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# Polymerization of Cyclodextrin-Ionic Liquid Complexes for the Removal of Organic and Inorganic Contaminants from Water

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## 1. Introduction

The removal of toxic contaminants from water still remains a huge challenge for water supplying companies and municipalities. Both organic and inorganic (mostly heavy metal) pollutants are often present in water distribution networks as a result of agricultural, domestic and industrial operations. To remove these pollutants from water distribution networks, effective techniques need to be developed. In our laboratories, research that involves the use of polymers of cone-shaped cyclodextrins (CDs) interconnected by linkers has been successfully demonstrated in the removal of organic pollutants from water. We have now undertaken a programme whereby polymers possessing moieties capable of removing both organic and inorganic contaminants from water, the so-called multifunctional complexes will be synthesised. To access these multifunctional complexes, CDs were attached to salts of organic cations (i.e. imidazolium and pyridinium) in a manner similar to the formation of ionic liquids (ILs). These cyclodextrin-ionic liquid (CD-IL) derivatives were then polymerised with bifunctional linkers with the expectation that the resulting polymers will be able to perform the dual role of removing a wide range of both organic and inorganic pollutants from water.

Pollutants from many industries often end up in water systems; other pollutants emanate from domestic and agricultural run-offs. Organic pollutants such as organic solvents, pesticides, fungicides and inorganic pollutants such as nitrates, cyanides and dissolved gases are present in many water systems (Schwarzenbach et al, 2003). When these pollutants are introduced into the environment, they are subjected to physical, chemical and biological processes, leading in the generation of derivatives possessing different environmental behaviour and effects (Schwarzenbach et al, 2003). These contaminants may leach into the soil and contaminate ground water. They also tend to bioaccumulate in the bodies of organisms. The small size and chemical inertness (or unreactiveness) of these pollutants make their removal from water using the current water treatment methods difficult (Li and Ma, 1999). Also, they have health effects such as kidney and liver damage, the destruction of nerve and circulatory systems and other psychological effects detrimental to human health. Since communities need ultra pure water, there is a need to remove pollutants even at very low concentrations to ensure the health and safety of water users.

Recent studies in our laboratories have involved the synthesis and application of standard (i.e. unfunctionalised) and functionalised CD polymers in the removal of organic contaminants from water at concentration levels as low as ppb ( $\mu\text{gL}^{-1}$ ). CDs can form inclusion complexes with organic compounds and thereby facilitating their removal. However, to apply CDs in the removal of organic pollutants from water, they need to be converted to water-insoluble polymers. Ionic liquids (ILs) on the other hand have demonstrated the ability to extract heavy metal ions from water. Although technologies for removing inorganic species from water are well known, to the best of our knowledge there is no general technique yet developed that is capable of removing organic and inorganic species from water simultaneously. Therefore, the use of CDs linked to ionic liquid appendages is envisaged to provide a dual system capable of removing both organic and inorganic pollutants from water at the same time. While the CD moiety in the polymer will retain its traditional role of absorbing organic contaminants, the IL component will perform the role of extracting the heavy metals present in water.

This work seeks to extend the application of cyclodextrin polymers to incorporate the removal of inorganic pollutants from water. The objectives of this study were the following:

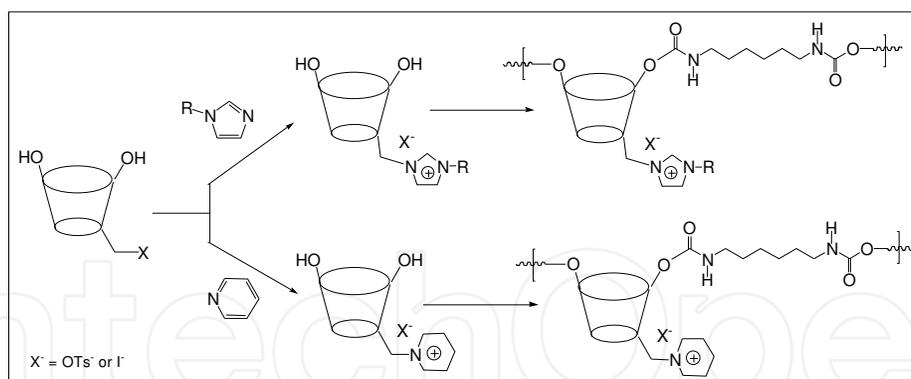
- i. To synthesise and characterise 6-deoxy-6-(*p*-tosyl)- $\beta$ -cyclodextrin (CDOTs) and 6-deoxy-6-iodo- $\beta$ -cyclodextrin (CDI) precursors. The aim here is to establish and optimize a reliable reaction path for the synthesis of CD-IL precursors. Characterisation of the CDOTs and the CDI precursors were carried out mainly by IR and NMR spectroscopy.
- ii. To synthesise and characterise CD-IL complexes by reacting CDOTs and CDI precursors synthesised in (i) with 3-alkylimidazole and pyridine. The CD-IL complexes were characterised with IR and NMR spectroscopy.
- iii. To polymerise the CD-IL complexes generated in (ii) with suitable bifunctional linkers such as hexamethylene diisocyanate and toluene-2,4-diisocyanate. IR spectroscopy was used for the characterisation of the polymers.
- iv. To study the thermal stability of the CD-IL polymers using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).
- v. To study the morphology of the polymers using scanning electron microscopy (SEM) and Brunauer-Emmet-Teller (BET).
- vi. To test the ability of the CD-IL polymers to remove organic and inorganic pollutants from water by performing model contamination experiments. These experiments involve deliberately placing the polymers into an aqueous solution containing known concentrations of the contaminants. GC-MS and UV-Visible spectroscopy were used to quantify the degree of absorption of the organic contaminants. Extraction of the inorganic contaminants was quantified by using atomic absorption (AA) spectroscopy.

A schematic representation for the synthesis of CD-IL complexes and CD-IL polymers are shown in Scheme 1.1.

## 2. Literature review

### 2.1 Organic pollutants

The problems associated with the use of the conventional water treatment techniques for the removal of these pollutants from the water systems and the approaches undertaken in our laboratories to address these problems are also described. The chapter then concludes with an overview of the applications of cyclodextrins and ionic liquids in the attempt to remove organic and inorganic contaminants from drinking water systems. Organic pollutants in



Scheme 1.1. Synthetic pathway for the preparation of CD-IL polymers

water pose a major threat to human health even when present at low concentrations. Some organic pollutants are referred to as persistent organic pollutants (POPs) because they remain in the environment for long periods of time. POPs can be absorbed by plants or animals thereby finding their way to poisoning food chains of living organisms (Oleszczuk and Baran, 2004). They have also been linked to adverse human effects such as cancer, nervous system damage, reproductive disorders, as well as the disruption of the immune system (EPA, 2006). POPs released in one part of the world can be transported globally *via* oceans and atmospherically, and their effects can be felt in regions which are distant from where they originate. POPs are mostly from human activity but there are other organics that are also of major concern.

Also, drinking water disinfection by-products pose a health risk to humans. Chlorine is still widely used for water disinfection. A residual amount of free chlorine (0.5-1.0 ppm) can keep levels of micro organisms such as bacteria to their lowest (Halmowitz, 1991). However, during chlorination, chlorine combines with water to form hypochlorous acid. Hypochlorous acid in turn reacts with NOM to form DBPs. The low volatility of DBPs, combined with their extreme stability, has led to their high persistence both in the environment and in the bodies of organisms after exposure (Gardio et al., 2006). They are mainly found in fatty tissues and bioaccumulate in food chains. DBPs are known to induce or aggravate adverse health problems in humans such as cancer, liver damage, failure of immune systems and the disruption of hormonal functions (Gardio et al., 2006). Due to the problems associated with DBPs, it is imperative to find better techniques to remove both NOM and its by-products from drinking water systems.

Phenolic compounds are common constituents of many industrial and commercial wastes (Rogers et al., 1999; Wikstrom and Marklund 2000). They may be introduced into the environment by accidental spills, illegal release of industrial and municipal wastewater, and excessive use of pesticides (Park et al., 1999). Phenolic compounds can be easily incorporated into the soil organic matter or dissolved humic materials because they are highly soluble in water. The presence of minute amounts of some phenolic compounds in water causes bad tastes and odours, which are greatly aggravated by the usual addition of chlorine for germicidal purposes (Niegowski, 1952; Kawaguchi 2004). Chlorinated and nitrated phenols pose a health hazard to both humans and animals. For instance, *para*-nitrophenol (PNP), though slightly soluble in water, is regarded as a possible mutagen to humans. 2,4,6-Trichlorophenol (TCP) is also known to affect the respiratory system and is a recognised carcinogen (NPI, 2007). Examples of important nitrated and chlorinated phenols are shown in Figure 2.1.

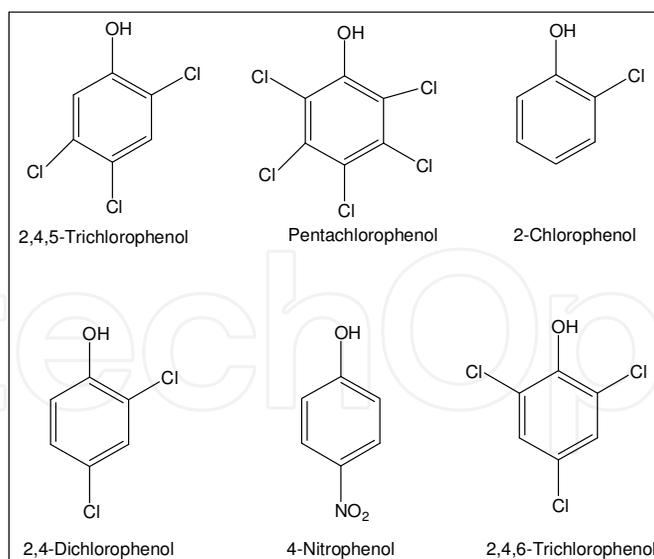


Fig. 2.1. Structures of chlorinated and nitrated phenols

The removal of phenolic compounds from industrial wastewater is currently an environmental and economic challenge. This effluent is resistant to conventional water treatment techniques due to the poor biodegradability and toxicity of phenolic compounds (Santos et al., 2007; Sabio et al., 2006). Moreover, it is also expensive to use these water treatment technologies to remove these organic pollutants at ppb levels ( $\mu\text{g}\cdot\text{L}^{-1}$ ).

## 2.2 Current water treatment methods for organic pollutants

Water treatment technologies used for the removal of organic species around the world include filtration using activated carbon, reverse osmosis, zeolites, and the use of dendrimers (Li and Ma, 1999). However, these techniques often do not remove organic contaminants to accepted levels. Due to the failure of most of the aforementioned water treatment techniques to remove organic pollutants from water, the world is facing challenges in meeting the rising demand for clean water. This is because the sources of available fresh water supplies are decreasing due to extended droughts, population growth and more stringent health-based regulations (Savage and Diallo, 2005). Also, water scientists are questioning the viability of current water treatment practices in meeting the water demands of all users according to regulations by the World Health Organisation (WHO). Since the current water treatment techniques fail to remove pollutants to the required levels due to their diversity and varying chemical properties, better technologies need to be developed. In our laboratories the use of cyclodextrin polyurethanes has been studied. These CD polymers have been found to have a high efficiency for the removal of organic pollutants from water, even at ppb levels (Mhlanga et al., 2007). Cyclodextrin polyurethanes are discussed in the following sections.

## 2.3 Cyclodextrins

Cyclodextrins (CDs) were first discovered by Villiers in 1891 (Szejtli, 1998). CDs are cyclic oligomers formed by the enzymatic hydrolysis of starch by *Bacillus macerans*. The glucose units in a CD molecule are linked by  $\alpha$ -(1,4) linkages (Bender and Komiyana, 1978; Croft and Bartsch 1983). Figure 2.2 illustrates the  $\alpha$ -(1,4) linkages and the numbering system in a typical CD moiety.

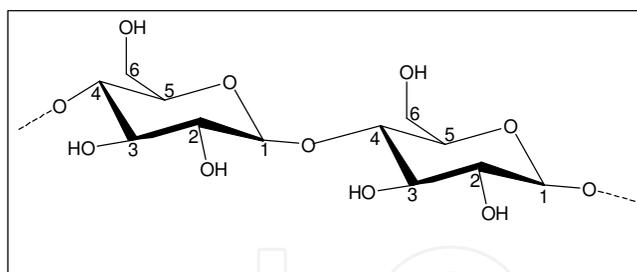


Fig. 2.2.  $\alpha$ -(1, 4) linkages and the numbering system in a CD molecule

### 2.3.1 Physical properties of cyclodextrins

The most common CDs are made of six, seven or eight glucose units and are called  $\alpha$ -,  $\beta$ - and  $\gamma$ -CDs, (Szejtli, 1998) respectively. The  $\beta$ -CD has been extensively studied by our research group and other researchers and was as a result used in this study. Higher molecular weight CDs are known, however their use is not common even in industry (Martin, 2004). Figure 2.3 shows the three common types of CDs.

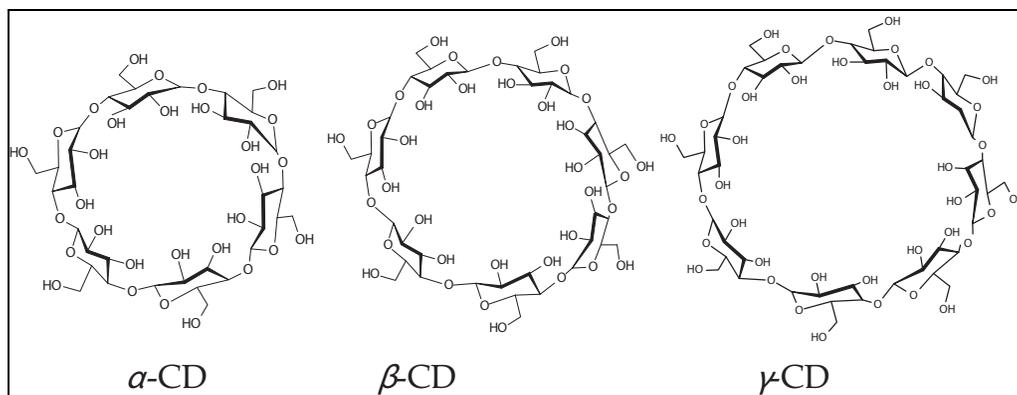


Fig. 2.3. Structures of  $\alpha$ -,  $\beta$  and  $\gamma$ -CDs, respectively showing the glucose units

CDs have a characteristic toroidal shape that form well defined cavities (Bender and Komiyana, 1978). These cavities are about 8Å deep. Depending on the number of the glucose units, the diameter of these cavities range between 5 and 10 nm. They have a hydrophobic interior because of the presence of carbon and hydrogen atoms and this feature allows them to host several compounds in their cavities. Their exterior cavities are hydrophilic because of the presence of hydroxyl groups and this makes them soluble in water. Figure 2.4 shows a representation of CD moiety with a hydrophilic exterior and a hydrophobic cavity.

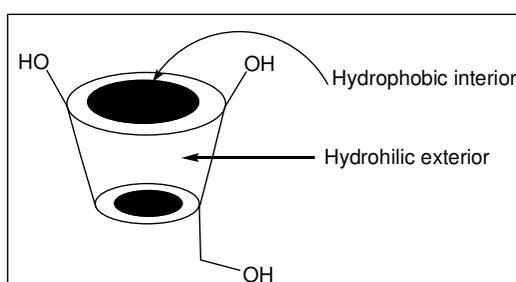


Fig. 2.4. Hydrophobic interior and hydrophilic exterior of a CD

### 2.3.2 Formation of inclusion complexes

Cyclodextrins can form inclusion complexes with various compounds (guests) of low molecular weight (Figure 2.5) (Li and Tan, 2001; Phan et al., 2002). Examples of the guest molecules include acids, apolar aliphatic and aromatic hydrocarbons and amines. The CD moiety harbours these small, suitably shaped organic compounds in its tubular cavities by shielding the bound species from the surrounding aqueous environment (Weinz et al., 1997). This phenomenon is a result of the hydrophobic-hydrophobic interaction between the host CD and the organic species (Liu et al., 2003; Weinz et al., 1997). The formation of inclusion complexes does not involve the formation of bonds but is an attraction between the host and guest as a result of their polarities (Szejtli, 1998).

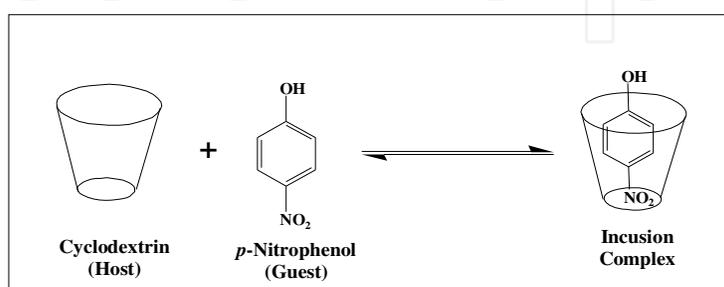


Fig. 2.5. Schematic representation of an inclusion complex

Because the lengths of the diameter of the CD vary, the organic species must be able to fit (at least partly) into the CD cavity (compatible geometry). The size of the organic compound and the type of the CD used is important for the formation of inclusion complexes. Direct exploitation of this phenomenon for water treatment is however limited by the solubility of CDs in water. Hence, making insoluble CD derivatives and polymers is a prerequisite if CDs are to be used in water treatment.

### 2.3.3 Cyclodextrin derivatives

The presence of hydroxyl groups in the outer cavity can be exploited in order to alter the physical and chemical properties of CDs (Li and Ma, 1999; Szejtli, 1998). For example, functionalising CDs can decrease their solubility, increase their stability in the presence of light, heat and oxidizing agents and also make them more volatile (Harada, 1997; Liu et al., 2003). The primary hydroxyl groups of a CD molecule (C-6 OHs) are more reactive compared to their secondary hydroxyl groups (C-2, C-3 OHs). These hydroxyl groups are shown in Figure 2.6. The C-2 hydroxyl groups are acidic. The C-3 hydroxyl groups are less

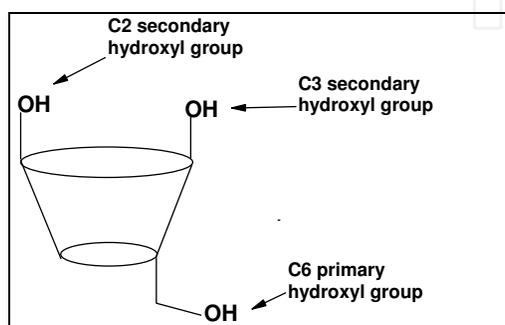


Fig. 2.6. The structure of a CD showing the three different hydroxyl groups.

reactive because they are not easily accessible due to steric hindrance. The primary hydroxyl groups at C-6 are basic hence an acid is used to remove the H in the OH, i.e.



and are the most easily accessible thus often more reactive during nucleophilic substitution reactions.

### 2.3.3.1 Monofunctionalisation of CDs

The purpose of functionalising CDs is to modify their physico-chemical properties and also to introduce groups with specific activity. The two most common types of CD substitution reactions are mono- and per-functionalisation reactions. Monofunctionalisation refers to the reaction of only one hydroxyl group while per-functionalisation involves the whole set of hydroxyl groups. In monofunctionalisation, regioselective reactions should be the target (Sutyagin et al., 2002). Regioselective reactions usually involve the protection of other OH groups to prevent them from participating in the reaction while exposing the target group to reactions. Monofunctionalisation at C-2 and C-3 is well documented (Rong and D'Souza, 1990; Fugita et al., 1984). In this study monofunctionalisation at C-6 was mainly exploited. Monofunctionalisation of C-6 can be achieved because in the presence of a base (e.g. NaOH), the proton at C-6 is removed to make O<sup>-</sup> which is a nucleophile that can be easily substituted. Thus when a CD is reacted with a tosyl group in a basic medium, a monofunctionalised CD derivative (CDOTs) is afforded (Byun et al., 1998; Muderawan et al., 2005; Zhong et al., 1998). The CDOTs is an important precursor for all C-6 CD derivatives because the tosylate is a good leaving group and can be easily replaced by other nucleophiles (e. g. halogens, azides and acetates). In this study, the CDOTs was also used as a precursor for the CD derivatives that were synthesised.

### 2.3.4 Cyclodextrin polymers

The solubility of CDs and their derivatives limits their application in water treatment. Converting them to water insoluble entities is therefore crucial if CDs are to be utilised in the removal of contaminants from water. To attain this property, CD derivatives have been polymerised with suitable bifunctional linkers in our laboratories to produce water insoluble polymers (Mhlanga et al., 2007; Mamba et al., 2007; Salipira et al., 2007). The presence of the OH groups in the CDs or CD-derivatives allows a reaction in which the monomers react with linkers to produce insoluble polymers. A reaction scheme for the polymerisation of CDs with diisocyanate linkers (hexamethylene diisocyanate (HDI)) is shown in Figure 2.7 (Li and Ma, 1999).

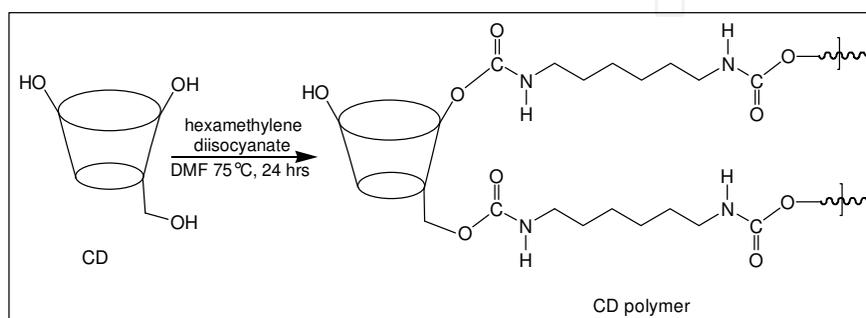


Fig. 2.7. Polymerisation of CDs with an isocyanate linker (HDI)

The CD polyurethanes have demonstrated a high efficiency for the absorption of organic pollutants in water (Mhlanga et al., 2007; Mamba et al., 2007; Salipira et al., 2007). However, in real water systems organic and inorganic contaminants co-exist; the challenge is to craft a water treatment system that is capable of simultaneously removing these contaminants from water. In an attempt to overcome this challenge, we functionalised CDs with ionic liquids (ILs). Since ILs are known to chelate heavy metals from aqueous media and CDs are able to remove organic pollutants from water, a system which combines CDs and ionic liquids is expected to absorb both organic and inorganic pollutants from water.

#### 2.4 Inorganic pollutants in water

Inorganic contaminants are compounds that typically do not contain the element carbon in their structure (waterborne, 2006). Inorganic pollutants are introduced into the environment naturally, for example, from weathering of parent rocks, industrial wastes and agricultural run-offs (waterborne, 2006; Petanen and Romantschuk, 2002). Inorganic pollutants include dissolved gases (e. g. oxygen, carbon dioxide, nitrogen and radon), heavy metals (e. g.  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{6+}$ ) and anions such as fluorides ( $\text{F}^-$ ), nitrates ( $\text{NO}_3^-$ ) and cyanides ( $\text{CN}^-$ ). These contaminants also pose health risks to living organisms because they bioaccumulate in the body resulting in chronic health effects (Morales et al., 1999). Inorganic contaminants are not biodegradable; hence they can typically poison the food chains of living organisms (waterborne, 2006).

#### 2.5 Ionic liquids

Ionic liquids (ILs) are salts of organic cations which have aroused an increasing interest for their promising role as alternative media for volatile solvents (Wei et al., 2003). Ionic Liquids (ILs) are low melting point molten salts composed of organic cations (e.g. pyridinium and imidazolium ions) and mostly inorganic anions like  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $[\text{PF}_6]^-$  and  $[\text{BF}_4]^-$ . Compared to conventional salts, ILs are liquid at room temperature (Wei et al., 2003). The most common types of organic cations are the imidazolium and pyridinium ions. Examples of the structures of ionic liquids are depicted below in Figure 2.8.

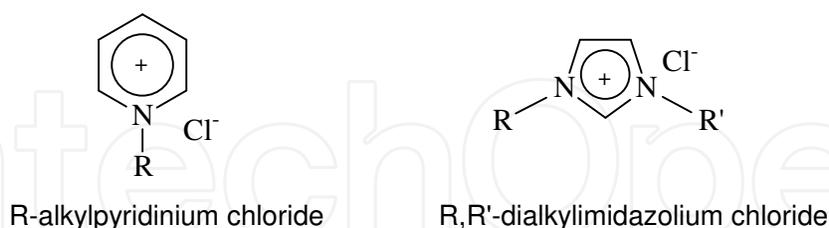


Fig. 2.8. Examples of ionic liquids

The organic cationic component and the alkyl substituents are known to be responsible for the low melting points associated with these compounds. The ability to dissolve organic solvents has also been linked to the cationic component and the alkyl substituents since both of them are organic in character (Welton, 1999). The alkyl group is usually an alkane chain whereby increasing the length of the alkane chain one can change the resulting properties (e.g., viscosity, hydrophobicity, and melting point) (Ferreira et al., 2000). Besides pyridinium and imidazolium cations, other less common organic cations have been used for the preparation of ionic liquids. These include ammonium, pyrrolidinium, sulfonium and phosphonium ions (Figure 2.9) (Pereiro et al., 2007).

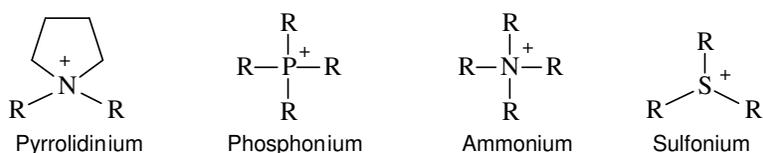
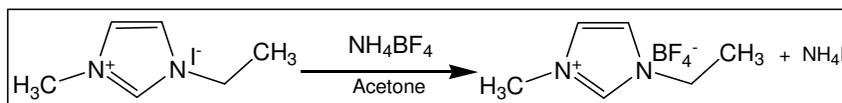


Fig. 2.9. Less common organic cations used for the synthesis of ILs.

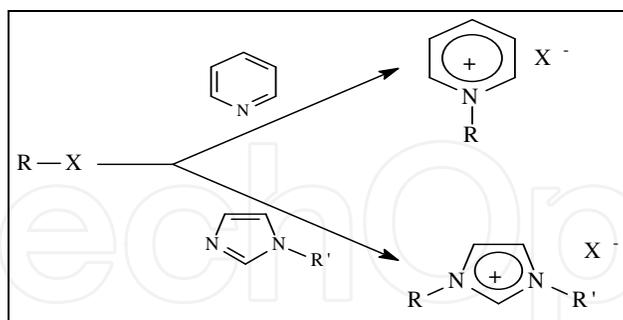
### 2.5.1 Synthesis of ILs

Ionic liquids are made up of both a cation and an anion, whose forces of attraction are not sufficiently strong to hold them together as solids at ambient temperatures. It is therefore possible, by proper choice of starting material, to synthesize ionic liquids that are liquid at or below room temperature (Ferreira et al., 2000). Volatile organic chemicals (VOC's) are used to prepare non-volatile ionic liquids which have negligible vapour pressure; therefore new and better methods need to be researched since many processes used for cleaning ionic liquids involve washing with water and VOC's. This will also help in terms of eliminating or decreasing the hazards in the system and eliminate the waste before it is produced. The two most common methods of synthesising ionic liquids are metathesis reaction involving a halide salt and acid-base neutralisation reactions (Welton, 1999). For example, the metathesis reaction of 1-ethyl-3-methylimidazolium iodide with ammonium tetrafluoroborate is shown in Scheme 2.1.



Scheme 2.1. Synthetic pathway for 1-ethyl-3-methylimidazolium tetrafluoroborate

Also, a reaction an alkyl halide with pyridinium and imidazolium cations yields ionic liquids, as shown in Scheme 2.2.



Scheme 2.2. Pathway for the synthesis of pyridinium and imidazolium based ILs

The anions, to a great extent influence both the chemical and physical properties of the ionic liquids. For example, although both anions are air- and moisture-stable,  $[BF_4]^-$  and  $[PF_6]^-$  anions are used for the preparation of water-miscible and water-immiscible ionic liquids, respectively (Ferreira et al., 2000). Besides anions such as hexafluorophosphate, tetrafluoroborate and halide ions, other common inorganic anions that are used for the preparation of ILs include  $[SbF_6]^-$  and  $[(CF_3SO_2)_2N]^-$ . The anion need not necessarily have to be inorganic; ILs possessing organic anions such as alkylsulfate, tosylate and methanesulfonate are known (Figure 2.10) (Sigma-aldrich, 2007).

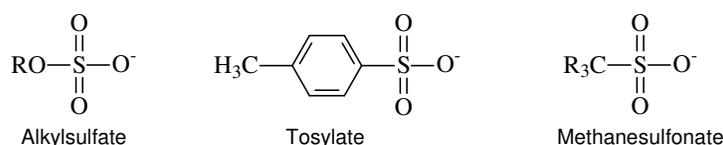


Fig. 2.10. Examples of organic anions used for the synthesis of ILs.

An example of such an IL (ethylpyridinium tosylate) is shown in Figure 2.11.

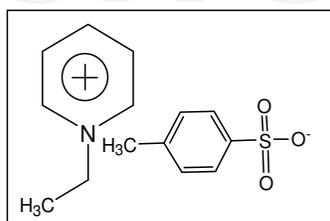


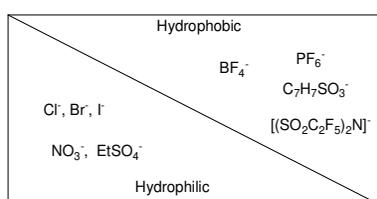
Fig. 2.11. Structure of ethylpyridinium tosylate

## 2.7.2 Physical properties of ILs

The physical properties of ionic liquids depend on the nature and the size of their cationic and anionic species (Visser and Rogers, 2004). These properties relate to the choice of the two ionic components (Ferreira et al., 2003; Visser and Rogers, 2004). Hence, ILs are sometimes referred to as “designer solvents”. ILs are gaining a wide recognition in analytical chemistry because they possess several unique properties (Liu et al., 2004). These physical properties include negligible vapour pressure (Liu et al., 2003), an ability to dissolve a wide range of organic and inorganic materials (Welton, 1999), high thermal stability (they have low melting points and high boiling points, for example, some ILs are liquid at 400°C, while others are liquid at -96°C) (Liu et al 2005) as well as variable viscosity and miscibility with water and other organic solvents (Liu et al., 2003). These physical properties have triggered an interest in applying ionic liquids in separation chemistry and synthesis. In addition, these properties form the basis for the utilisation of ILs in replacing traditional toxic, flammable and volatile organic compounds (VOCs), which are not environmentally friendly. To this end, ILs have the potential to be used as alternative reaction media for “Green Chemistry” (Wei et al., 2003).

### 2.7.2.1 Hydrophobic and hydrophilic ILs

The hydrophilic and hydrophobic nature of ILs depends on the type of anion used in the synthesis of the target ionic liquid (Welton, 1999; Cocalia et al., 2006). This characteristic feature determines the extent of miscibility of ILs with water and other organic solvents. It also provides an alternative for the use of ILs in nonaqueous, polar phase separation systems, i.e. liquid-liquid extraction (Welton, 1999). For instance, hydrophobic ILs can be used as immiscible polar phases with water. Examples of common hydrophobic and hydrophilic anions are shown in Figure 2.11. In this study, one hydrophobic (tosylate) and one hydrophilic (iodide) anion were utilised in the synthesis of ionic liquids.



Key:  $[\text{PF}_6]^-$  = hexafluorophosphate,  $[\text{BF}_4]^-$  = tetrafluoroborate,  $[\text{C}_7\text{H}_7\text{SO}_3]^-$  = tosylate  $[(\text{SO}_2\text{C}_2\text{F}_5)_2\text{N}]^-$  = bis (triflyl) imide and  $[\text{EtSO}_4]^-$  = ethylsulfonate.

Fig. 2.11. Examples of hydrophobic and hydrophilic IL anions

### 2.7.3 Chemical properties of ILs

Ionic liquids have been widely considered as greener solvents which are suitable for application in a wide range of organic chemical reactions (Chowdhury et al., 2007). Applications of ILs include control of product distribution, enhanced reactivity rates, recyclability, catalysis and ease of recovering products from a reaction mixture (Chowdhury et al., 2007). Further, they have shown to possess much needed properties such as inflammability and less volatility. Thus they are emerging as novel replacements for the widely used VOC's which are detrimental to the environment (Liu et al., 2003; Cruz and Moens, 2000). ILs are generally referred to as polar solvents because they are able to dissolve and stabilise dipolar and charged solutes (Welton, 1999). The localisation of the anions and the delocalisation of the cationic charge also influence the polarity of ILs. Ionic liquids can be applied in battery industries since they are good electrolytes and good solvents for Friedel-Crafts alkylations, hydrogenations and Diels-Alder reactions, to mention just a few (Welton, 1999; Cruz and Moens, 2000). However, the reactivity of ILs is also affected by the acidity and basicity of the IL under investigation.

#### 2.7.3.1 Acidic and basic ILs

The acidic and basic nature of ionic liquids is largely determined by the ability of the salt to act as a hydrogen bond donor (acid) or acceptor (base) (Welton, 1999; Chowdhury et al., 2007). Incorporation of an aliphatic carboxylic group to the cationic component of an IL can result in the formation of an acidic ionic liquid. Also, reacting the cationic component with an acidic anion, e. g.  $[\text{HSO}_4]^-$ , results in an acidic IL (Chowdhury et al., 2007). Increasing the acidity of the anion has been found to improve the catalytic activity of the IL. On the other hand, basic ILs are a result of combining the cationic component of the IL with a basic anion, e. g.  $[\text{OH}]^-$ . Knowing the acidic and basic nature of an IL is important because it allows for the proper choice of an IL for a specific application. This has led to a tailored synthesis of task specific ionic liquids (TSILs).

### 2.7.4 Applications and uses of ILs

The application of any ionic liquid depends on the purpose for which it is designed. ILs that have been specifically designed for use in catalysis, chromatography, spectrometry, electrochemical applications, as chemo sensors and extraction solvents have been reported in a number of publications (Visser and Rogers, 2004; Liu et al., 2004; Cruz and Moens, 2000). Task specific ionic liquids that have been synthesised for the purposes of metal extraction from aqueous media have also been reported (Pereiro et al., 2007; Liu et al., 2005; Visser et al., 2002). Metal ions such as  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  have been removed from

aqueous media using ILs (Visser and Rogers, 2004). The ability of ILs to form complexes with most metal-halides, especially transition metal-halides, is the basis for their application in metal extraction from aqueous media (Welton, 1999). Metal ions form complexes with both the anion and cation of the IL with a specific coordination. The coordination mechanism depends on the ionisation state of the metal ion. For instance, metals with ionisation state of two, [M (II)], form complexes with bidentate coordination (Welton, 1999). To enhance the metal ion extraction capability of ionic liquids, metal ligating groups such as urea and sulphur, are used (Visser et al., 2002). Affiliating such ligands on the IL cations improve the extraction efficiency of the targeted metal ions.

### **2.8 Problems associated with current water treatment technologies**

Current water treatment techniques can either absorb organic or inorganic pollutants from an aqueous medium, but not both. In addition, these technologies fail to remove pollutants to the required levels and this is attributed to the diversity and varying chemical properties of organic pollutants. Furthermore, in real water systems organic and inorganic pollutants co-exist hence techniques that can remove both contaminants simultaneously would be ideal. Cyclodextrin polyurethanes have been applied in the removal of organic pollutants from water (Mhlanga, 2006). The new challenge is to functionalise these polymers such that they are capable of removing both organic and inorganic pollutants present in water. One possibility is to functionalise the CD moieties with salts of organic cations known as ionic liquids. On their own, ionic liquids have demonstrated the ability to remove inorganic contaminants (heavy metal ions such as  $\text{Hg}^{2+}$ ,  $\text{As}^{3+}$  and  $\text{Cr}^{3+}$ ) from an aqueous solution (Visser et al., 2002; Tran and De Paoli, 2002). Since cyclodextrin polyurethanes and ionic liquids have independently shown the capability to remove organic and inorganic contaminants, respectively, it is expected that cyclodextrin polymers functionalised with ionic liquids can simultaneously remove organic and inorganic contaminants from water.

### **2.9 Summary**

From the literature overview in this section, the health risk associated with the presence of organic and inorganic pollutants in water has been highlighted. The failure of conventional water treatment technologies to remove organic and inorganic pollutants to ppb levels remains an ongoing research concern. Water insoluble CD polymers have demonstrated the ability to remove organic pollutants at ppb levels. On the other hand ILs are able to remove metal ions from water. To the best of our knowledge, there is no known technique that simultaneously removes organic and inorganic contaminants from water. Water insoluble polymers of CDs functionalised with ILs should provide a dual system that is capable of removing both organic and inorganic pollutants from water simultaneously

## **3. Experimental methodology**

### **3.1 Reagents and solvents**

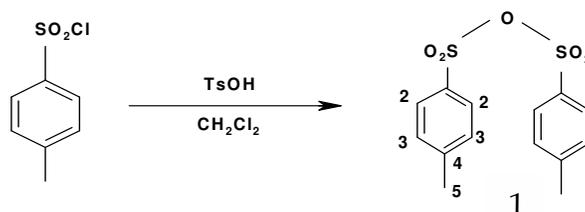
Unless otherwise specified, all chemicals and reagents were obtained from suppliers and used without further purification. All reactions were carried out under inert conditions of argon or nitrogen. All solvents used in this study were dried over calcium hydride for 2 days and distilled before being used. The distilled solvents were stored under molecular sieves.

### 3.2 Synthetic procedures

The synthesis of monosubstituted cyclodextrins mainly takes place at the C-6 hydroxyl group. A strong nucleophilic reagent (i.e. sulfonic anhydride ( $\text{Ts}_2\text{O}$ )), was used for the displacement of the hydroxyl group at the C-6 position. Monotosylated cyclodextrins are generally good precursors for derivatives of CDs due to the ease of formation of the monotosylate and ease with which the tosyl leaving group can be replaced. Therefore, in order to access a CD monotosylate,  $\text{Ts}_2\text{O}$  had to be first synthesised.

#### 3.2.1 Synthesis and characterisation of *p*-toluene sulfonic anhydride ( $\text{Ts}_2\text{O}$ )

*p*-Toluene sulfonyl chloride (2.00g, 10.4mmol) was dissolved in dichloromethane (12.5mL) and *p*-toluene sulfonic acid ( $\text{TsOH}$ ) (0.52g, 2.63mmol) was added gradually with vigorous stirring under nitrogen atmosphere. The resulting mixture was stirred overnight at room temperature. The milky reaction mixture was then filtered through silica gel to remove the unreacted *p*-toluene sulfonic acid. Hexane (50mL) was added to the clear filtrate and a precipitate was afforded. The crystals of  $\text{Ts}_2\text{O}$  (1) were collected as white needle-shaped granular/solids after drying overnight under vacuum.



Scheme 3.1. Synthetic pathway for the preparation of *p*-toluene sulfonic anhydride.

IR/KBr,  $\text{cm}^{-1}$ : 3095 (CH, Ar), 3058 (CH, Ar), 2925 (C-H), 1928, 1809, 1652, 1592, 1488 ( $\text{SO}_2$ ), 1373, 1305, 1925, 1175 ( $\text{SO}_2$ ), 1121, 1079, 1015.  $^1\text{H}$  NMR,  $\text{DMSO}-d_6$ : 7.40 (d, 4H, H-2), 7.0 (d, 4H, H-3), 2.0 (s, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR,  $\text{DMSO}-d_6$ : 145 (C-1), 139 (C-2), 129.0 (C-3), 126.0 (C-4), 21.5 (C-5). Yield: 5.89g, 18.1mmol, 73%. M.pt = 124-126°C. TLC: Eluent: 2:1 hexane/ethylacetate,  $R_f$ : 0.80.

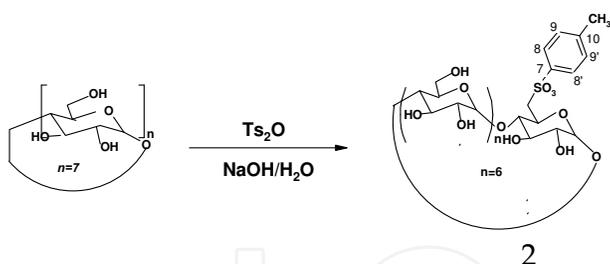
### 3.7.2 Synthesis of monofunctionalised CD precursors

#### 3.7.2.1 Synthesis and characterisation of mono-6-deoxy-6-(*p*-tosyl)- $\beta$ -cyclodextrin (2) ( $\beta$ -CDOTs)

A solution of  $\beta$ -CD (2.86g, 2.53mmol), *p*-toluene sulfonic anhydride (1.24g, 3.80mmol) and distilled water (60 mL) was stirred at room temperature under an inert atmosphere. A solution of NaOH (1.25g, 31.3mmol) in water (13 mL) was then added after 2 hours. After 10 minutes, unreacted  $\text{Ts}_2\text{O}$  was removed by filtration through silica gel. The pH of the filtrate was adjusted to  $\sim 8$  by the addition of ammonium chloride (3.36g). Overnight refrigeration of the resultant precipitate followed by drying under reduced pressure led to the isolation of 2 as a white powdery solid (2.25g, 1.75mmol, 68%).

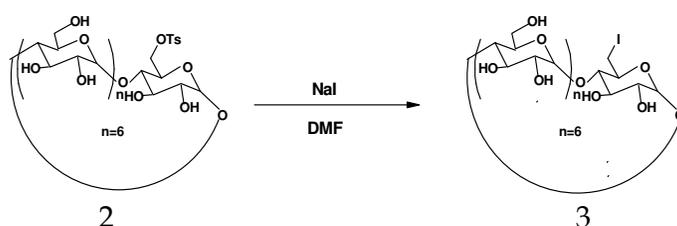
#### 3.7.2.2 Synthesis and characterisation of mono-6-iodo- $\beta$ -cyclodextrin ( $\beta$ -CDI)

Dry  $\beta$ -CDOTs (1.00g, 0.88mmol) was dissolved in anhydrous DMF (40 mL). To this solution, sodium iodide (1.20g, 7.76mmol, 10 equiv), was added under nitrogen with vigorous stirring which was continued for 5 hours at 90°C in an inert atmosphere. Addition of acetone (25 mL) led to the formation of a precipitate. The mixture was filtered and thereafter



Scheme 3.2. A synthetic pathway for the synthesis of  $\beta$ -CDOTs

IR/KBr,  $\text{cm}^{-1}$ : 3377 (O-H), 2934 (C-H), 1635 (C=C), 1599 (C-C), 1357 ( $\text{SO}_2$ , Assy.), 1156 ( $\text{SO}_2$ , Sym), 1037 (C-O).  $^1\text{H}$  NMR/ppm,  $\text{DMSO-d}_6$ : 7.53(d,  $\text{H}_{\text{Ar}}$ , 2H), 7.21 (d,  $\text{H}_{\text{Ar}}$ , 2H), 4.55 (s, OH-6), 5.40-5.80 (m, H-6, 2H), 4.0 (m, H-6), 3.20-3.55 (m, H-3, H-5, H-6), 5.40-5.80 (br, OH-2, OH-3), 2.90-3.20 (m, H-2, H-4) 4.63 (d, H-1, 7H), 2.21, (s,  $-\text{CH}_3$ , 3H).  $^{13}\text{C}$  NMR/ppm,  $\text{DMSO-d}_6$ : 145.0 ( $\text{C}_{\text{Ar}}$ ), 132.8 ( $\text{C}_{\text{Ar}}$ ), 129.9 ( $\text{C}_{\text{Ar}}$ ), 127.6 ( $\text{C}_{\text{Ar}}$ ), 101.9 (C-1), 81.5 (C-4), 72.4 (C-2), 73.1 (C-3), 72.2 (C-5), 59.9 (C-6), 21.2 ( $-\text{CH}_3$ ). Yield = 2.25g, 1.75mmol, 69%. M.pt = 171-174°C. TLC:  $R_f$  = 0.49.



Scheme 3.3. Synthetic pathway for the preparation of  $\beta$ -CDI.

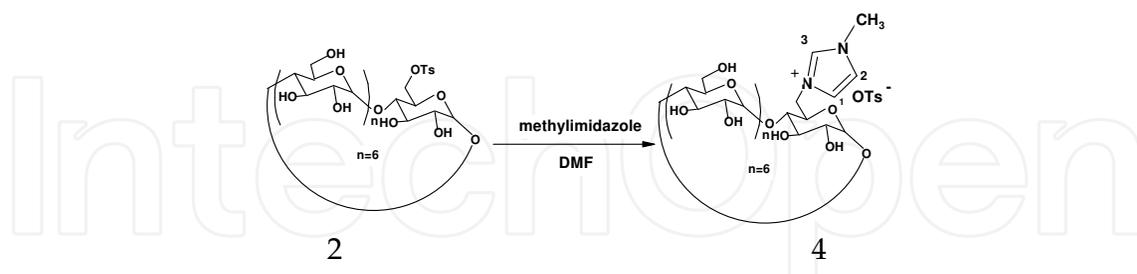
FTIR/KBr,  $\text{cm}^{-1}$ : 3346 (O-H), 2924 (C-H), 1027 (C-O), 586 (C-I).  $^1\text{H}$  NMR/ppm,  $\text{DMSO-d}_6$ : 5.40-5.63 (m, OH-2, OH-3), 4.62 (d, H-1), 4.30 (br, OH-6), 4.30(m, H-6), 3.20-3.55 (m, H-3, H-5, H-6), 3.00-3.20 (m, H-2, H-4), 1.90 ( $\text{CH}_2\text{-I}$ ).  $^{13}\text{C}$  NMR/ppm,  $\text{DMSO-d}_6$ : 102.0 (C-1), 81.6 (C-4), 73.1 (C-3), 72.4 (C-2), 72.1 (C-5), 60.0 (C-6), 30.9 (C-6') M.pt = 206-209°C. TLC:  $R_f$  = 0.43.

washed with acetone (100 mL). The acetone was then removed under reduced pressure (rotary evaporator). To ensure complete removal of unreacted NaI, this procedure (washing and evaporation of acetone) was repeated three times. The resulting solid was dissolved in deionised water (50 mL) and precipitated by the addition of copious amounts of acetone. The precipitate was filtered off and dried in a desiccator to give 3 as white powdery solid (0.79g, 0.63 mmol, 82%).

### 3.7.3 General procedure for the synthesis of CD-IL complexes

Typically an alkyl imidazole or pyridine (10 equiv.) was added dropwise to a stirred solution of dry  $\beta$ -CDI or  $\beta$ -CDOTs (1.00g, 0.88mmol) dissolved in anhydrous DMF (40 mL). Stirring was continued at elevated temperatures (80°C and 90°C for  $\beta$ -CDI and  $\beta$ -CDOTs, respectively) under nitrogen for a further 24 hours. After cooling to room temperature, acetone (25 mL) was added to precipitate the product. The reaction mixture was then stirred for 30 minutes. Evaporation of organic solvents using a rotary evaporator afforded a white solid. The solid was finally dissolved in deionized water (50 mL) and precipitated by the addition of acetone (200 mL). The precipitate was filtered off and dried under vacuum to yield a white powdery solid.

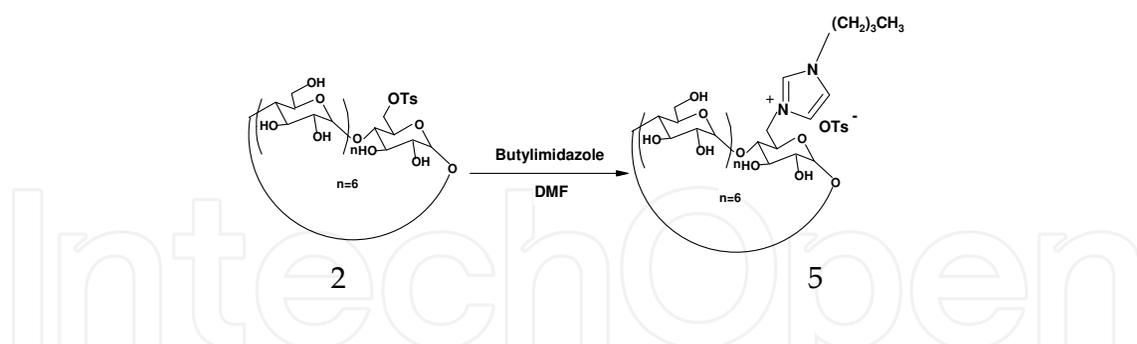
### 3.7.3.1 Synthesis and characterisation of mono-6-deoxy-6-(3-methylimidazolium)- $\beta$ -cyclodextrin tosylate (4) ( $\beta$ -CD-MIMOTs)



Scheme 3.4. Synthetic pathway for the preparation of  $\beta$ -CD-MIMOTs

IR/KBr,  $\text{cm}^{-1}$ : 3388 (O-H), 2929 (C-H), 1027 (C-O), 1641 (C=C), 1156 (C-N).  $^1\text{H}$  NMR/ppm,  $\text{DMSO-d}_6$ : 8.99 (s, =CH<sub>imid</sub>), 7.92 (s, =CH<sub>imid</sub>), 7.65 (s, =CH<sub>imid</sub>), 7.45 (d, H<sub>Ar(ortho)</sub>), 7.09 (d, H<sub>Ar(meta)</sub>), 5.20-6.21 (OH-2, OH-4), 4.76 (s, H-1), 4.27 (t, OH-6) 3.87 (s, H-6), 3.40-3.66 (m, H-3, H-5, H-6), 3.20-3.41 (m, H-2, H-4), 2.25 (s, -CH<sub>3imid</sub>), 2.04 (s, -CH<sub>3OTs</sub>).  $^{13}\text{C}$ NMR/ppm,  $\text{DMSO-d}_6$ : 145.4 (C<sub>Ar(meta)</sub>), 137.9 (C<sub>Ar(ortho)</sub>), 128.3 (C<sub>Ar(ipsos)</sub>), 125.6 (C<sub>Ar(para)</sub>), 137.2 (C<sub>im</sub>) 123.17 (C<sub>im</sub>), 123.0 (C<sub>im</sub>), 102.0 (C-1), 81.6 (C-4), 73.1 (C-3) 72.5 (C-2), 72.1 (C-5), 60.1 (C-6), 48.76 (C-6'). Yield = 0.91g, 0.66 mmol, 97%. M.pt = 226-229°C, TLC: = 0.58.

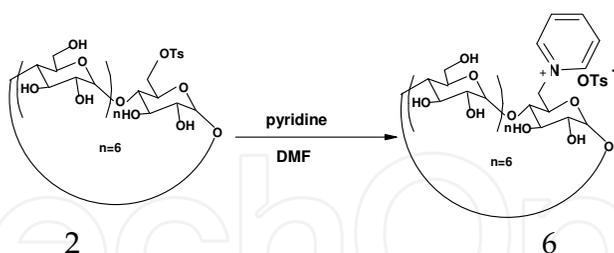
### 3.7.3.2 Synthesis and characterisation of mono-6-deoxy-6-(3-butylimidazolium)- $\beta$ -cyclodextrin tosylate(5) ( $\beta$ -CD-BUTIMOTs)



Scheme 3.5. Synthetic pathway for the preparation of the  $\beta$ -CD-BUTIMOTs

IR/KBr,  $\text{cm}^{-1}$ : 3346 (O-H), 2924 (C-H), 1035 (C-O), 1633 (C=C), 1156 (C-N).  $^1\text{H}$ NMR/ppm  $\text{DMSO-d}_6$ : 9.06 (s, CH<sub>-im</sub>), 7.74 (s, CH<sub>-im</sub>), 7.68 (CH<sub>-im</sub>), 7.57 (d, CH<sub>Ar(ortho,OTs)</sub>), 7.08 (d, CH<sub>Ar(meta,OTs)</sub>), 5.52-5.82 (OH-2, OH-3), 4.49 (d, H-1), 4.10 (t, OH-6), 3.41-3.72 (m, H-3, H-5, H-6), 3.10-3.41 (H-2, H-4), 2.08 (t, N-CH<sub>2-</sub>), 1.76-2.00 (m, -CH<sub>2-</sub>), 1.20-1.40 (m, -CH<sub>2</sub>-CH<sub>3</sub>) 0.84 (CH<sub>3-OTs</sub>), 0.005 (s, CH<sub>3-im</sub>).  $^{13}\text{C}$ NMR/ppm  $\text{DMSO-d}_6$ : 145.4 (C-2'<sub>OTs</sub>), 137.1 (C-2<sub>OTs</sub>), 128.2 (C-3<sub>OTs</sub>), 125.6 (C-3'<sub>OTs</sub>), 138.0 (C-8<sub>but</sub>), 123.5 (C-10<sub>but</sub>), 123.1 (C-9<sub>but</sub>), 102.0 (C-1), 81.6 (C-4), 73.1 (C-3), 72.49 (C-2), 72.09 (C-5), 60.00 (C-6), 48.71 (C-6'), 31.55 (N-CH<sub>2</sub>), 31.2 (-CH<sub>2-</sub>), 21.29 (-CH<sub>2</sub>-CH<sub>3</sub>), 19.3 (CH<sub>3-OTs</sub>), 13.75 (CH<sub>3-im</sub>). Yield: 0.96g, 0.67 mmol, 98%, M.pt: 240-243°C. TLC: R<sub>f</sub>= 0.61.

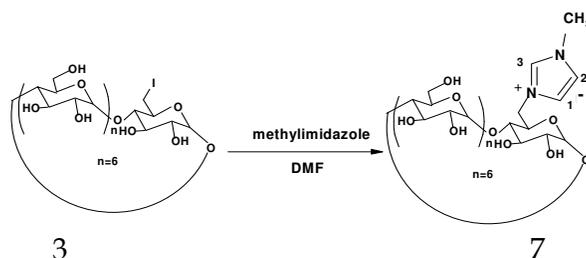
### 3.7.3.3 Synthesis of mono-6-deoxy-6-pyridinium- $\beta$ -cyclodextrin tosylate (6) ( $\beta$ -CD-PYROT)



Scheme 3.6. A synthetic pathway for the preparation of  $\beta$ -CD-PYROT

IR/KBr,  $\text{cm}^{-1}$ : 3395 (O-H), 2933 (C-H), 1033 (C-O), 1636 (C=C), 1159 (C-N).  $^1\text{H}$  NMR/ppm,  $\text{DMSO-d}_6$ : 9.08 (d,  $=\text{CH}_{\text{pyr}}$ ), 8.20 (t,  $=\text{CH}_{\text{pyr}}$ ), 7.80 (dd,  $=\text{CH}_{\text{pyr}}$ ), 7.57 (br d,  $\text{H}_{\text{Ar(ortho)}}$ ), 7.21 (d,  $\text{H}_{\text{Ar(meta)}}$ ), 5.01 (s, H-1), 4.40-4.82 (m, OH-2, OH-3), 3.98 (t, OH-6), 3.52-3.88 (m, H-3, H-5, H-6), 3.21-3.52 (m, H-2, H-4), 2.15 (d,  $-\text{CH}_3\text{OTs}$ ).  $^{13}\text{C}$  NMR/ppm,  $\text{DMSO-d}_6$ : 147.69 ( $\text{C}_{\text{py(C-8)}}$ ), 145.16 ( $\text{C}_{\text{py(C-9)}}$ ), 125.66 ( $\text{C}_{\text{py(C-10)}}$ ), 143.00 ( $\text{C}_{\text{OTs(C-1)}}$ ), 138.25 ( $\text{C}_{\text{OTs(C-2)}}$ ), 137.92 ( $\text{C}_{\text{OTs(C-3)}}$ ), 128.38 ( $\text{C}_{\text{OTs(C-4)}}$ ), 102.08 (C-1), 81.68 (C-4), 73.22 (C-3), 72.53 (C-2), 72.17 (C-5), 60.09 (C-6), 45.42 (C-6'). Yield = 2.49g, 0.70 mmol, 90.7%. M.pt = 242-245°C. TLC:  $R_f$  = 0.55.

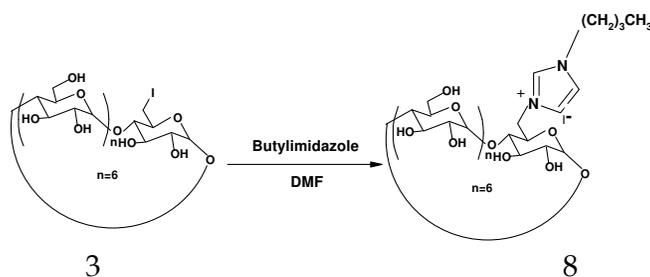
### 3.7.3.4 Synthesis and characterisation of mono-6-deoxy-6-(3-methylimidazolium)- $\beta$ -cyclodextrin iodide (7) ( $\beta$ -CD-MIMIOD)



Scheme 3.7. A synthetic scheme for the preparation of  $\beta$ -CD-MIMIOD

FTIR/KBr,  $\text{cm}^{-1}$ : 3393 (O-H), 2919 (C-H), 1027 (C-O), 1645 (C=C), 1156 (C-N).  $^1\text{H}$  NMR/ppm,  $\text{DMSO-d}_6$ : 5.60-5.80 (br m, OH-2, OH-3), 4.81 (s, H-1), 4.54 (br, OH-6), 3.41-3.80 (m, H-3, H-5, H-6), 3.22-3.41 (m, H-2, H-4), 7.48 (d,  $\text{H}_{\text{Ar-1}}$ ), 7.10 (d,  $\text{H}_{\text{Ar-2}}$ ), 7.92 (s,  $\text{H}_{\text{Ar-3}}$ ), 2.06 (s,  $-\text{CH}_3$ ).  $^{13}\text{C}$  NMR/ppm,  $\text{DMSO-d}_6$ : 128.4 ( $\text{C}_{\text{Ar-imid}}$ ), 125.7 ( $\text{C}_{\text{Ar-imid}}$ ), 102.2 (C-1), 81.8 (C-4), 73.2 (C-3), 72.6 (C-2), 72.2 (C-5), 60.1 (C-6), 30.9 ( $-\text{CH}_3\text{-imid}$ ). Yield = 0.86g, 0.63 mmol, 92%, M.pt: 197-202°C. TLC:  $R_f$  = 0.54.

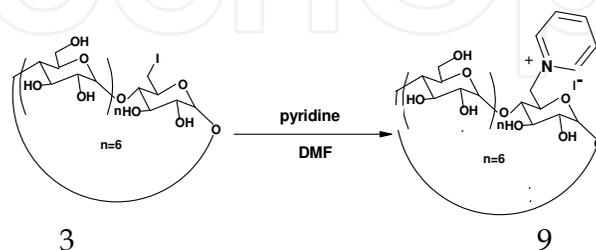
### 3.7.3.5 Synthesis and characterisation of mono-6-deoxy-6-(3-butylimidazolium)- $\beta$ -cyclodextrin iodide (8) ( $\beta$ -CD-BUTIMIOD)



Scheme 3.8. Synthetic pathway for the preparation of  $\beta$ -CD-BUTIMIOD

FTIR/KBr,  $\text{cm}^{-1}$ : 3378 (O-H), 2924 (C-H), 1032 (C-O), 1655 (C=C), 1151 (C-N).  $^1\text{H}$  NMR/ppm,  $\text{DMSO-d}_6$ : 7.10 (d,  $\text{H}_{\text{Ar}}$ ), 7.46 (d,  $\text{H}_{\text{Ar}}$ ), 7.92 (s,  $\text{H}_{\text{Ar}}$ ), 5.60-5.81 (m, OH-2, OH-3), 4.81 (s, H-1), 4.43-4.62 (br, OH-6), 3.29-3.65 1.73 (s,  $\text{CH}_2\text{-im}$ ), 1.21 (s,  $\text{CH}_2\text{-im}$ ), 0.85 (s,  $\text{CH}_2\text{-im}$ ), (m, H-3, H-5, H-6), 3.15-3.39 (m, H-2, H-4), 2.27 (m), 2.06 (s), 1.93 (s).  $^{13}\text{C}$  NMR/ppm,  $\text{DMSO-d}_6$ : 128.3( $\text{C}_{\text{Ar-imid}}$ ), 125.6( $\text{C}_{\text{Ar-imid}}$ ), 102.1 (C-1), 81.7 (C-4), 73.2 (C-3), 72.5 (C-2), 72.2 (C-5), 60.1 (C-6), 30.9(- $\text{CH}_3\text{-imid}$ ), 36.0(- $\text{CH}_2\text{-imid}$ ), 20.9. Yield = 0.82g, 0.58 mmol, 85%. M.pt: 219-221°C. TLC:  $R_f$  = 0.57.

### 3.7.3.6 Synthesis and characterisation of mono-6-deoxy-6-pyridinium $\beta$ -cyclodextrin iodide (9) ( $\beta$ -CD-PYRIOD)



Scheme 3.9. A schematic pathway for the preparation of  $\beta$ -CD-PYRIOD

FTIR/KBr,  $\text{cm}^{-1}$ : 3388 (O-H), 2929 (C-H), 1027 (C-O), 1656 (C=C), 1151 (C-O).  $^1\text{H}$  NMR/ppm,  $\text{DMSO-d}_6$ : 9.01 (d,  $\text{H}_{\text{Ar}}$ ), 7.48 (d,  $\text{H}_{\text{Ar}}$ ), 7.12 (t,  $\text{H}_{\text{Ar}}$ ), 5.50-5.84 (m, OH-2, OH-3), 4.81 (s, H-1), 4.51 (t, OH-6), 3.42-3.78 (m, H-3, H-5, H-6), 2.98-3.42 (m, H-2, H-4).  $^{13}\text{C}$  NMR/ppm,  $\text{DMSO-d}_6$ : 128.2 ( $\text{C}_{\text{Ar}}$  (ortho)), 125.6 ( $\text{C}_{\text{Ar}}$  (meta)), 120.3 ( $\text{C}_{\text{Ar}}$  (para)), 102.4 (C-1), 81.9 (C-4), 73.6 (C-3), 72.8 (C-2), 72.4 (C-5), 60.4 (C-6) 48.3 (C-6'). Yield = 0.855g, 0.63 mmol, 88%, M.pt: 216-218°C. TLC:  $R_f$  = 0.51

### 3.8 Synthesis of CD-IL polymers

The CD-IL complexes (both tosylate and iodide derivatives) were reacted with bifunctional diisocyanate linkers to produce CD-IL polymers. Typically, the  $\beta$ -CD-IL complex (1.00g, 0.88 mmol) was dissolved in DMF (20 mL), and reacted with the bifunctional linker (10 equiv.) in DMF at 75°C for 18-24 hours. Two bifunctional linkers were used for the polymerisation of the CD-IL complexes. These are hexamethylene diisocyanate (HDI) and toluene-2,4-diisocyanate (TDI). The polymerisation reaction was monitored by IR spectroscopy. The completion of the polymerisation was confirmed by the total disappearance of the isocyanate peak at 2270  $\text{cm}^{-1}$  after 18-24 hours (Li and Ma, 1999). The reaction mixture was then precipitated by the addition of acetone (100 mL). The solid formed was then left to settle in acetone for 10 minutes to allow for the removal of residual DMF from the polymers. To remove traces of DMF which may have been present, the polymers were filtered and washed with copious amounts of acetone (100 mL). The polymers were then dried overnight under reduced pressure. The examples of the synthesised polymers are shown in Figures 3.10 and 3.11.

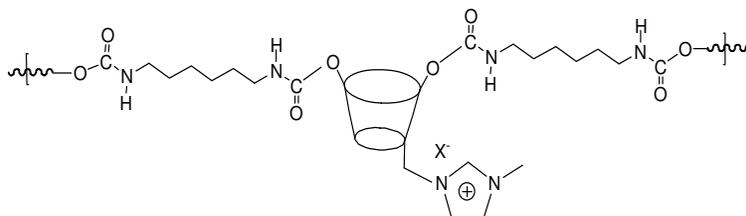


Fig. 3.1. Structure of CD-IL hexamethylene diisocyanate polymer

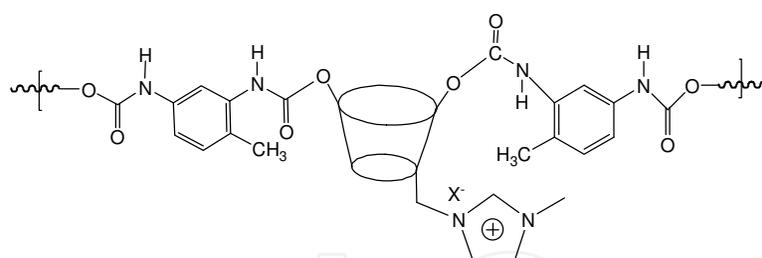


Fig. 3.2. Structure of CD-IL toluene-2,4-diisocyanate polymer

### 3.9 Absorption studies of the CD-IL polymers

The synthesized CD-IL polymers were found to be insoluble in water and other organic solvents, an important feature for their application in the removal of organic and inorganic pollutants from water. Using model contamination experiments, the ability of the polymers to absorb organic and inorganic pollutants from an aqueous medium was studied. In these model experiments, a known concentration of the pollutant in water was passed through the polymers. Quantification of organic pollutants was achieved by using UV-visible spectroscopy and GC-MS analysis. Inorganic pollutants (heavy metals) were quantified using AAS.

#### 3.9.1 UV-Visible spectroscopy absorption experiments

To measure the UV absorbance of *para*-nitrophenol (PNP), a Cary 50 UV-visible spectrophotometer was used. PNP was chosen because phenolic compounds are prevalent as pollutants in most aquatic systems. Compounds that can be analysed by this technique must have chromophores (i.e. covalently bonded but unsaturated groups such as NO<sub>2</sub>, C=C and C=O) that absorb electromagnetic radiation in the ultraviolet and visible regions of the spectrum (Field et al., 1995). An added advantage of using PNP is that it can be easily monitored by UV-visible spectroscopy since it strongly absorbs at 318 nm (visible region of the spectrum). A 10 mm quartz cuvet cell was used as a sample holder. The instrument was calibrated using PNP standards (2, 5, 10, 15 and 20 ppm) and a calibration curve was plotted and used to determine the amount of the PNP absorbed by the polymers. For the actual analysis of the pollutants, the pollutant under investigation, (30 mL, 10 mg.L<sup>-1</sup>) was typically passed through a CD-IL polymer (300 mg) (i.e. HDI and TDI polymers) packed in a C-18 SPE chromatography column. PNP was allowed to pass through the polymers at a flow rate of 5 mL per minute. It was observed that after the extraction process that the polymers assumed the colour of the pollutant (i.e. turned yellow) while the filtrate became clearer. The filtrate was then analysed for the amount of PNP present after it had been passed through the polymer. The residual concentration of PNP absorbed by the polymers was determined from a calibration curve drawn from standards.

#### 3.9.2 GC-MS analysis

The GC-MS uses gas chromatography and mass spectroscopy as a combined analytical technique for analysing mixtures of compounds (Frederic, 2004). GC analysis separates the components in a sample and provides a representative spectral output while MS identifies the substances by electrically charging the specimen molecules; this entails accelerating them through a magnetic field thus breaking them into charged fragments and detecting the mass ions. By combining these techniques, a solution containing a number of compounds

can be analysed qualitatively and quantitatively. The sample is injected into the injector port and passed through the column by a mobile phase. Helium was used as a carrier gas in all experiments in this study. The gas sweeps the analyte into a column packed with a 0.25  $\mu\text{m}$  coating of a polymeric stationary phase in order to promote maximum separation. As the compounds emerge from the column, a signal is created whenever a compound is detected. The time duration that a compound is retained in the GC column is referred to as the retention time ( $T_R$ ). Though the retention time can assist in differentiating between compounds, it is sometimes not a reliable determiner since similar compounds can have similar retention times. Therefore, more information other than retention times is required to identify a particular compound. As the compounds elute, the MS identifies the substances by electrically charging the specimen molecules, accelerating them through a magnetic field, breaking them into charged fragments and thus detecting the different charges. These fragments are charged ions with a specific mass. The mass of the fragments divided by the charge is called mass to charge ratio ( $m/z$ ). The mass spectrum can thus be used to confirm the identity of a given compound using  $m/z$  values. Also, an internal library system can be used to relate an unknown compound by comparing the mass spectrum of a compound with mass spectra of compounds having similar fragmentation patterns and  $m/z$  values.

### 3.9.2.1 Preconcentration of water samples

The concentration of water samples when performing analyses at low concentrations is crucial because it ensures that samples are within the detection limit of the instrument (Valerie, 2003). The method used for this procedure was EPA Method 525.2, which is an EPA method for the analysis of semi-volatile organic compounds in drinking water samples (Zymark Corporation, 2001). It utilises solid phase extraction (SPE) for isolation and concentration of the analyte and GC-MS for the determination of the preconcentrated analyte. For the purposes of this study, this method was used with some modifications. For instance, a 30 mL water sample, instead of a 1000 mL, was loaded onto a conditioned C-18 SPE cartridge. The cartridge was then dried and eluted with ethyl acetate (EtOAc) and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ). After this the sample was concentrated under nitrogen to about 1 mL before analysis. The first step involved in the SPE method is the conditioning of the column with methanol. The second step involves loading of the sample in the solid sorbent. Thirdly, the sorbent is washed with a solvent that has low elution strength and lastly, the desired analyte is eluted with a suitable solvent

#### 3.9.2.1.1 2,4,6-Trichlorophenol absorption tests

2,4,6-Trichlorophenol (TCP) was selected as an additional organic pollutants to be studied because it is known to affect the respiratory system and is a recognised carcinogen. For the preparation of 50 ppm TCP standard solution (1000 mL), TCP (0.500 g) was dissolved in acetone (2 mL) and then made up to the mark by adding  $\text{CH}_2\text{Cl}_2$ . Serial dilutions were then carried out to prepare 1, 2, 5, 10, 15 and 20 ppm standard solutions. Residual TCP was determined using a calibration curve obtained from these standards. An empty C-18 SPE cartridge was filled with the polymer under investigation (0.300 g). The cartridge was then connected to a filtering unit comprising of separating funnel and a receiving Erlenmeyer flask. The Erlenmeyer flask was in turn connected to a suction pump (see Figure 3.3 for the manual set up of the SPE) to enhance a smooth and controlled flow of the water samples through the polymer. The polymer was conditioned by first passing through  $\text{CH}_2\text{Cl}_2$  (5 mL) after which a spiked water sample (30 mL, 10 ppm) was passed through the polymer at a

flow rate that was maintained between 3 and 5 mL per minute. Residual TCP was extracted from the eluent with  $\text{CH}_2\text{Cl}_2$ .

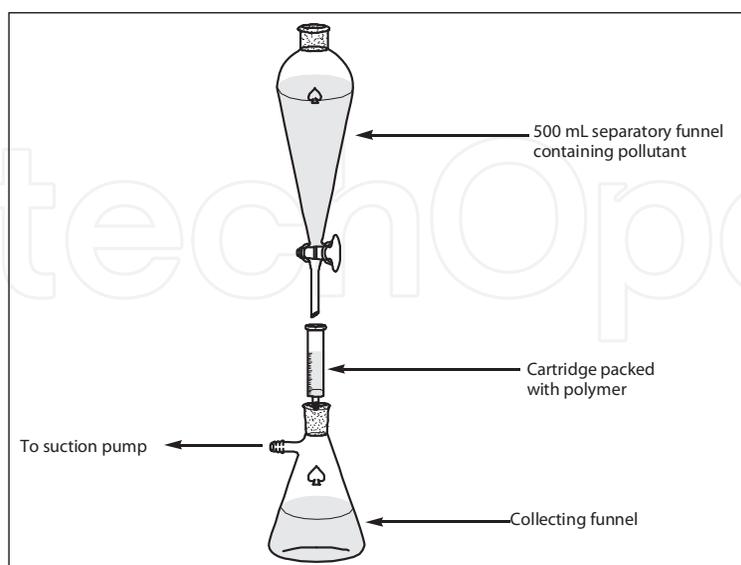


Fig. 3.3. Diagram showing the manual SPE used in this project

### 3.10 Extraction of heavy metals

Chromium and cadmium were used as model pollutants for the extraction study of heavy metals from water by the polymers. Besides being available in our laboratory, these pollutants were selected because they are toxic and lethal to the human body, particularly the central nervous system. Apparently these metals bind to sulphur bonds of enzymes resulting in the malfunctioning of the enzymes. A chromium standard ( $1000 \text{ mg.L}^{-1}$ , 1000 mL) was prepared by dissolving potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) (2.84 g), which was first pre-dried in an oven at  $110^\circ\text{C}$  for 2 hours, in distilled water (200 mL).  $\text{HNO}_3$  (1.5 mL) was then added. To prepare cadmium standard solution ( $1000 \text{ mg.L}^{-1}$ , 1000 mL), cadmium metal (1.00 g) was dissolved in a 1:1 solution of distilled water/HCl.  $\text{La}(\text{NO}_3)_2$  (1.00g) was added to stabilise the cadmium standards.

#### 3.10.1 AAS analysis

For AAS analysis, serial dilutions were made from the  $1000 \text{ mg.L}^{-1}$  standard chromium and cadmium solutions. This led to the preparation of 2, 4, 5, 6 and 8 ppm for chromium standards and 0.4, 0.6, 0.8, 1, 1.5 and 2 ppm for cadmium standards. These concentrations were chosen based on the detection limits for chromium and cadmium. These are 0.2-10 ppm and 0.05-2 ppm, respectively. Absorption of chromium was determined at 5 ppm while cadmium was measured at 1 ppm. Distilled water was used to zero the instrument as a reference sample. All measurements were performed at room temperature.

## 4. Results and discussions

### 4.1 CD-IL complexes/derivatives

The CD-IL derivatives were successfully synthesized and their physical parameters are summarised in Table 4.1.

CD and CD-IL derivatives	Melting point (°C)	Colour and form	Yield (%)
$\beta$ -CDOTs (2)	171-174	White fine powder	68
$\beta$ -CDI (3)	206-209(dec)	White fine powder	82
$\beta$ -CDMIMOTs (4)	229-229(dec)	White solid	98
$\beta$ -CDBUTIMOTs (5)	240-242	White powder	97
$\beta$ -CDPYROTs (6)	242-245(dec)	White solid	91
$\beta$ -CDMIMIOD (7)	197-202(dec)	White solid	92
$\beta$ -CDBUTIMIOD (8)	219-221(dec)	White powder	85
$\beta$ -CDPYRIOD (9)	216-218(dec)	White powder	88
$\beta$ -CDOTs: mono-6-tosyl, .. $\beta$ -CDMIMOTs: mono-6-methyl imidazolium tosylate $\beta$ -CDBUTIMOTs: mono-6-butyl imidazolium tosylate, $\beta$ -CDPYROTs: mono-6-pyridinium tosylate, $\beta$ -CDI: mono-6-CD iodide, $\beta$ -CDMIMIOD: mono-6-methyl imidazolium iodide $\beta$ -CDBUTIMIOD: mono-6-butyl imidazolium iodide, $\beta$ -CDPYRIOD: mono-6-pyridinium iodide. Dec = decomposes at its melting point.			

 Table 4.1. Yields and physical properties of the  $\beta$ -CD-IL complexes

The melting points of the synthesised CD-IL derivatives were found to range between 190 and 245°C. With the exception of the  $\beta$ -CDBUTIMOTs derivative, all the CD-IL complexes melted with decomposition. These compounds were found to be soluble in water and several organic solvents (e.g. DMF, ethanol, DMSO and ethyl acetate). For application in water treatment, it was therefore necessary to polymerise the CDI-IL complexes into water-insoluble polymers. The synthetic reactions and characterisations of these CD-IL polymers are discussed in the section that follows.

#### 4.2 Synthesis and characterisation of the CD-IL polymers

Polymerisation of the CD-IL complexes was performed as per the procedure described in section 3. Each CD-IL complex was polymerised with bifunctionalised linkers; hexamethylene diisocyanate (HDI) and toluene 2,4-diisocyanate (TDI). The polymerisation reactions were monitored using infrared spectroscopy. Figures 4.12a and 4.12b show the gradual disappearance of the isocyanate peak (N-C=O) at 2270  $\text{cm}^{-1}$  as the polymerisation reaction proceeded. The complete disappearance of the isocyanate peak at 2270  $\text{cm}^{-1}$  (after 24 hrs) marked the end of the polymerisation reaction.

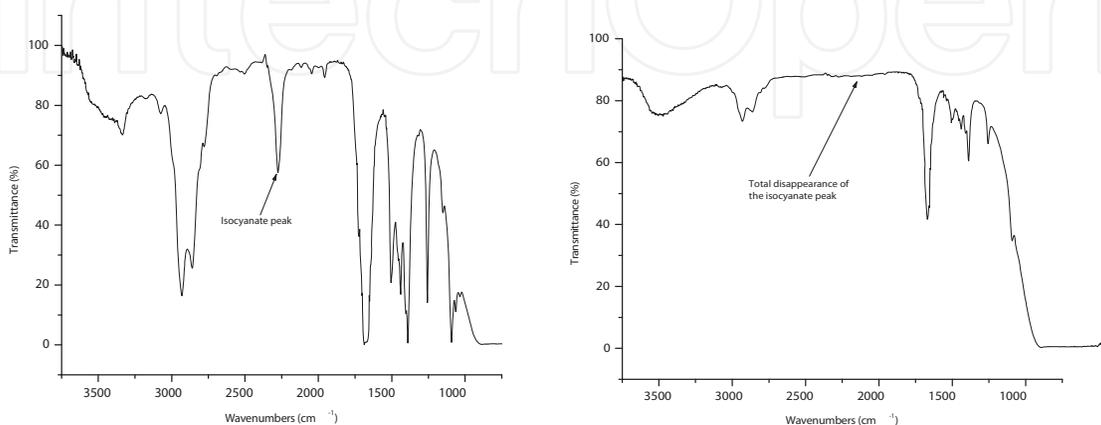


Fig. 4.12. IR spectrum showing isocyanate peak at 00 mins and after 24 hrs

### 4.3 Physical properties of the $\beta$ -CD-IL polymers

The physical properties (colour, texture and the yields) of the synthesised CD-IL polymers are shown in Table 4.2.

CD-IL polymer	Texture	Colour	Yield (%)
B-CD/HDI	Powder	White	100
B-CD/TDI	Powder	White	98
$\beta$ -CDMIMOTs/HDI	Powder	White	97
$\beta$ -CDMIMOTs/TDI	Powder	Light brown	99
$\beta$ -CDBUTIMOTs/HDI	Powder with granules	Crème white	95
$\beta$ -CDBUTIMOTs/TDI	Powder	Light brown	96
$\beta$ -CDPYROTs/HDI	Granulated powder	White	93
$\beta$ -CDPYROTs/TDI	Powder	Yellowish brown	96
$\beta$ -CDMIMIOD/HDI	Granulated powder	Crème white	100
$\beta$ -CDMIMIOD/TDI	Granulated powder	Light brown	97
$\beta$ -CDBUTIMIOD/HDI	Powder	White	100
$\beta$ -CDBUTIMIOD/TDI	Powder with granules	Light brown	95
$\beta$ -CDPYRIOD/HDI	Crystalline with powder	Beige	100
$\beta$ -CDPYRIOD/TDI	Crystalline	Yellow	94
$\beta$ -CDMIMOTs: mono-6-methyl imidazolium tosylate $\beta$ -CDBUTIMOTs: mono-6-butyl imidazolium tosylate $\beta$ -CDPYROTs: mono-6-pyridinium tosylate $\beta$ -CDMIMIOD: mono-6-methyl imidazolium iodide $\beta$ -CDBUTIMIOD: mono-6-butyl imidazolium iodide $\beta$ -CDPYRIOD: mono-6-pyridinium iodide.			

Table 4.2. Physical properties of the  $\beta$ -CD-IL polymers

While these polymers were produced in high yields, it should be noted that they are insoluble in water, an important feature for their application in water treatment. Unfortunately, NMR studies could not be performed due to the unavailability of solid-state NMR equipment. However, to study the morphology of these polymers SEM and BET surface area analyses were carried out. SEM is important because it gives us an idea of the physical morphology of the polymers while BET analysis provides an insight into the effect of the pore volume and surface area on the absorption efficiency of the polymers.

### 4.4 Scanning electron microscopy (SEM) analysis of the polymers

SEM was utilised in order to determine and compare the surface features of both the native  $\beta$ -CD and the CD-IL polymers. The SEM micrographs of both the  $\beta$ -CD/HDI and the CD-IL/HDI polymers are shown from Figure 4.13a to Figure 4.13e.

SEM images of the TDI linked polymers were also investigated and the SEM micrographs are presented in Figures 4.13 h-n.

From these SEM micrographs it can be observed that the SEM micrographs of the native  $\beta$ -CD/HDI or TDI polymers and the CD-IL polymers are different. Some of the polymers exhibit a spongy surface (e.g.  $\beta$ -CDPYROTs/HDI and  $\beta$ -CDMIMOTs/TDI) while others are crystalline (e.g.  $\beta$ -CDBUTIMIOD/HDI and  $\beta$ -CDMIMIOD/TDI). From these results it can be concluded that the type of cation (pyridine or alkyl imidazole) or anion (iodide or tosylate)

have an effect on the physical surface of the polymers. However, it is not clear at this stage whether these differences are as a result of some discrepancies during the processing of the polymers, thus BET analysis was carried out to further elucidate their physical properties.

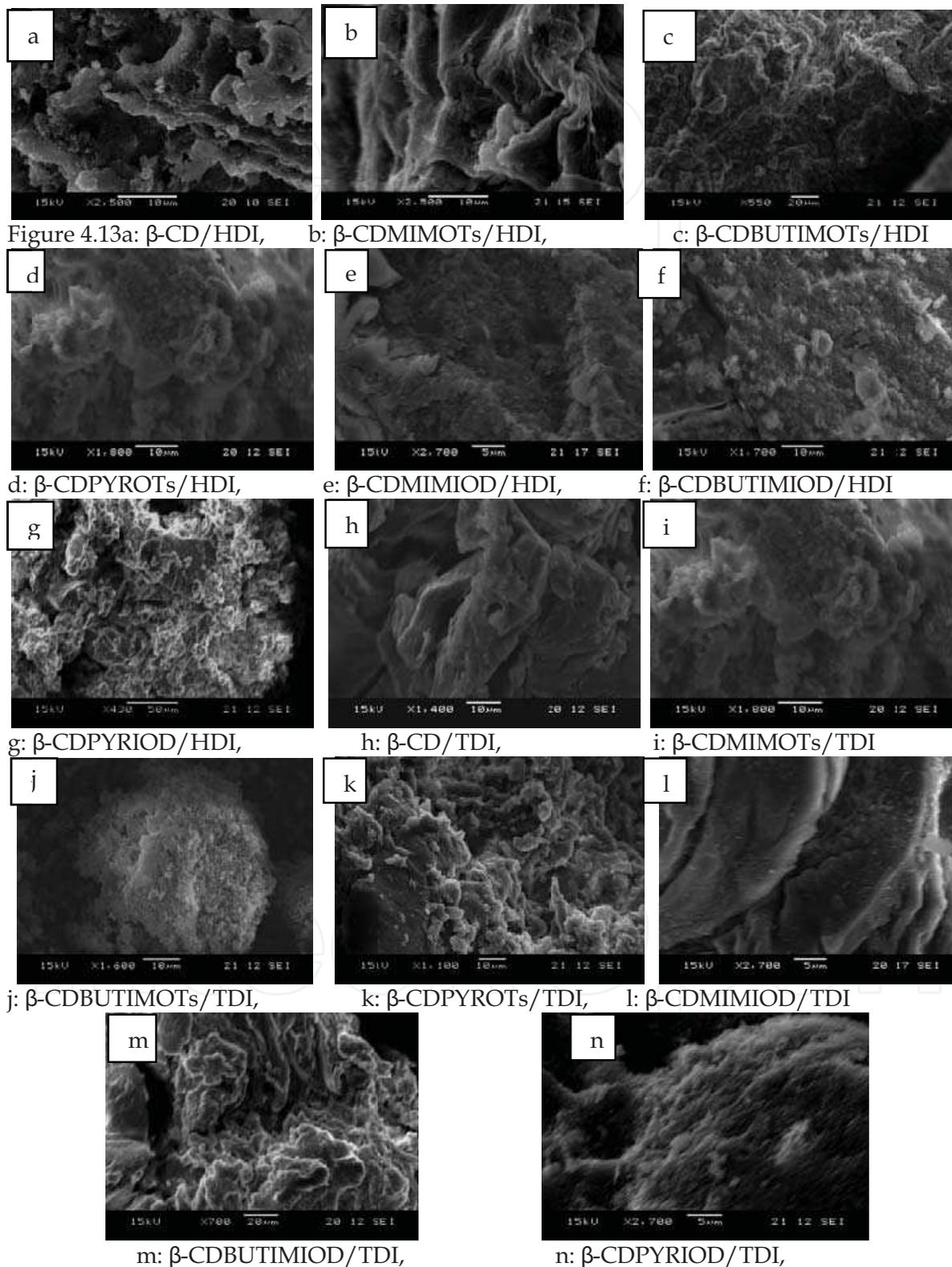


Fig. 4.13.

#### 4.5 BET analysis of the polymers

Polymers	HDI		TDI	
	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)
B-CD	2.53	0.009	1.706	0.009
$\beta$ -CDMIMOTs	23.26	0.084	22.71	0.11
$\beta$ -CDBUTIMOTs	2.99	0.014	10.51	0.023
$\beta$ -CDPYROTs	2.89	0.063	1.64	0.026
$\beta$ -CDMIMIOD	2.51	0.012	1.81	0.080
$\beta$ -CDBUTIMIOD	10.88	0.058	1.78	0.0066
$\beta$ -CDPYRIOD	0.4427	0.0036	7.00	0.030

Table 4.3. BET results of the polymers

These BET results show that there is no pattern observed between the surface area and the incorporation of the imidazolium or pyridinium ring onto the CD backbone. For example, the highest surface area recorded was for the  $\beta$ -CDMIMOTs/HDI polymer (23.26 m<sup>2</sup>/g) while the lowest was 0.4427 m<sup>2</sup>/g ( $\beta$ -CDPYRIOD/HDI polymer). However, the surface area significantly increased for the  $\beta$ -CDMIMOTs (both HDI and TDI polymers).

#### 4.6 Thermal analysis of the polymers

To determine the stability, melting and decomposition temperatures of the polymers, thermal analysis of the polymers was carried out using TGA and DSC. The findings of this study are presented in the following sections.

##### 4.6.1 TGA analysis of the polymers

The polymers generally had similar heating profiles. Representative TGA graphs of the native  $\beta$ -CD/HDI,  $\beta$ -CDMIMIOD/HDI and  $\beta$ -CDPYROTs/TDI polymers are shown in Figure 4.14. Other TGA thermographs are shown in Appendix B.

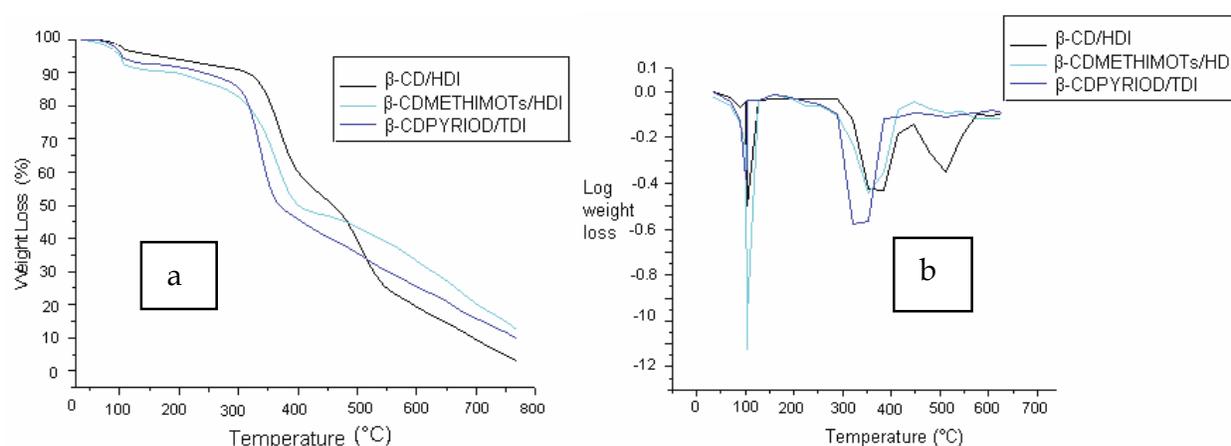


Fig. 4.14. (a) TGA thermographs and (b) derivative curves of the native  $\beta$ -CD and CD-IL polymers

The TGA thermographs (Figure 4.14(a)) showed some differences between the native  $\beta$ -CD polymers and the CD-IL polymers. The polymers showed a three step degradation process;

the first step at about 100°C (loss of water), the second step at about 350°C (melting point of the polymer) and lastly the decomposition of the polymers at about 520°C. However, to fully study the thermal behaviour of these polymers derivative curves of both the  $\beta$ -CD polymers and the CD-IL polymers were done. These derivative curves are presented in Figure 4.14(b). Analysis of the derivative curves confirmed that the native  $\beta$ -CD polymers showed three different regions which were characterised by the loss of water at 100°C, the melting point at about 350°C and the decomposition of the polymers at about 520°C. The imidazolium CD-IL polymers on the other hand showed only two regions; loss of moisture at 100°C and the melting point was accompanied by degradation at about 350°C. However, the pyridinium based CD-IL polymers had lower melting points at 320°C.

#### 4.6.2 DSC analysis of the polymers

DSC analysis was also performed in order to compare the thermal properties of the polymers with or without the attachment of the imidazolium or pyridinium moieties. Noteworthy is that the DSC thermograms are generally similar thus Figure 4.16 shows representative DSC thermographs of the polymers.

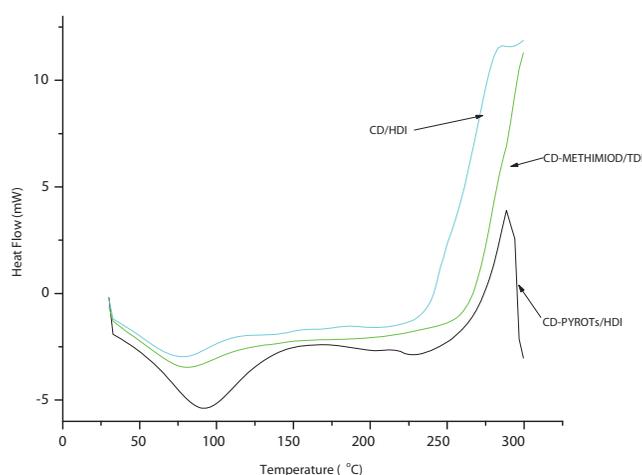


Fig. 4.16. DSC chromatograms of the native  $\beta$ -CD and CD-IL polymers

The DSC thermograms all showed an endothermic peak associated with the evaporation of water and other organic solvents at about 95°C. The thermograms also showed an extra endothermic peak at 250°C which corresponds to the melting points of these polymers. For all three polymers degradation occurred at around 300°C.

#### 4.7 Absorption studies of the polymers

Four pollutants (two organic and two inorganic) were used as model pollutants for the study of the absorption capabilities of the polymers. These pollutants are *para*-nitrophenol (PNP), 2,4,6-trichlorophenol (TCP), chromium VI and cadmium II and were readily available in our laboratory.

##### 4.7.1 Absorption of *para*-nitrophenol (PNP) and 2,4,6-trichlorophenol (TCP)

*p*-Nitrophenol (PNP) was chosen as a model pollutant because phenolic compounds are prevalent as pollutants in most aquatic systems. Also, PNP can be easily monitored by UV-Visible spectroscopy because of its yellow colour. Polymers formed by cross-linking the

synthesised CD-IL complexes with HDI and TDI linkers were investigated for their ability to absorb PNP. *p*-Nitrophenol (30 mL, 10mg.L<sup>-1</sup>) was passed through the polymers (300 mg) as described in section 3. The absorbance values were recorded in triplicates at room temperature. TCP, which is known to affect the respiratory system and is carcinogenic, was also used as a model pollutant and was studied using GC-MS. TCP standard solution (30 mL, 10 mg.L<sup>-1</sup>) was used to determine the absorption efficiencies of the polymers. The residual amount of the TCP was extracted by liquid-liquid extraction with CH<sub>2</sub>Cl<sub>2</sub> as outlined in section 3 after it was passed through the polymers. Results obtained from these analyses are summarised in Tables 4.3. The native  $\beta$ -CD polymer was included in the study for comparison purposes.

Polymers	Amount of PNP and TCP removed (%)			
	HDI linker		TDI linker	
	PNP	TCP	PNP	TCP
$\beta$ -CD	64	54	68	58
$\beta$ -CDMIMOTs	80	69	77	69
$\beta$ -CDBUTIMOTs	68	69	64	77
$\beta$ -CDPYROTs	15	63	40	60
$\beta$ -CDMIMIOD	65	75	55	74
$\beta$ -CDBUTIMIOD	63	67	71	71
$\beta$ -CDPYRIOD	24	69	48	61

Table 4.3. Percentage absorption efficiency of PNP by HDI and TDI polymers

As mentioned in section 2, the amount of the pollutant absorbed can be affected by the type of cation or anion, or the length of the alkyl chain attached to the imidazolium or pyridinium ring. It was, therefore, necessary to study the effect of these properties on the absorption efficiency of PNP and TCP by the polymers. Also, the effect of the linker on the overall performance of the polymer was investigated. These variations are discussed in the section that follows.

#### 4.7.1.1 Effect of the type of the cation on the extraction of the organic pollutants

It is very clear from Table 4.3 that the incorporation of the imidazolium ring onto the CD backbone generally enhances the absorption efficiencies of the polymers (i.e. with respect to PNP). In fact, the highest absorption (80%) was recorded for  $\beta$ -CDMIMOTs/HDI. However, the pyridinium-based showed less affinity for PNP. For example, the absorption efficiencies of  $\beta$ -CDPYROTs/HDI and  $\beta$ -CDPYRIOD/HDI were a mere 15% and 24%, respectively. The corresponding TDI polymers followed a similar pattern. In contrast, both the imidazolium- and pyridinium-based polymers are better at absorbing TCP when compared to the native cyclodextrin polymers. It is not clear at this stage why the extraction of PNP is influenced by the type of cation.

#### 4.7.1.2 Effect of the imidazolium alkyl chain on the extraction of the organic pollutants

The effect of the length of the alkyl chain attached to the imidazolium ring on the absorption efficiency of the polymers was investigated. According to previous studies (Visser et al, 2001; Pandey, 2006), the longer the alkyl chain the less effective is the ionic liquid for metal ion extraction. In our study, two substituents (methyl and butyl) have been incorporated onto the ionic liquid component (imidazolium) of the polymer and this allowed us to test

this concept. Results presented in Table 4.3 indeed confirmed that the alkyl chain had an effect on the amount of pollutant absorbed by the polymers. As expected, the methylimidazolium polymers were generally found to have a higher absorption efficiencies compared to their butylimidazolium counterparts.

#### 4.7.1.3 Effect of the type of anion on the extraction of the organic pollutants

To further study the absorption efficiencies of the polymers, the effect of the counter-anion (tosylate and iodide) on the absorption capacity of the polymers was investigated. It was observed that the amount of pollutant absorbed and the type of anion present in the polymer were not well correlated. As summarised in Figure 4.17a and Figure 4.17b, the type of the anion does not seem to significantly affect the absorption of both PNP and TCP.

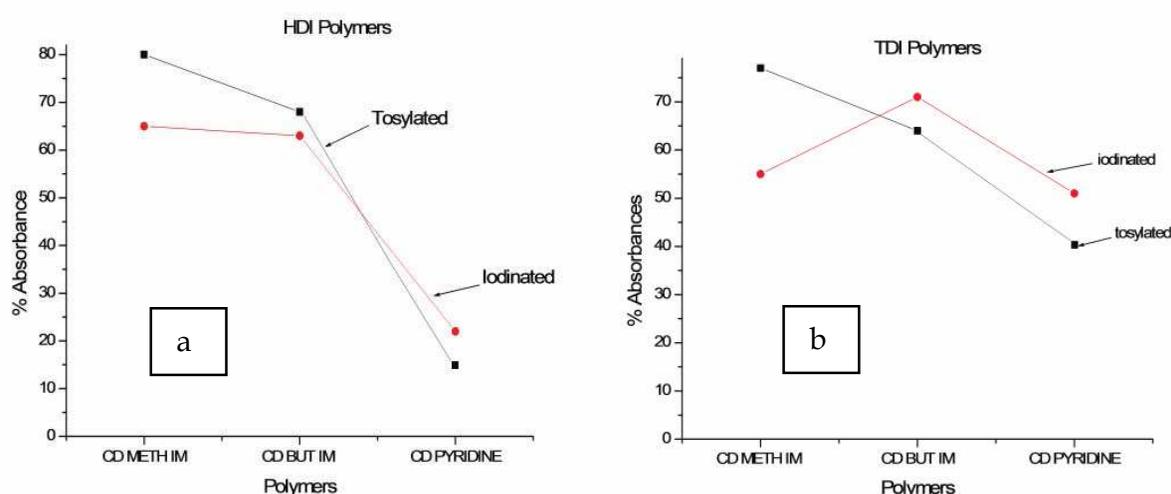


Fig. 4.17. Comparison of PNP absorbed by tosylated versus iodinated HDI-linked (a) and (b) TDI-linked polymers.

#### 4.7.1.4 Effect of the linker on the extraction of the organic pollutants

Figures 4.17a and 4.17b were also used to determine how the linkers affected the absorption efficiency of the polymers. According to these results, the tosylated polymers showed better absorption efficiencies than the TDI linked polymers (especially the imidazolium polymers) for the HDI-linked polymers. However, this was not the case with the pyridinium polymers where higher absorption efficiency was observed for the iodinated polymers. For the TDI-linked polymers, it was observed that the iodinated polymers had better absorption efficiencies compared to the tosylated polymers with the exception of  $\beta$ -CD-methylimidazolium tosylate polymer.

#### 4.7.2 Absorption of chromium ( $\text{Cr}^{6+}$ ) and cadmium ( $\text{Cd}^{2+}$ ) by the polymers

Chromium is a toxic inorganic pollutant (heavy metal), especially when present in water as  $\text{Cr}^{6+}$ . This metal ion can penetrate the skin causing irritation, liver and kidney damage as well as a decrease in male sperm counts (Li and Ma, 1999; Morales et al., 1999). Chromium standards were prepared as outlined in Chapter 3 and a  $\text{Cr}^{6+}$  concentration of  $5 \text{ mg.L}^{-1}$  ( $30 \text{ mL}$ ) was passed through the polymers ( $300 \text{ mg}$ ). The detection limit of  $\text{Cr}^{6+}$  by AAS is  $0.002 \text{ mg.L}^{-1}$ . A working range of  $0.2\text{-}10 \text{ mg.L}^{-1}$  was recommended thus  $5 \text{ mg.L}^{-1}$  was used for its analysis. Cadmium ion ( $\text{Cd}^{2+}$ ) was also used as a model inorganic pollutant to study the absorption

efficiencies of the CD-IL polymers. Cadmium was studied because it is toxic and even lethal to the human body, particularly the central nervous system (Morales et al., 1999). This metal ion has a great affinity for sulphur hence it attacks the sulphur bonds of enzymes making them to function improperly (Lewis and Evans, 2001). Cadmium standards were prepared as outlined in section 3 and a concentration of  $\text{Cd}^{2+}$  ( $1 \text{ mg.L}^{-1}$ , 30 mL) was passed through the polymers (300 mg). The detection limit of  $\text{Cd}^{2+}$  by AAS is  $0.002 \text{ mg.L}^{-1}$ . Since a working range of  $0.005\text{--}2 \text{ mg.L}^{-1}$  is recommended, a  $1 \text{ mg.L}^{-1}$  was used for  $\text{Cd}^{2+}$  analysis. After passing the  $\text{Cr}^{6+}$  and the  $\text{Cd}^{2+}$  spiked water sample through the CD-IL polymers, AAS analysis of the eluent was performed. Results obtained are shown in Table 4.4. Native  $\beta$ -CD polymers were also used to see if they can absorb inorganic pollutants from an aqueous medium.

Polymers	Amount of $\text{Cr}^{6+}$ and $\text{Cd}^{2+}$ removed (%)			
	HDI linker		TDI linker	
	$\text{Cr}^{6+}$	$\text{Cd}^{2+}$	$\text{Cr}^{6+}$	$\text{Cd}^{2+}$
$\beta$ -CD	34	18	60	24
$\beta$ -CDMIMOTs	100	33	100	28
$\beta$ -CDBUTIMOTs	98	32	97	23
$\beta$ -CDPYROTs	100	24	95	20
$\beta$ -CDMIMIOD	69	15	43	18
$\beta$ -CDBUTIMIOD	51	21	95	17
$\beta$ -CDPYRIOD	34	10	60	13

Table 4.4. Comparison of absorption efficiency of  $\text{Cr}^{6+}$  by HDI and TDI polymers

It is clear from Table 4.4 that the incorporation of the ionic liquid component onto the CD backbone resulted in high absorption of  $\text{Cr}^{6+}$ . Absorption of  $\text{Cd}^{2+}$  was however significantly reduced. For example,  $\beta$ -CDMIMOTs/HDI polymer absorbed 100% of the  $\text{Cr}^{6+}$  but only 33% of the  $\text{Cd}^{2+}$  was absorbed. This can be attributed to the fact that ionic liquids are selective in the absorption of heavy metal ions (Welton, 1999; Chowbury et al., 2007). For example, the incorporation of sulphur or urea in the alkyl chain of the cation has been reported to greatly enhance the absorption of  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  from an aqueous medium (Visser et al., 2002). This observation suggests that, to improve the extraction of  $\text{Cd}^{2+}$ , further studies that incorporate sulphur or urea on the cations need to be carried out. A discussion on how variations of cation, anion, alkyl chain as well as the linker impact on the extraction efficiency of the polymers follows in the next section.

#### 4.7.2.1 Effect of the type of the cation on the extraction of the inorganic pollutants

The incorporation of the imidazolium or pyridinium rings onto the CD backbone was found to have no bearing on the amount of the pollutant absorbed by the polymers. Some imidazolium-based polymers (e.g.  $\beta$ -CDMIMOTs) and some pyridinium-based polymers (e.g.  $\beta$ -CDPYROTs) had 100% absorption efficiencies for  $\text{Cr}^{6+}$  while some imidazolium-based polymers (e.g.  $\beta$ -CDBUTIMIOD/HDI) and some pyridinium-based polymers (e.g.  $\beta$ -CDPYRIOD/HDI) had low absorption efficiencies of 51 and 34%, respectively. The same polymers, however, showed less efficiency in the absorption of  $\text{Cd}^{2+}$ .

#### 4.7.2.2 Effect of the imidazolium alkyl chain on the extraction of the inorganic pollutants

The length of the alkyl chain of the imidazolium ring was also investigated to determine its effect on the absorption efficiency of the polymers. From Table 4.4 it was observed that

increasing the alkyl chain of the imidazolium ring did not have much bearing on the amount of either  $\text{Cr}^{6+}$  or  $\text{Cd}^{2+}$  absorbed by the polymers. No pattern could be established between the amount of pollutant (either  $\text{Cr}^{6+}$  or  $\text{Cd}^{2+}$ ) absorbed and the length of the alkyl chain attached to the imidazolium ring.

#### 4.7.2.3 Effect of the type of anion on the extraction of the inorganic pollutants

The type of anion of the ionic liquid seems to have an effect on the amount of  $\text{Cr}^{6+}$  and  $\text{Cd}^{2+}$  absorbed by the polymers (Table 4.4). The tosylated polymers (both HDI and TDI) showed high absorption efficiencies of  $\text{Cr}^{6+}$  and  $\text{Cd}^{2+}$  than the iodinated polymers (Figure 4.18). The tosylate anion enhances the chelation (hexavalent dentition) of the chromium with the cationic component of the CD-IL polymers because it is a hydrophobic anion (Welton, 1999), while the iodide anion is a hydrophilic anion; hence the tosylate anion enhances the chelation of the heavy metal by repelling the water molecules from the cationic component (Cocalia et al., 2006).

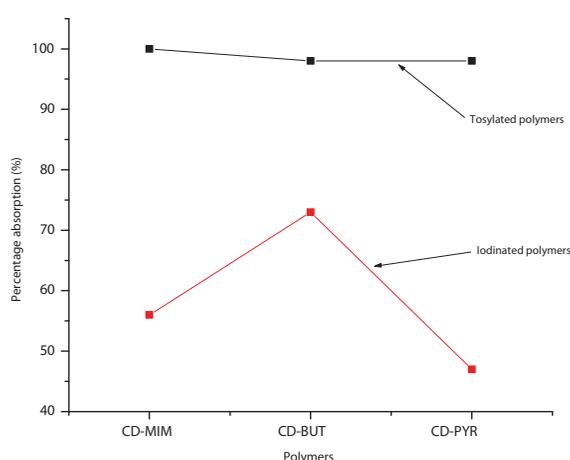


Fig. 4.18. Comparison of  $\text{Cr}^{6+}$  absorbed by average tosylated versus average iodinated polymers (both (TDI and HDI))

#### 4.7.2.4 Effect of the linker on the extraction of the inorganic pollutants

For the absorption of  $\text{Cd}^{2+}$  and the  $\text{Cr}^{6+}$ , there appears to be no correlation between the amount of pollutant absorbed and the type of linker used. For instance, the  $\beta$ -CDMIMOTs polymer absorbed 100% of  $\text{Cr}^{6+}$  irrespective of the linker used. However, it is noteworthy that the native  $\beta$ -CD polymers were able to absorb some chromium and cadmium from water. The HDI and TDI polymers showed 34% and 60% of  $\text{Cr}^{6+}$ , respectively, while 18 and 24% absorption efficiencies were respectively observed for the  $\text{Cd}^{2+}$  polymers. This observation is attributed to the ability of cyclodextrins to form complexes with chromium (Cardas et al., 2005). Similar findings (Brusseau et al., 1997), confirm that not only can modified cyclodextrins form complexes with organic compounds, but they can also complex with cationic heavy metals.

### 4.8 Comparison of absorption and surface area

After attaining the absorption efficiencies of the polymers, it was necessary to see if there was any correlation between the amount of pollutant absorbed and the surface area of the polymers. The results obtained are summarised in Table 4.5.

Sample	HDI					TDI				
	Surface area (m <sup>2</sup> /g)	% PNP absorbed	% TCP absorbed	% Cr <sup>6+</sup> absorbed	% Cd <sup>2+</sup> absorbed	Surface area (m <sup>2</sup> /g)	% PNP absorbed	% TCP absorbed	% Cr <sup>6+</sup> absorbed	% Cd <sup>2+</sup> absorbed
$\beta$ -CD	2.53	64	54	34	18	1.706	68	58	60	24
$\beta$ -CDMIMOTs	23.26	80	69	100	33	22.71	77	69	100	28
$\beta$ -CDBUTIMOTs	2.99	68	69	98	32	10.51	64	77	97	23
$\beta$ -CDPYROTs	2.89	15	63	100	24	1.64	40	60	95	20
$\beta$ -CDMIMIOD	2.51	65	75	69	15	1.81	55	74	43	18
$\beta$ -CDBUTIMIOD	10.88	63	67	51	21	1.78	71	71	95	17
$\beta$ -CDPYRIOD	0.4427	24	69	34	10	7.00	48	61	60	13

Table 4.5. Comparison of surface area versus percentage absorption

From these results, it was observed that there is no direct relationship between the amount of pollutant absorbed and the surface areas of the polymers. For example, both  $\beta$ -CDMIMOTs/HDI and  $\beta$ -CDPYROTs/HDI polymers showed 100% absorption efficiency for PNP yet their surface areas are significantly different, 23.26 m<sup>2</sup>/g and 2.89 m<sup>2</sup>/g, respectively.

#### 4.9 Absorption efficiencies of the polymers on a mixture of organic and inorganic pollutants

In real water samples, organic compounds and heavy metals co-exist (Brusseau et al., 1997). It was, therefore, necessary to study the absorption efficiency of the CD-IL polymers in a synthetic mixture containing both organic and inorganic pollutants. These experiments were carried out to determine if the organic and inorganic pollutants would compete for the absorption sites of the CD-IL.

##### 4.9.1 PNP and chromium

From the absorption studies of PNP and Cr<sup>6+</sup>, it was evident that the CD-IL polymers exhibited enhanced absorption efficiencies on exclusive absorption tests; hence studies to investigate whether they would still exhibit such enhanced efficiencies were carried out. PNP and Cr<sup>6+</sup> were thus chosen to study the effect of the presence of both organic and inorganic pollutants on the absorption efficiency of the polymers (Table 4.6).

Polymers	HDI linked		TDI linked	
	PNP absorbed	Cr <sup>6+</sup> absorbed	PNP absorbed	Cr <sup>6+</sup> absorbed
$\beta$ -CD	63 (64)	14 (34)	60 (68)	40 (60)
$\beta$ -CDMIMOTs	62 (80)	72 (100)	34 (77)	36 (100)
$\beta$ -CDBUTIMOTs	13 (68)	21 (98)	34 (64)	50 (97)
$\beta$ -CDPYROTs	27 (15)	23 (100)	40 (40)	29 (95)
$\beta$ -CDMIMIOD	16 (65)	36 (69)	20 (55)	14 (43)
$\beta$ -CDBUTIMIOD	69 (63)	25 (51)	47 (71)	27 (95)
$\beta$ -CDPYRIOD	14 (24)	10 (34)	43 (48)	50 (60)

Values in parenthesis refer to individual absorption of the pollutant by the polymer

Table 4.6. Comparison of HDI and TDI linked CD-IL polymers on the absorption efficiencies of a mixture of PNP (10 ppm) and Cr<sup>6+</sup> (5 ppm)

From the results in Table 4.6, it was observed that the presence of both organic and inorganic pollutants generally resulted in reduction in the absorption efficiency of the pollutants. This is an indication that there is competition between the organic and inorganic pollutants for complexing sites on the polymers. However, for  $\beta$ -CDBUTIMIOD/HDI and  $\beta$ -CDPYROTs/HDI polymers, the presence of  $\text{Cr}^{6+}$  enhanced the absorption efficiency of PNP.

#### 4.8.2 PNP and cadmium

Since the CD-IL polymers showed low absorption efficiency for the mixture of PNP and chromium spiked water samples (though separate analysis showed high absorption efficiencies), a mixture of PNP and cadmium spiked water samples was passed through the polymers in order to determine if the same observations would be seen. The results for this analysis are shown in Table 4.7.

Polymers	HDI linked		Amount removed $\text{Cd}^{2+}$ (%)	
	% PNP absorbed	% $\text{Cd}^{2+}$ absorbed	% PNP absorbed	% $\text{Cd}^{2+}$ absorbed
$\beta$ -CD	24 (64)	12 (18)	42 (68)	17 (24)
$\beta$ -CDMIMOTs	48 (80)	33 (33)	23 (77)	28 (28)
$\beta$ -CDBUTIMOTs	15 (68)	32 (32)	25 (64)	23 (23)
$\beta$ -CDPYROTs	18 (15)	24 (24)	51 (40)	20 (20)
$\beta$ -CDMIMIOD	16 (65)	15 (15)	23 (55)	18 (18)
$\beta$ -CDBUTIMIOD	66 (63)	21 (21)	43 (71)	17 (17)
$\beta$ -CDPYRIOD	13 (24)	10 (10)	37 (48)	13 (13)

Values in parenthesis refer to individual absorption of the pollutant by the polymer

Table 4.7. Comparison of HDI and TDI linked CD-IL polymers on the absorption efficiencies of PNP (10 ppm) and  $\text{Cd}^{2+}$  (1 ppm)

From Table 4.7 it was observed that the absorbances of the CD-IL polymers remain the same, (low regardless of the type of heavy metal ion used (i.e. whether  $\text{Cd}^{2+}$  or  $\text{Cr}^{6+}$ )). It was observed that the absorption efficiency of the polymers generally decreased in the presence of both organic and inorganic pollutants an indication that  $\text{Cd}^{2+}$  retards the absorption of both organic and inorganic pollutants from water. However, a thorough investigation needs to be carried out to ascertain these observations.

## 5. Conclusions

Based on the aims and objectives of this investigation as set out earlier in the chapter, it can be concluded that this study was successful and the following conclusions can therefore be drawn:

Alkyl imidazolium and pyridinium based CD-IL complexes were successfully synthesised from monotosylated and monoiodinated CDs in relatively high yields and they were successfully characterised using IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopic techniques. The CD-IL complexes were successfully polymerised using hexamethylene diisocyanate (HDI) and toluene-2,4-diisocyanate to form CD-IL polymers. Unlike the water soluble CD-IL complexes, the synthesised CD-IL polymers were insoluble in water and common organic

solvents such as DMF,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{OH}$ . This property is very important because it is usually exploited thus allowing their application in water treatment. Further analysis of the polymers using SEM revealed that some of the polymers (e.g.  $\beta$ -CDPYROTs/HDI and  $\beta$ -CDMIMOTs/TDI) had a spongy surface while others were crystalline (e.g.  $\beta$ -CDMIMIOD/TDI and  $\beta$ -CDBUTIOD/HDI). However, it could not be determined whether this phenomenon was due to the incorporation of the pyridinium or the imidazolium rings. Also, BET results were not conclusive because no relationship could be established between the pore volume, surface area and the amount of pollutant absorbed by the polymers.

Thermal analyses of the polymers revealed that not only were CD-IL polymers more stable than the native CD polymers, the thermal stability of the CD-IL polymers were affected by the type of cation. It was established that the polymers containing pyridinium-based polymers are less stable than the imidazolium-based polymers. The CD-IL polymers were effective at the removal of organic and inorganic pollutants from water. The  $\beta$ -CDMIMOTs/HDI polymer showed high absorption efficiency for both organic (80% with respect to PNP) and inorganic (100% with respect to  $\text{Cr}^{6+}$ ) pollutants. The CD-IL polymers showed very little affinity for cadmium. This implies that the CD-IL polymers we synthesised are not suitable for the absorption of  $\text{Cd}^{2+}$  from an aqueous media. From the results obtained from this study, it was found that the absorption efficiency of the CD-IL polymers was generally retarded when a synthetic mixture of organic and inorganic pollutants was analysed. This therefore revealed that the organics and inorganics compete for complexing sites of the CD-IL polymers.

## 6. Future work

Also, as part of future work on this subject, the following is under study for future work. This study only explored the use of imidazolium and pyridinium cations in the synthesis of CD-IL complexes. Synthesis of CD-IL complexes using other cations like ammonium and phosphonium cations need to be explored. Other anions such as hexafluorophosphate ( $\text{PF}_6$ ), tetrafluoroborate ( $\text{BF}_4$ ) and trioctylmethylammonium thiosalicylate (TOMATS) have also not been tried. Conversion of the tosylate or iodide anions (of the CD-IL complexes we synthesised) into hydrophobic anions (e.g. the less toxic TOMATS) would generate new and insoluble CD-IL complexes. This would thus eliminate the need for the preparation of the CD-IL polymers. Attachment of thio, thioether, thiourea and urea on the cationic components of the ionic liquid has been reported to have high complexation capabilities for cadmium and mercury (Visser et al., 2002). Such attachments, especially on the imidazolium ring, need to be explored.

Above that, absorption efficiencies of the polymers were done only at high concentrations (ppm levels) and using only four pollutants. It would be important to test these polymers at lower concentrations (ppb levels) and on a wide range of organic and inorganic pollutants. The preliminary studies in our laboratory have shown that there is competition for complexation sites between the anion and the cation, conditions that would decrease this competition need to be found to exploit the full extent of the absorption capabilities of the polymers. Since the effectiveness of the polymers was studied for only one cycle, more multiple cycles need to be studied in order to test the strength of the polymers and their ability to still absorb pollutant species after a number of cycles.

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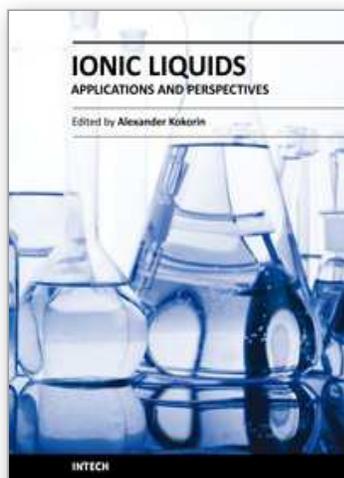
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