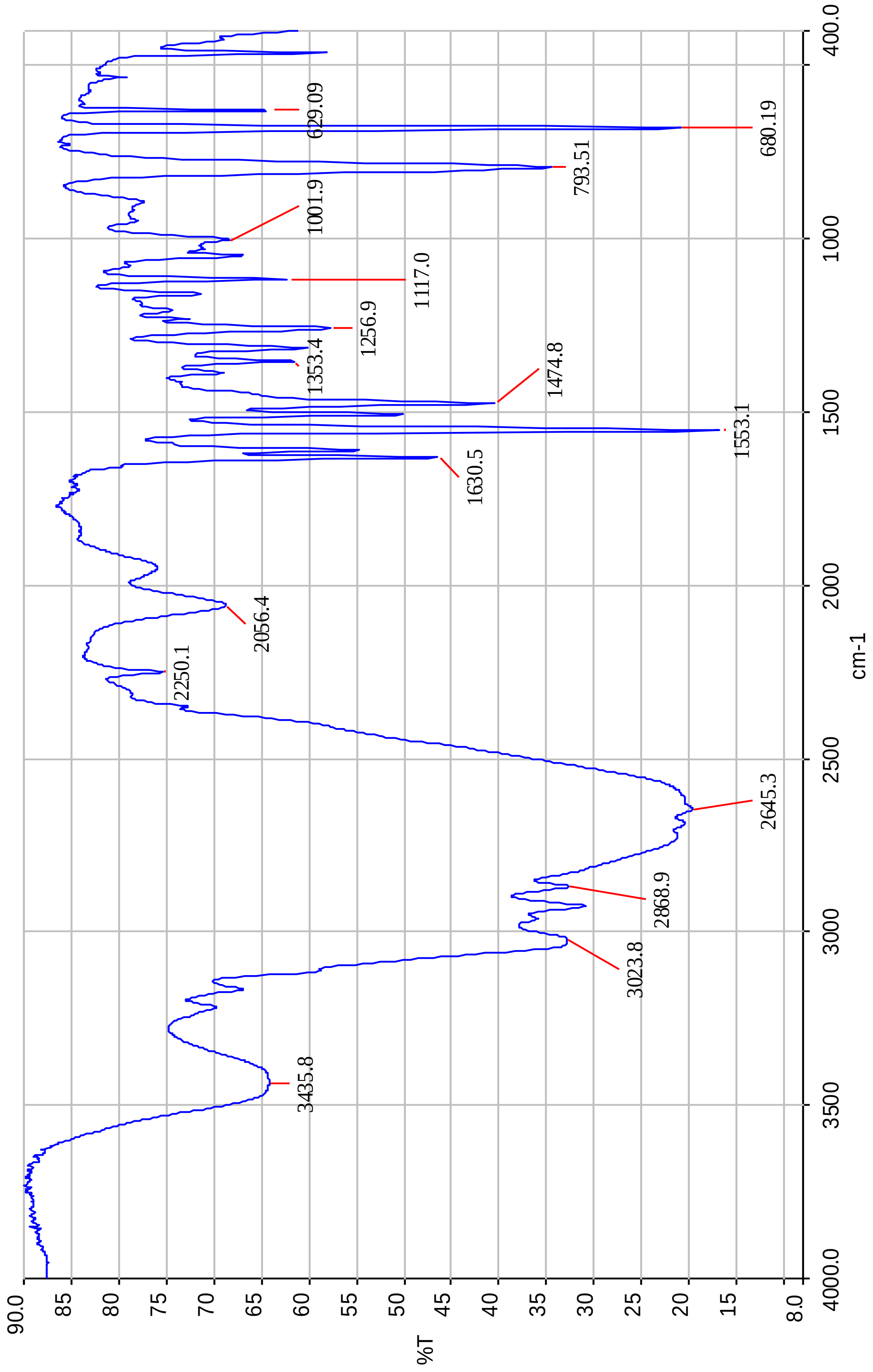
1-hexyl-3-methylpyridinium bromide [C6MPy][Br]



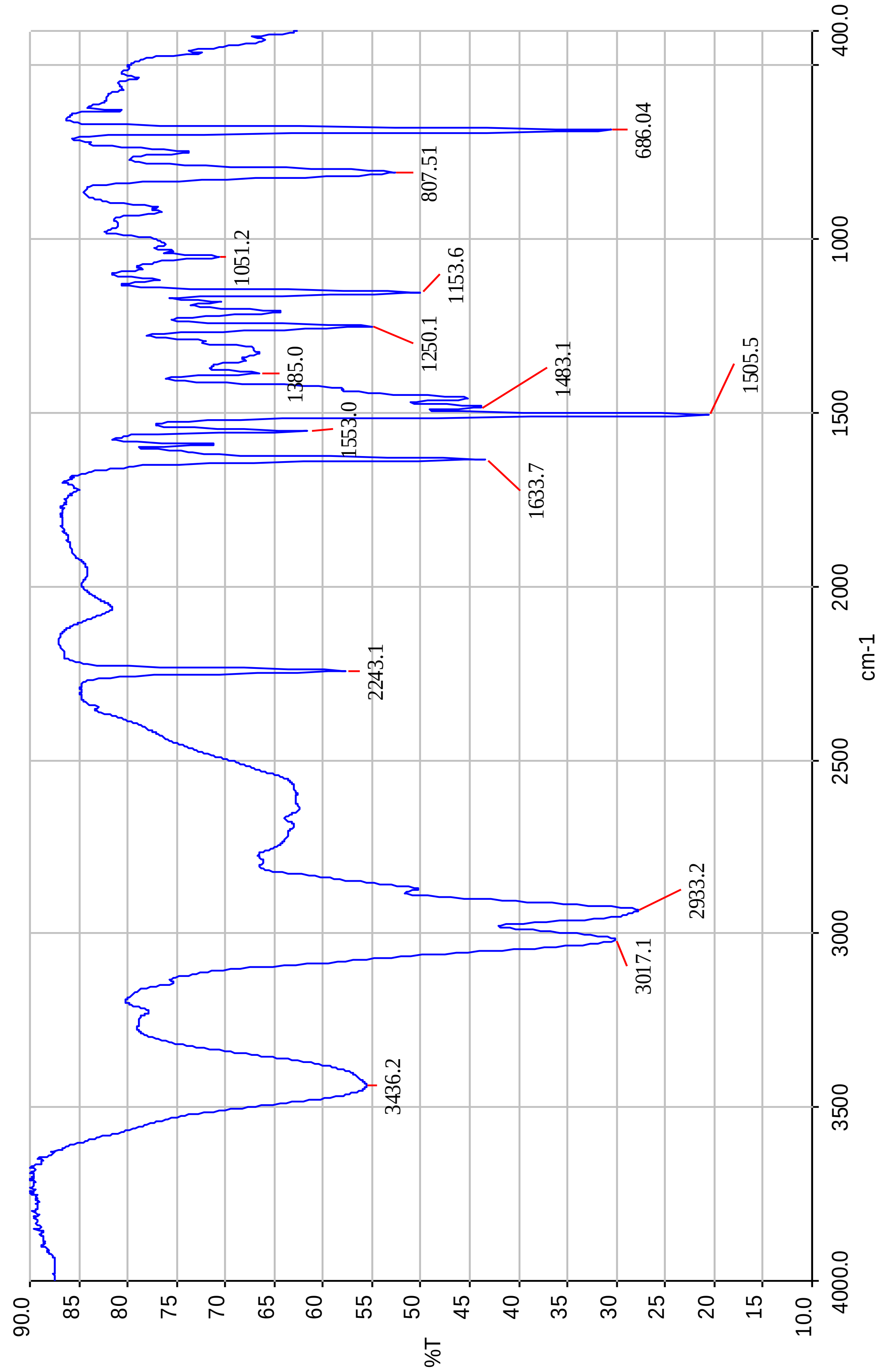
1-octyl-3-methylpyridinium bromide [C8MPy][Br]



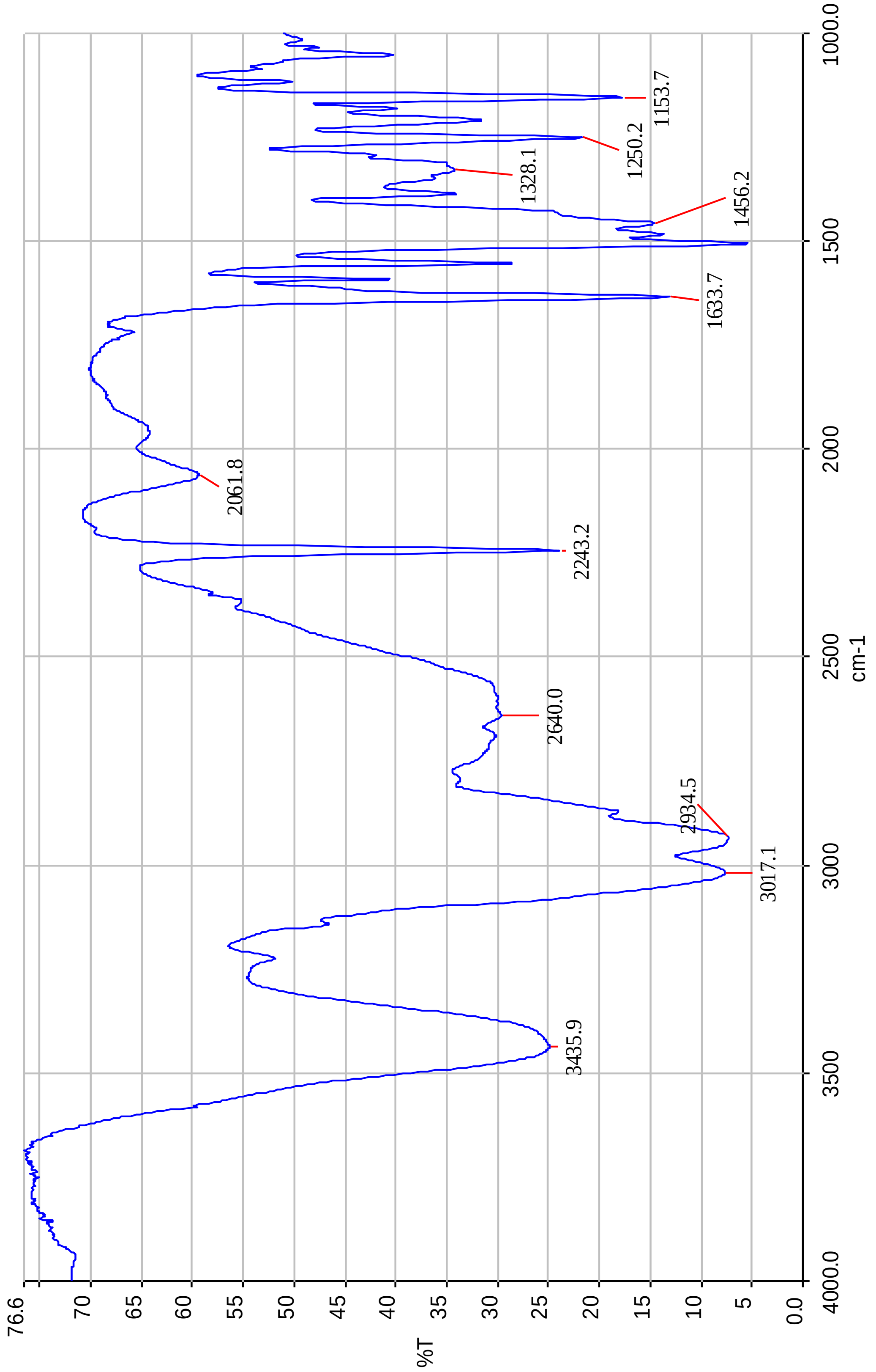
1-(2-cyanoethyl)-3-methylpyridinium bromide [CNC2MPy][Br]



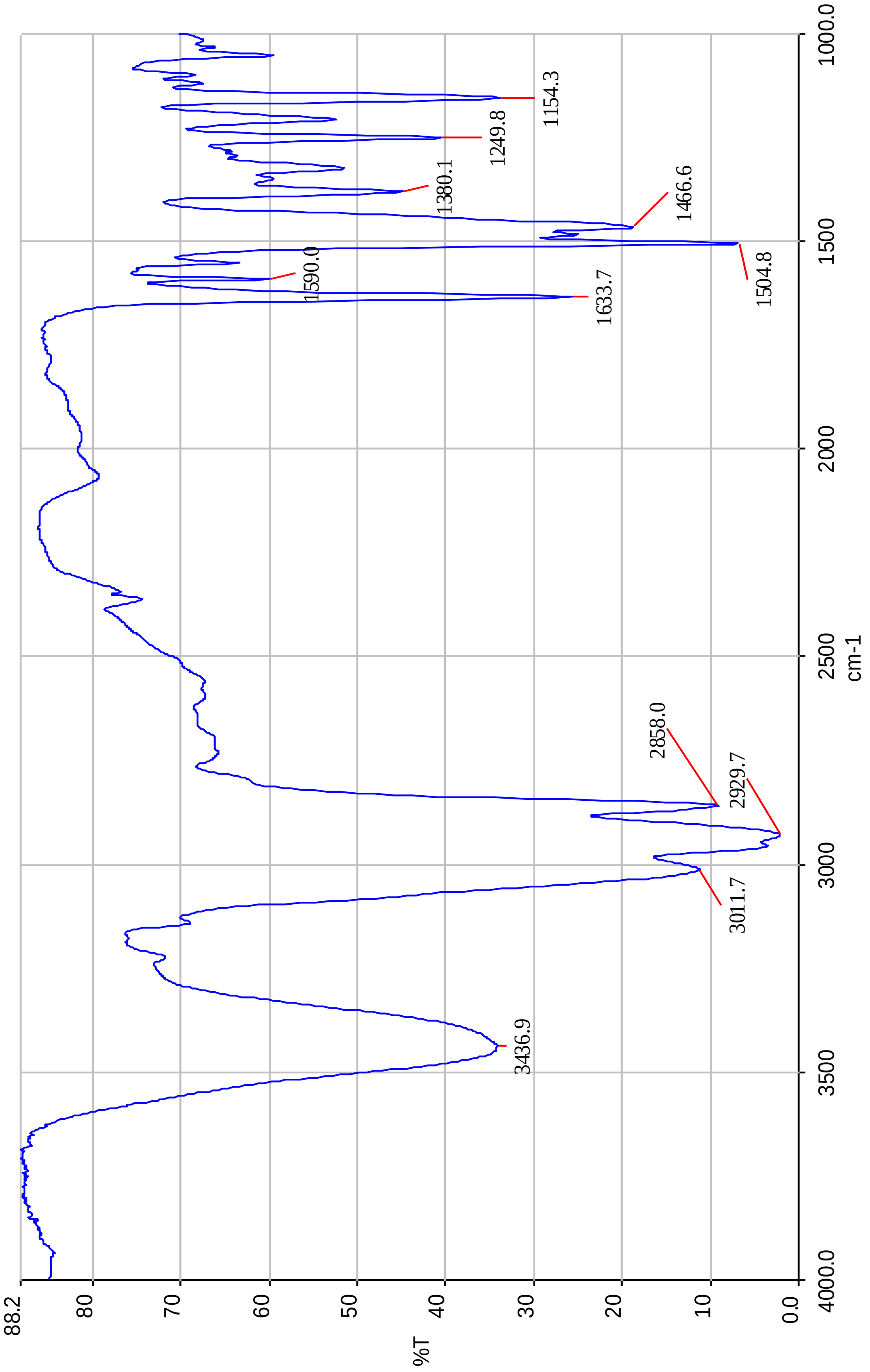
1-(4-cyanobutyl)-3-methylpyridinium bromide [CNC4MPy][Br]



1-(6-cyanohexyl)-3-methylpyridinium bromide [CNC6MPy][Br]



1-hexylpyridinium bromide [C6Py][Br]



Annex E: Hydrophobicity of IL: measurement of k’

This annex aims at reporting the retention times of the ILs at different eluent composition (Table I) in order to quantify the hydrophobicity, and compare it to the logarithm of the octanol/water partition coefficient, logP, calculated using a prediction software. The retention factor k’, as defined in Section 2.4.4.1, was calculated and its logarithm was extrapolated at 0% methanol (Table II) to only account for hydrophobic interactions of the solute (IL) with the stationary phase.

Table I: Retention time of the IL at various solvent compositions (two replicates)

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Table II: log k’and regression of log k’ at 0% MeOH

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The grey zone in Table I and Table II indicated that the corresponding percentage of eluent has not been tested, either because the retention time would have been too long or too short to be measured accurately.

Annex E: CuO dissolution: raw results and calculation

This annex aims at reporting the copper concentrations, as given by FAAS, and the method of calculation that led to the determination of the concentration of copper in the ionic liquids.

FAAS concentration values for dissolution of CuO diluted in water (or acetonitrile) are reported in Table III and Table IV, along with dilution factor (DF) and calculated concentration of copper in the IL.

Table III: Experimental values from the dissolution experiments of CuO in water

Sample	*[Cu] (mg.L^{-1})*	*DF*	*Initial Volume (ml)*	*mIL (g)*	*[Cu] in IL (mg per g)*	*Mw (IL)*	*[Cu] in IL (mol%)*
blank	0.0	100	100	2.001	0.1	219.1	0.0
[C4MIM][Br]	0.3	100	100	2.081	1.6	219.1	0.6
[C6MIM][Br]	0.2	100	100	2.044	0.8	247.2	0.3
[C8MIM][Br]	0.2	100	100	2.074	1.0	275.2	0.4
[CNC2MIM][Br]	4.9	100	100	2.279	21.6	216.1	7.3
[CNC4MIM][Br]	0.3	100	100	2.094	1.5	244.2	0.6
[CNC6MIM][Br]	0.2	100	100	1.994	0.9	272.2	0.4
$[CN(CH_2)_2C5MIM]$ *[Br]*	0.2	100	100	2.106	1.0	286.2	0.5
[COOHC2MIM][Br]	3.1	100	100	2.204	13.9	235.1	5.2
[COOHC5MIM][Br]	0.2	100	100	2.607	0.9	277.2	0.4
[OHC2MIM][Br]	1.9	100	100	2.018	9.3	207.1	3.0
[OHC6MIM][Br]	0.2	100	100	2.106	0.7	263.2	0.3
[C6MPy][Br]	0.2	100	100	2.070	1.0	258.2	0.4
[CNC2MPy][Br]	1.9	100	100	2.094	9.2	227.1	3.3
[CNC4MPy][Br]	0.5	100	100	2.105	2.4	255.2	1.0
[CNC6MPy][Br]	2.4	10	100	2.014	1.2	283.2	0.5
blank	0.0	100	100	1.997	0.2	219.1	0.1
[C4MIM][Br]	0.3	100	100	2.148	1.2	219.1	0.4
[C6MIM][Br]	0.2	100	100	2.118	0.9	247.2	0.4
[C8MIM][Br]	0.2	100	100	1.891	1.3	275.2	0.6
[CNC2MIM][Br]	5.2	100	100	2.244	23.2	216.1	7.9
[CNC4MIM][Br]	0.4	100	100	2.299	1.6	244.2	0.6
[CNC6MIM][Br]	0.2	100	100	2.126	1.0	272.2	0.4
[CN(CH2)2C5MIM] [Br]	0.2	100	100	2.215	0.8	286.2	0.3
[COOHC2MIM][Br]	2.8	100	100	2.015	13.8	235.1	5.1
[COOHC5MIM][Br]	0.3	100	100	2.837	1.0	277.2	0.4
[OHC2MIM][Br]	2.2	100	100	1.849	12.1	207.1	3.9
[OHC6MIM][Br]	0.1	100	100	2.042	0.6	263.2	0.3
[C6MPy][Br]	0.1	100	100	2.227	0.7	258.2	0.3
[CNC2MPy][Br]	1.7	100	100	2.184	7.8	227.1	2.8
[CNC4MPy][Br]	0.6	100	100	2.039	3.0	255.2	1.2
[CNC6MPy][Br]	2.0	10	100	2.014	1.0	283.2	0.5

Table IV: Experimental values from the dissolution experiments of CuO in acetonitrile

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The calculation of the concentration of copper in the IL was done using Equation I for the massic concentration of CuO ($mg.g^{-1}$) or Equation II for the molar concentration of copper.

$$[CuO] = \frac{C \times \frac{M_{CuO}}{M_{Cu}} \times DF \times V}{m_{IL}}$$

Equation I

$$[Cu] = \frac{C \times DF \times V}{m_{IL}} \times \frac{M_{IL}}{M_{Cu}}$$

Equation II

Where C was the average concentration of the two replicates given by the FAAS measurement, DF was the dilution factor of the sample, V was the volume of the flask used to dilute the IL filtrate, m_{IL} was the mass of ionic liquid used for the dissolution test and M is the molecular mass of a compound in $g.mol^{-1}$.

Annex F: Development of the chromatographic method for the quantification of DBDE

This annex regroups the sensitive numerical values used to test the quality of the quantification method designed to quantify DBDE in sample containing ionic liquids (in that case [C8MIM][Cl]). Table V compiles the chromatography results for different standard, which were used to assess the reproducibility of the measure.

Table V: Summary of peak areas for various DBDE concentrations

[DBDE]	***Peak area (µV.min)***
0.5	27565
0.5	28239
0.5	29728
1	52751
1	54285
1	53002
2.5	141058
2.5	141093
5	283426
5	283830

Annex G: Raw data and calculation method for leaching of DBDE

The standard curves of DBDE have been established using linear regression in Excel. More precisely, the function LINEST estimated the best fit line through the method of least squares. The coefficients of determination reported were always very high ($R^2>0.95$), proving that the standard curve is linear enough to allow quantitative measurement. The raw results and calculation of [DBDE] were reported below, sorted out in three sections: one for leaching in various IL, one for different temperatures, and one for different ration of polymer to IL. Calculations included the massic concentration of [DBDE] (Equation III) and percentage of DBDE extracted from the polymer (Equation IV).

$$[DBDE] = \frac{C \times V_{sample}}{m_{IL\ in\ sample}}$$ **Equation III**

$$\%DBDE = \frac{[DBDE] \times m_{IL}}{m_{DBDE\ in\ HIPS}} \times 100$$ **Equation IV**

C was the concentration of DBDE given by HPLC, $m_{IL\ in\ sample}$ was the mass of IL taken out of leaching media, V_{sample} was the final volume in which $m_{IL\ in\ sample}$ was diluted, m_{IL} was the mass of IL used for leaching minus the IL already removed for the analysis of DBDE, and $m_{DBDE\ in\ HIPS}$ was the mass of DBDE in the polymer subjected to leaching (4.4 percent of the HIPS weighted).

F.1 Leaching tests in IL at 90 °C

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F.2 Leaching of DBDE at different temperatures in [C8MIM][Br]

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F.3 Leaching of DBDE at different ratio of [C8MIM][Br] : HIPS

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