CHAPTER 1

INTRODUCTION

1.1) Background study

Ionic liquids can be defined as ionic compounds which are liquid below 100°C. For the past decade ionic liquid had gathered significant interest in academic purposes as well as recognized as new alternatives to modern chemical application and industries. This is due to the fact that ionic liquid emerge as feasible alternatives for more “green” and environmental friendly solvents. It is important to note that ionic liquids are also referred with different terminologies such as room temperature ionic liquid (RTIL) (Berthod&Broch, 2002), non-aqueous ionic liquid, molten salts and fused salts.

As stated in its definition above, ionic liquids are a liquid. However it is wholly composed of ions (G.Singh&A.Kumar, 2008). Even though ionic liquids looked like a classical liquid, ionic liquids do not composed of molecules. Instead, they are composed of cations and anions. The cations of an ionic liquid may be organic or inorganic while the anions are inorganic. The cations and anions of an ionic liquid presents at exactly equal number which contribute to its electrical neutrality properties.

The fascinations toward ionic liquids as “green solvents” expand exponentially in recent years because ionic liquid have no measurable vapor pressure. Consequently, it does not emit volatile organic compounds (VOCs) (Earle & Seddon, 2000). Ionic liquids show other unique properties such as non-volatility, non-flammability and low viscosity, chemical and electrochemical stability (Wilker & Zaworotko, 1992; Fuller et al., 1994; McEwen et al., 1999). Other than that, ionic liquids are also reported to have good electricity conductivity, high ionic mobility and excellent chemical stabilities (Chauvin & Olivier, 1995; Ngo et al., 2000).

Ionic liquids had been used extensively in analytical chemistry for example, as solvent in liquid-liquid extractions, as an addictive in HPLC, as an electrolyte in Capillary Electrophoresis, as matrixes for MALDI-TOF MS and as stationary phase in Gas Chromatography (Berthod&Broch, 2002). Other than that, ionic liquids are widely used in chemical reactions or catalysis (Wasserscheid, 2003), have potential usage in petroleum industry (Koel et al., 2003) and utilization as solvents in polymerization industry (Carlin & Wilkes, 1990; Tang & Osteryoung, 1991).

Cyclodextrins was first discovered by a French scientist, A.Villiers in 1891. In his paper, Villiers reported that he had isolate 3g of crystalline substance from bacterial digest of 1000g of starch (Villiers, 1891). Ever since its discovery, there are immense interests in chemical and industrial development of cyclodextrines.

Cyclodextrins are cyclic oligosaccharides consisting of 6, 7, 8 or more glucopyranose units linked by α-(1, 4) bonds (Dadziuk, 2006; Martin Del Valle, 2003). Cyclodextrines of 6, 7 or 8 glucopyranose units are known as α-cyclodextrin, β-cyclodextrin and γ-cyclodextrin respectively (Dadziuk, 2006; Martin Del Valle, 2003). Cyclodextrines are also known as cycloamyloses, cyclomaltose and Schardinger dextrines (Villiers, 1891; Eastburn et al., 1994). They are produced as a result of intramolecular transglycolation reaction from degradation of starch by cyclodextrins glucanotransferase (CGTase) enzyme (Szetjli, 1998)

The three major cyclodextrins (α-cyclodextrin, β-cyclodextrin and γ-cyclodextrin) are crystalline, homogeneous and nonhygroscopic substances. They are torus-like macro-rings structure with a central cavity (Freudenberg & Meyer-Delius, 1938; Freudenberg et al., 1939). Cyclodextrins exhibit hydrophobic inner cavity and hydrophilic exterior. These features make cyclodextrins an excellent supramolecular host. The main interest in cyclodextrin lies in their ability to form inclusion complexes (host-guest) with several other compounds. Stoddart (1989) had referred cyclodextrins as all-purpose molecular containers for organic, inorganic, organometallic and metalloorganic compounds that may be neutral, cationic, anionic or even radicals.

In addition cyclodextrins are safe and proven to be practically non-toxic to human body. These macrocyclic molecules are widely used in cosmetics industry, personal care and toiletry products manufacturing, food formulations and flavoring, applications in pharmaceutical industry, agricultural and chemical industries (Valle, 2003), environmental engineering and environmental protection (Morillo et al., 2001; Jozefaciuk et al., 2003).

Inclusion complexes are a complex in which one compound (the host) contain a cavity or spaces in which another molecular entity (the guest) are located. There is no covalent bonding occurs between the host and the guest. The inclusion complexation of these host-guest systems occurs through various interactions such as hydrogen bonding, Van Der Waals, electrostatic or hydrophobic interactions. The need to understand the interaction between ionic liquid and cyclodextrins is of importance for analytical chemistry and material synthesis.

In this paper, an inclusion complex interaction between β-cyclodextrins (β-CD) and ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) were investigated. The host molecule used in this work was β-CD and [bmim][BF_4] was used as the guest molecule. The behavior of the inclusion complex of β-CD-[bmim][BF_4] were tested through several analytical methods of the following; Fourier Transfer-Infra Red (FTIR) spectra, H1-NMR spectra, Differential Scanning Calorimetry (DSC) and Termogravimetric Analysis (TGA).

1.2) Research Objectives

The objectives of this research are;

1. To synthesis the inclusion complex of β-cyclodextrin (β-CD) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]).
2. To study the characteristics of the β-CD-[bmim][BF_4] inclusion complex through the following instrumentions
    a. Fourier Transfer-Infra Red (FTIR) spectra
    b. H1-NMR spectra
    c. Differential Scanning Calorimetry
    d. Termogravimetric Analysis (TGA)
3. To propose possible structure of β-CD-[bmim][BF_4] inclusion complex.

CHAPTER 2

LITERATURE REVIEW

2.1 Ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]).

Ionic liquid is considered as a “green alternatives” to the conventional volatile solvents and referred as environmental friendly solvents for various usages in chemical industries. This notable green solvents exhibit advantageous physicochemical properties such as negligible vapor pressure, excellent thermal stability, strong ability to dissolve many chemicals, high electrical conductivity, wide electrochemical window and ability of repetitive utilization (Consorti et al., 2005; Li et al., 2006; Gao et al., 2006). Among various ionic liquids, the alkylimidazolium salts, 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF_6), 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF_4) and 1-butyl-3-methylimidazolium chloride (bmimCl) are widely investigated (He & Shen, 2008).

In general, an ionic liquid consists of a cation, which is normally a bulk organic structure with low symmetry. The anion of ionic liquid may be organic or inorganic. These factors had contributed ionic liquid attribute of having lower melting point since the lattice energy of the crystalline form of the salt had been reduce (Earle & Seddon, 2000). Weak intermolecular interactions and a good distribution of charge in the cation favor low melting point of ionic liquid (Fenin et al., 1984). The forces operating between cation and anion of an ionic liquid are columbic in nature thus, making ionic liquid exhibiting practically no vapor pressure. Ionic liquids with $[BF_4]^-$and $[PF_6]^-$ anions are air stable and neutral. The ionic liquid can react exothermically with Lewis acids and water (Khupse & Kumar, 2010). The molecular structure of [bmim][BF_4] is shown in Figure 2.1 . While the physical and chemical properties are summarize in Table 2.1

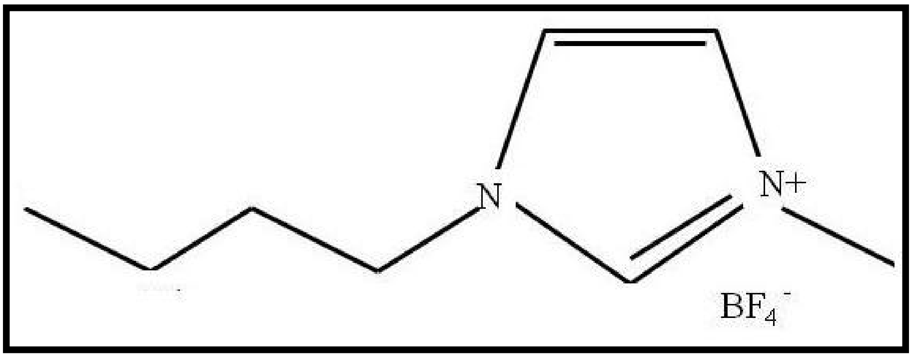


Figure 2.1 Chemical structure of [bmim][BF_4]

Property	Information
Empirical formula	$C_8H_{15}BF_4N_2$
Molecular weight	226.03
Chemical Family	Organic amine salt
Color and Form	Yellow liquid
Melting Point	-75°C
Vapor Pressure	Not applicable.
Specific Gravity	1.2
Odor	None
Solubility in Water	Soluble
Stability	Hygroscopic

(Strem Chemicals Inc., 2012)

Table 2.1 Physical and chemical properties of [bmim][BF_4]

Ionic liquids have been described as designer solvents (Freemantle, 1998) since their properties can be adjusted to be suit to the requirements of particular process. Properties such as melting point, viscosity, density, and hydrophobicity can be varied by simple changes to the structure of the ions. For example, the viscosity of [bmim][BF_4] increased by 25% in the present of 0.5 mol/kg of chloride content (Khupse & Kumar, 2012). Another important property that changes with structure is the miscibility of water in these ionic liquid (Earle & Seddon, 2000).

The potential usage of [bmim][BF_4] for engineering design was conducted through systematic study about how water affects the physical properties of aqueous solutions of RTIL [bmim][BF_4] (Liu et al., 2006). The study had concluded that the physical properties changed sharply in different concentration regions. Duan et al. (2006) conducted a study on esterification of tert-butanol by acetic anhydride which is the typical acid-base catalytic reaction in neutral ionic liquid [bmim][BF_4] . The study had resulted with excellent selectivity and high yield. Many other tertiary alcohols could also be successfully converted to the corresponding esters in [bmim][BF_4]. Other than that, ionic liquid [bmim][PF_6] solvent was reported to be an excellent a replacement for DMF solvent in the Heck coupling reaction because the yield of the reactions in [bmim][PF_6] were comparable and solvent as well as the catalyst are reusable several times. This supports the requirement of positive environmental and cost implications (Howarth & Dallas, 2000).

The potential to reduce pollution in industrial processes had led to investigations of ionic liquids as alternative reaction media for a variety of application. Ionic liquid are consider as replacement for organic solvents in catalysis. According to Wassercheid, 2003 and Earle, 2002, ionic liquid plays an active role in the catalysis rather than used simply as solvents. Moreover RTILs provide unique solvation environment for ionic species such as metal neutral ligand complexes, and have been shown to be highly effective as replacements for conventional organic diluents in liquid-liquid extraction of metal ions (Dai et al., 1999 & Visser et al., 2001).

Amrstrong et al., (1999) demonstrated the applications of RTIL as mixture for ultraviolet matrix-assisted laser desorption ionization (UV-MALDI) mass spectrometry (MS). It was demonstrated that vacuum-stable liquid consistency of RTIL matrix sample preparations considerably enhanced MALDI-MS analysis in terms of shot-to-shot reproducibility. Another study by Carda-Borch et al., (2003) describes the wide utilization of ionic liquid in liquid-liquid extraction. In their study, they had used 1-butyl-methylimidazolium hexafluorophosphate [bmim][PF_6] ionic liquid to form biphasic liquid system with water in liquid-liquid extraction. Apart from that, in some capillary electrophoresis (CE) studies, alkylammonium salts have been used as electroosmotic flow (EOF) modifiers (Huang et al., 1989; Harrold et al., 1993). Poole et al., (1986) studied the properties of tetraalkylammonium nitrate and thiocyanate ionic liquid in gas and liquid chromatography. In this study, the salts had been observed to have strong orientation and proton acceptor interactions with weak proton donor capacity as well as can be used in the temperature range from around room temperature to 150°-180°C at which temperature they exhibit significant vapor pressure.

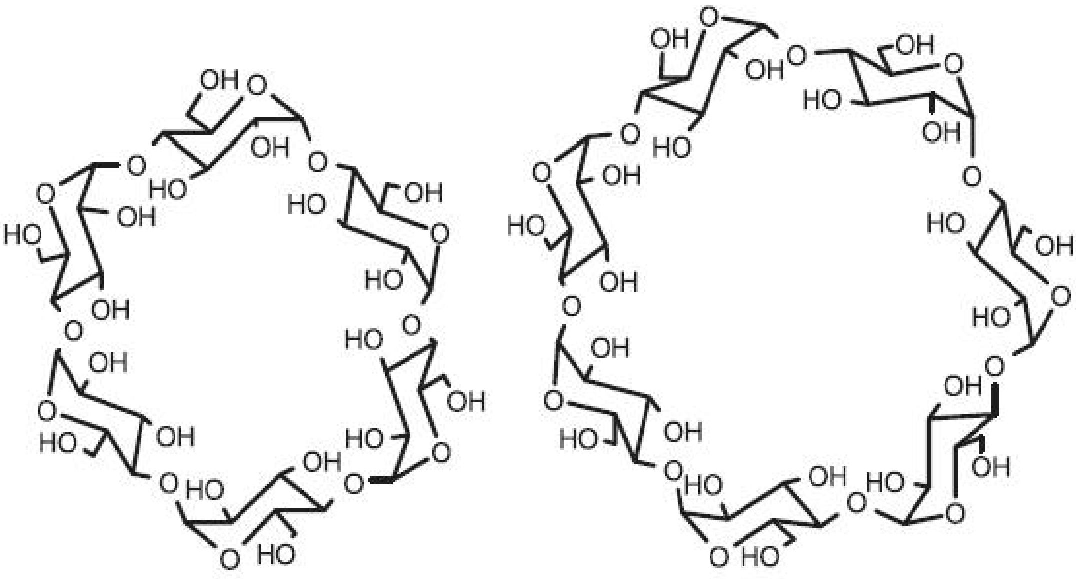
To date, there are continuous proliferation of interest and effort in studying the potential of ionic liquid. Table 2.2 summarizes the important properties of ionic liquid and their potential and current applications.

IONIC LIQUIDS	
Properties	**Applications**
• **Thermal stability** • **Low vapor pressure** • **Electric conductivity** • **Interesting solvent properties** • **Possible biphasic system** • **Liquid crystalline structures** • **High electro elasticity** • **High heat capacity** • **Non-flammability**	1) Lubricants and additives i. Lubricants ii. Fuel additives
	2) Electroelastic materials i. Artificial muscles ii. Robotics
	3) Analytics i. MALDI-TOF-matrices ii. GC-Head-space-solvents iii. Protein-crystallization
	4) Solvents i. Bio-catalysis ii. Organic reactions and catalysis iii. Nano-particle synthesis iv. Polymerization
	5) liquid crystals i. Displays
	6) Heat storage i. Thermal fluids
	7) Electrolytes i. Fuel cells ii. Sensors iii. Batteries iv. Supercaps v. Metal finishing vi. Coating
	8) Separation i. Gas separations ii. Extractive distillation iii. Extraction iv. Membranes

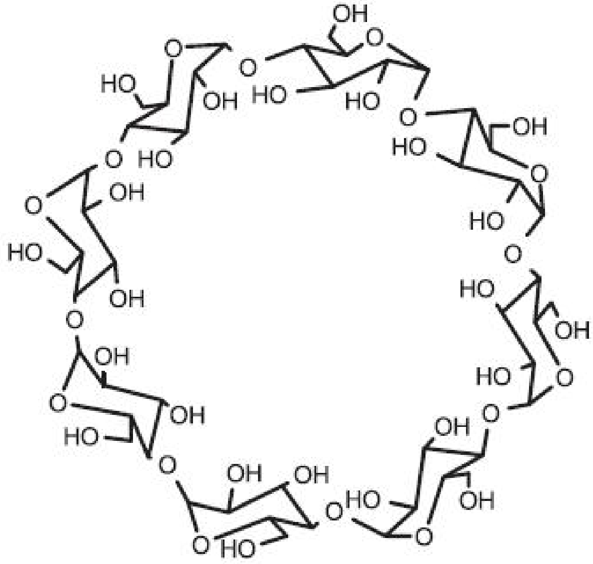
Table 2.2 Properties of Ionic liquid and their potential and current applications

2.2 Cyclodextrins

Cyclodextrins (CDs) are of three types: α-cyclodextrin, β-cyclodextrin and γ-cyclodextrin referred to as first generation or parent cyclodextrin. α-cyclodextrine, β-cyclodextrine and γ-cyclodextrine are composed of six, seven and eight α-(1,4)-linked glycosyl units respectively (Valle, 2003). β-cyclodextrin is the most accessible, the lowest-priced and generally the most useful.



α-cyclodextrin β-cyclodextrin



γ -cyclodextrin

Figure 2.2 Chemical structures of cyclodextrins

Cyclodextrins are generally crystalline, water-soluble, cyclic, homogeneous, non-reducing and the oligosaccharides compounds are built up from glucopyranose units (Ghodke et al., 2008). Table 2.3 summarizes the chemical and physical properties of parent cyclodextrins.

Physicochemical properties	**α-CD**	**β-CD**	**γ-CD**
• **No. of glucopyranose units**	6	7	8
• **Molecular weight**	972	1135	1297
• **Central cavity diameter (Å)**	4.7-5.3	6.0-6.5	7.5-8.3
• **Water solubility at 25°C (g/100mL)**	14.5	1.85	23.2

(Singh et al., 2010)

Table 2.3 Chemical and physical properties of α-CD, β-CD and γ-CD

Cyclodextrins in reality is a cylinder (conical cylinder) which occasionally describe as doughnut or wreath-truncated cone. The glucopyranose units that made up the cyclodextrins are built in the $^4C_1$ conformation (Dodziuk, 2006). Due to this conformation, all secondary hydroxyl groups are situated on one of the two edges of the rings, whereas all the primary ones are placed on the other edge (Szejtli, 2004). In other words the secondary hydroxyl groups (C_2 and C_3) are located on the wider edge of the ring and the primary hydroxyl groups (C_6) on the smaller edge, and that the apolar C_3 and C_5 hydrogens and ether-like oxygens are at the inside of the torus-like molecules (Valle, 2003). This had resulted the hydrophilic properties on the outside ring which can be dissolve in water and hydrophobic property on the inner ring of the molecule, describe as ‘micro heterogeneous environment’ (Valle, 2003; Sjejtli, 1989)

The C-2-OH group of one glucopyranose unit can form a hydrogen bond with the C-3-OH group of the adjacent glucopyranose unit. In β-CD molecule, a complete secondary belt is formed by these hydrogen bonds, therefore making β-CD a rather rigid structure. These intramolecular H-bond formations justify the lowest water solubility of β-CD among all CDs molecules (Szejtli, 2004).The central cavity is lined up with relatively non-polar lipophilic groups (Subramaniam et al., 2005). Thus, cyclodextrins is considered as an empty capsule of molecular size and can take up guest molecules of appropriate size to form host-guest-type inclusion complexes. Cyclodextrins capability to form encapsulation, affects the physical properties of the guest to desirable purposes.

The formation of inclusion complexes with wide variety of guest molecules is one of the most interesting properties of cyclodextrins. Inclusion complex of CD and guest molecules can occur in solid and solution state. The changes towards the physicochemical properties of guest molecule can be characterize through several methods in order to ensure whether the guest molecules are really included in the cyclodextrin cavity. Inclusion complex formed between the guest and cyclodextrin molecules can be characterized by SEM, XRD, IR Spectroscopy, TLC, NMR, UV/VIS, Electrochemistry, polarography, polarimetry and spectroscopy methods (Singh et al., 2010).

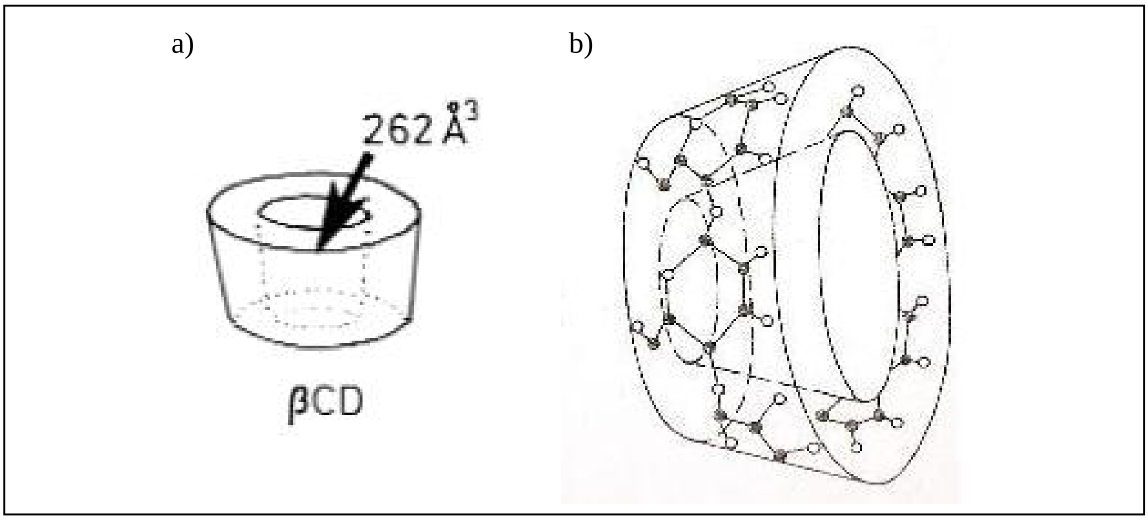


Figure 2.3 a) Central cavity of β-CD, b) Doughnut or wreath-truncated cone shape of β-CD molecule

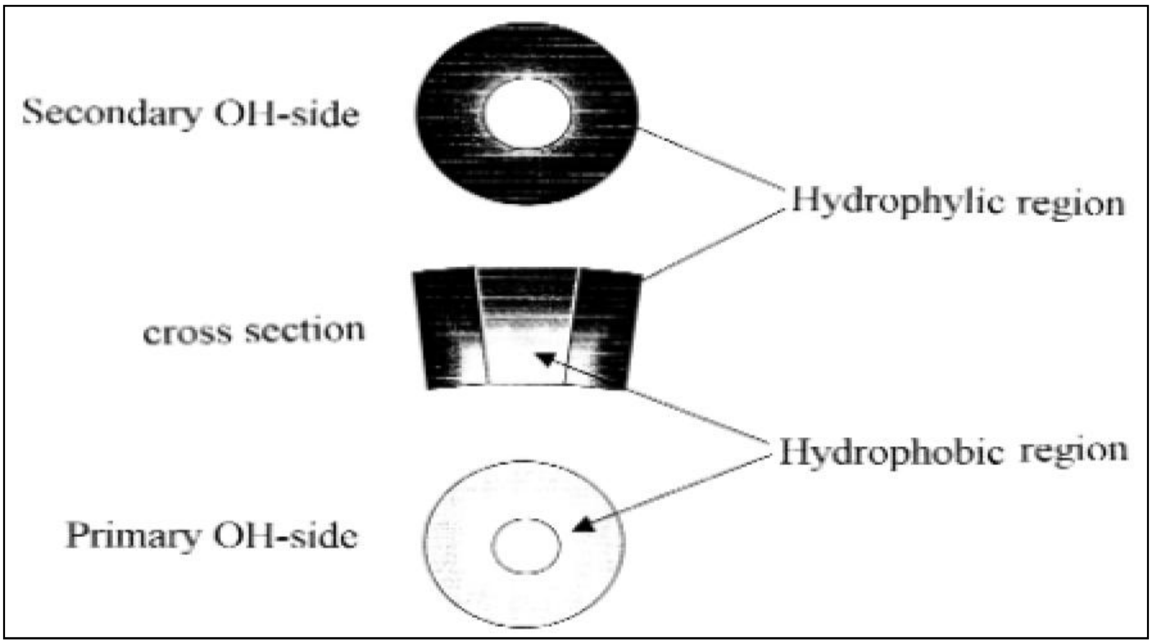


Figure 2.4 Dimensions and hydrophilic/hydrophobic regions of the CD molecules.

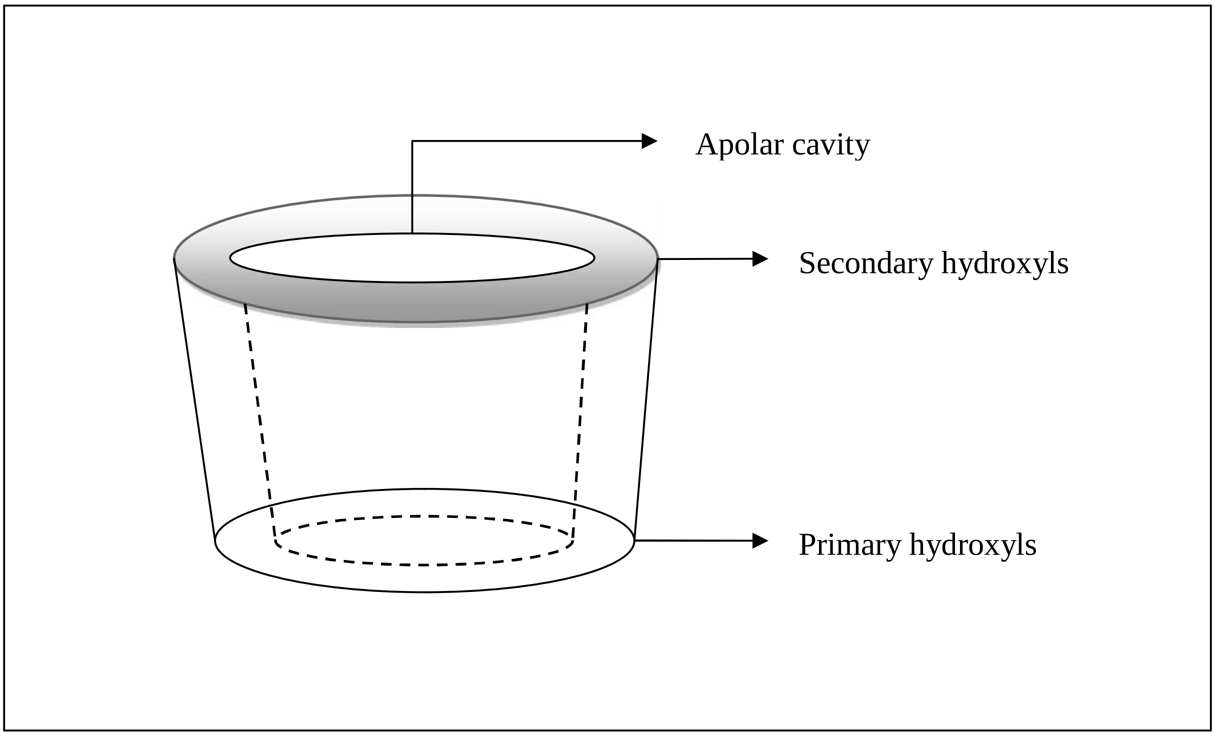


Figure 2.5 Cyclodextrin with empty cylinders rings structure (Connors, 1997)

2.3 Inclusion complex

The ability of CDs form host-guest inclusion complex with various organic and inorganic guest molecules (Kawaguchi et al., 2003) makes CDs widely used in pharmaceuticals, pesticides, foodstuff, toilet articles and textile processing (Szejtli, 1998; Kaifer, 1999). Apart from industrial applications, inclusion complexes are related to molecular recognition and self-assembly, selectivity, molecular encapsulation, chemical stabilization and intermolecular interactions (Kaifer, 1999; Krishnaveni et al., 2003).

In aqueous solution, the slightly apolar cavity of cyclodextrin is occupied by a small quantity of water molecules that energetically unfavored and therefore can be readily substituted by appropriate guest molecules that are less polar than water. The guest molecule prefers to penetrate the empty cavity, leading to the formation of an inclusion compound through host-guest interaction (Gao et al., 2006). The dissolved cyclodextrin is the ‘host’ molecule, and part of the ‘driving force’ of the complex formation is the substitution of the high entalphy water molecules by an appropriate guest molecules. In other word, no covalent bonds are broken or form during formation of inclusion complex (Schneiderman et al., 2000). Figure 2.6 is the schematic representation of the host-guest inclusion complex.

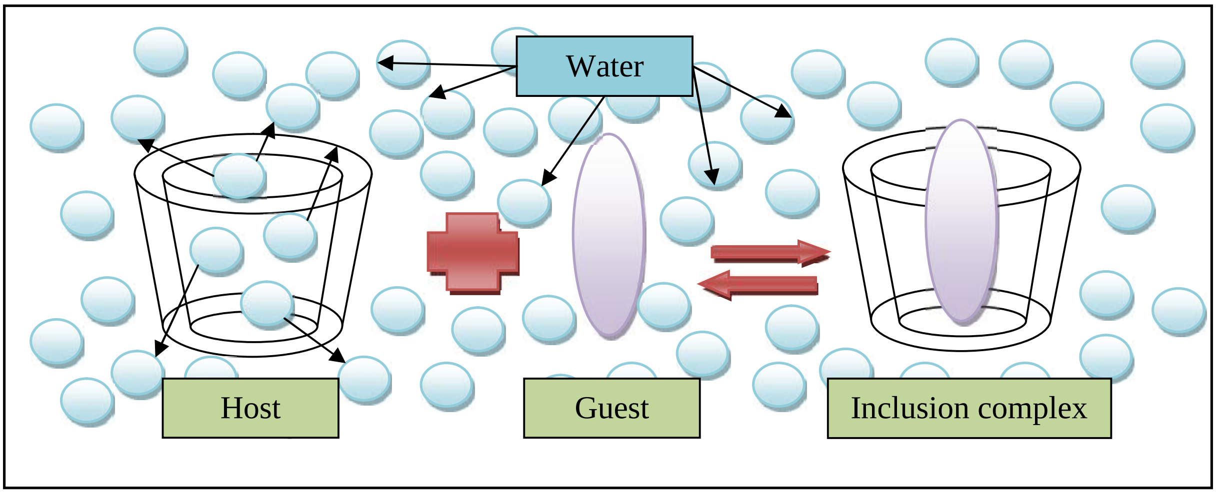


Figure 2.6 Schematic representation of host-guest inclusion complex formation.

In the complex one, two or three CD molecules contain one or more guest molecules. The host-guest ratio is usually 1:1 which is the essence of molecular encapsulation (Szejtli, 2004). However host-guest ratio of 2:1, 1:2 and 2:2 and high order complex equilibrium do exist almost always simultaneously. The binding of guest molecules within the host CD is not permanent but rather a dynamic equilibrium. Binding strength of inclusion complex depends on how well the host-guest complex fit together and on specific local interaction between surface atoms (Valle, 2003). Weak Van der Waals forces, hydrogen bonds and hydrophobic interaction keep the complex together (Hak et al.,2003)

According to Valle (2003) there are two factors that determine the ability of cyclodextrin to form an inclusion complex with a guest molecule.

1. Steric and depends on the relative size of the cyclodextrin to the size of the guest molecule.
2. The thermodynamic interactions between the different components of the system (cyclodextrin, guest, solvent). A favorable net energetic driving force must present to pulls the guest into the cyclodextrin central cavity.

2.4 Inclusion complex between cyclodextrins and ionic liquids

There have been several studies on inclusion complex (IC) formation between cyclodextrins and ionic liquids. Gao et al. (2006) had conducted a study on inclusion complex between three kinds of ionic liquid surfactants namely C_{12}-mimPF$_6$, C_{14}mimPF$_6$, and C_{16}mimPF$_6$ with β-cyclodextrin. These inclusion compounds formed in this study were characterized by XRD, ^{13}C CP/MAS NMR, ^{1}H NMR, rotating frame nuclear Overhauser effect spectroscopy (ROESY), and thermogravimetry (TGA). The host-guest system presented a channel-type structure, and each glucose unit of β-CD was in a similar environment. It was suggested that hydrophobicity played a crucial role in supporting the formation of inclusion complexes formed in this study.

Ionic liquid,C_{12}-mimPF$_6$ and β-CD inclusion complex formation also been studied by Li et al., (2007). In this researched the inclusion complexation interaction was confirmed by FT-IR spectra. Additionally, the inclusion complex was also characterized by XRD, NMR and TGA. Other than that, a study on the interaction between different type of ionic liquid and β-CD had been conducted by He et al., (2009). In this study, the alkyl side chain on the imidazolium ring was found to enter into β-CD molecule instead of the imidazolium ring itself. According to the association constants, the sequence of interaction strength of some IL with β-CD was obtained as well.

Different characterization techniques had been conducted to study the formation of inclusion complex of TetraPhimBr with β-CD (Puvaneswary et al., 2010). The techniques employ in this research are FTIR, XRD, NMR and TGA analysis. The resulting new products exhibit characteristics that are different from those of originating host and guest molecules. While Li et al., (2010) had conducted an investigation about interaction of ionic liquid with α-CD, β-CD and γ-CD and suggest 1:1 and 1:2 ratio of inclusion complex had been form. From this study as well it had been established that poor interaction such as hydrogen bond and Van der Waals occur between host-guest complex.

According to He & Shen (2008) in a study of interaction between [bmim][PF$_6$], [bmim][BF$_4$] and [bmim][Cl] with β-CD using 2(p-aminophenyl)-3,3-dimethyl-5-carboethyoxy-3H-indole as a fluorenscent probe through a competitive method. In this study the formation of the 1:1 (gues-host) inclusion complex was suggested and the associations constant at different temperatures were estimated. The negative entropy and enthalpy changes indicated that the formation of inclusion complexes was entropically unfavorable and enthalphy-driven. The ability for ionic liquids to associate with β-CD followed the order of [bmim][PF_6] » [bmim][BF_4] » [bmim][Cl].

Other than that, a research on interaction between α-CD, β-CD and γ-CD with ionic liquids, [bmim][BF_4] and [omim][BF_4] have been conducted with titration microcalorimetry and UV and NMR spectra at 298.15K. Hydrophobic interaction of CD molecular cavity with alkyl chain of ionic liquid cation had been studied. In addition, the change in iceberg structure formed by water molecules existing around tail of the ionic liquids was discussed as well. The ^{1}H NMR spectra reveal that chemical shift data of all protons in α-CD, β-CD and γ-CD molecules move to high field in the presence of ionic liquids. UV absorbance for the CD-IL systems had been detected indicating that the inclusion complex is formed through weak interaction (Li et al., 2010).

2.5 Inclusion complex between of β-cyclodextrins with various compounds

Other than ICs of β-CD with ionic liquids, inclusion complex with various type of compound such as drug, pesticide, cosmetics and other type of compound were widely investigated. Table 2.4 summaries inclusion complexes studies of previous work and their finding.

Nu.	**Research**	**Findings**	**References**
1.	Inclusion complexes of carotenoids with cyclodextrins: ^{1}H NMR, EPR and Optical studies	Carotenoid forms a stable 1:1 inclusion complex with β-CD	Polyakov et al.,(2004)
2.	Spectrophotometric and electrochemical study of the IC between β-CD and furnidipine	The phase solubility profile was classified as AL-type. 1:1 stoichiometric was formed	Yanez et al., (2004)
3.	NMR studies of the IC between β-CD and paroxetine	1:1 stoichiometry and an association constant value of the order 2 x10^3 have been formed.	Bernini et al., (2004)
4.	Spectrophotometric and thermoanalytical study of cypermethrin/CD complexes	Complexes made by coprecipitation, suspension and kneading methods contained cypermethrin in complexed and uncomplexed form. Heating technique showed to be completely complexed.	Orgovanyi et al., (2005)
5.	Study of IC formation between tropaelin OO and β-CD by spectrophotometry and Infrared spectroscopy	1:1 host-guest complex with an apparent constant of 1.5 x 10^3 L/mol	Wang et al., (2006)
6.	A study on the supramolecular structure of IC of β-CD with prazosin hydrochloride	The 1:1 stoichiometry of complexation was achieved by phase solubility study. XRD patterns of β-CD and IC belonged to the channel-type packing structure.	Liu & Zhu (2007)

7.	UV-Vis and FTIR spectroscopic analyses of IC of nonylphenol and nonyphenol ethoxylate with β-CD.	At the structural level, the data from FTIR spectroscopic study have indicated alkyl chains of NP and NP9EO can form Van der Waals interactions with the cavity of β-CD.	Bonenfant et al., (2009)
8.	Spectroscopic studies of IC of β-CD and benzidine diammonium dipicrate.	1:2 guest-hosts have been established by UV, 1H NMR, 13NMR, IR spectra and powder XRD.	Hamdi et al., (2010)

Table 2.4 S Previous studies on inclusion clusion complexes and their finding.

CHAPTER 3

METHODOLOGY

3.1 Equipments and chemicals

The equipments and chemicals used in this study were shown in Appendix E. β-CD (99%) was purchased from Acros (Hungary). Other reagents and chemicals were of analytical reagent grade and were used as received. Double distilled water was used throughout.

3.2 Instrumentation

The IR spectra were recorded on Perkin-Elmer RX1 FT-IR spectrometer with samples prepared as KBr pellets. All the spectra were run in the range of 400-4000cm^{-1} at room temperature. For pH adjustment pHS-3C digital pH-meter (Shanghai Lei Ci Device Works, Shanghai, China) was used for pH adjustment. The ^{1}H NMR spectra were recorded in DMSO on a Lambda JEOL 400 MHz FT-NMR spectrometer. Thermogravimetric analyses (TGA) were made using a TA instruments Q500. Samples were heated at 20°C C/min from room temperature to 900°C in a dynamic nitrogen atmosphere. The Differential Scanning Calorimetry (DSC) curves were obtained on TA DSC-2010 with heating rate of 10°Cmin^{-1} under a nitrogen atmosphere.

3.3 Preparation of β-CD-[bmim][BF$_4$] inclusion complex by Kneading method.

4g of β-CD was mix with ethanol in agate mortar and kneaded to form a paste. Then equimolar of [bmim][BF4], 0.77g (3.524 x 10^{-3} mol) and ethanol were added. The sample was kneaded for approximately 60min and dried to constant mass at 105°C. White precipitate was obtained as final product. The final product will be characterized by using various instruments.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Characterization of inclusion complex

4.1.1 Fourier Transfer-Infra Red (FTIR) Analysis

Inclusion complex formation can be confirmed through FT-IR spectrometry. The inclusion of guest molecule into the host molecule results in band shift and alteration in the intensity of IR spectrum (Tang et al., 2002). The variation of the shape, shift and intensity of the absorption peaks of the guest or host provide proof for the formation of inclusion complex (Szente et al., 1996). Thus FT-IR analysis able to provide confirmation of interaction between guest-host system i.e β-CD-[bmim][BF_4] in this study. The FT-IR spectra of pure β-CD, ionic liquid,[bmim][BF_4] and inclusion complex, β-CD-[bmim][BF_4] will be compare. If differences observed in the spectra comparison, the existence of inclusion complex formation can be confirmed (Szente et. al., 1996).

The preparation of inclusion complex through kneading method had yield white color powder. The first method to characterize the inclusion complex is through FT-IR analysis. The FT-IR spectra obtained were measured in 400-4000 cm^{-1} region. The bands detected are assigned to C-O, C-C, C-O-C stretching and O-H in planar angular deformation vibrations (νC-O, νC-C, νC-O-C and δO-H) (Bonenfant et al., 2009). Figure 4.1 shows the FT-IR spectra of β-CD, [bmim][BF_4] and β-CD-[bmim][BF_4] respectively. While Table 4.1 shows the overall interpretation of IR spectrum in this study. The result obtained from the table proved the formation of β-CD-[bmim][BF4] inclusion complex since the bands of β-CD-[bmim][BF_4] were shifted compared to the pure β-CD and [bmim][BF_4].

Wavenumber (cm^{-1})in 400-4000 cm^{-1} region		
Mode	**β-CD**	**β-CD-[bmim][BF_4]**
δO-H	3369.72	3368.33
νCH2	2925.80	2929.26
νC-O	1157.63	1156.74
νC-C	1079.60	1076.43
νC-O-C	1031.41	1030.10

Table 4.1 Wavenumber of FT-IR bands of β-CD and β-CD-[bmim][BF_4].

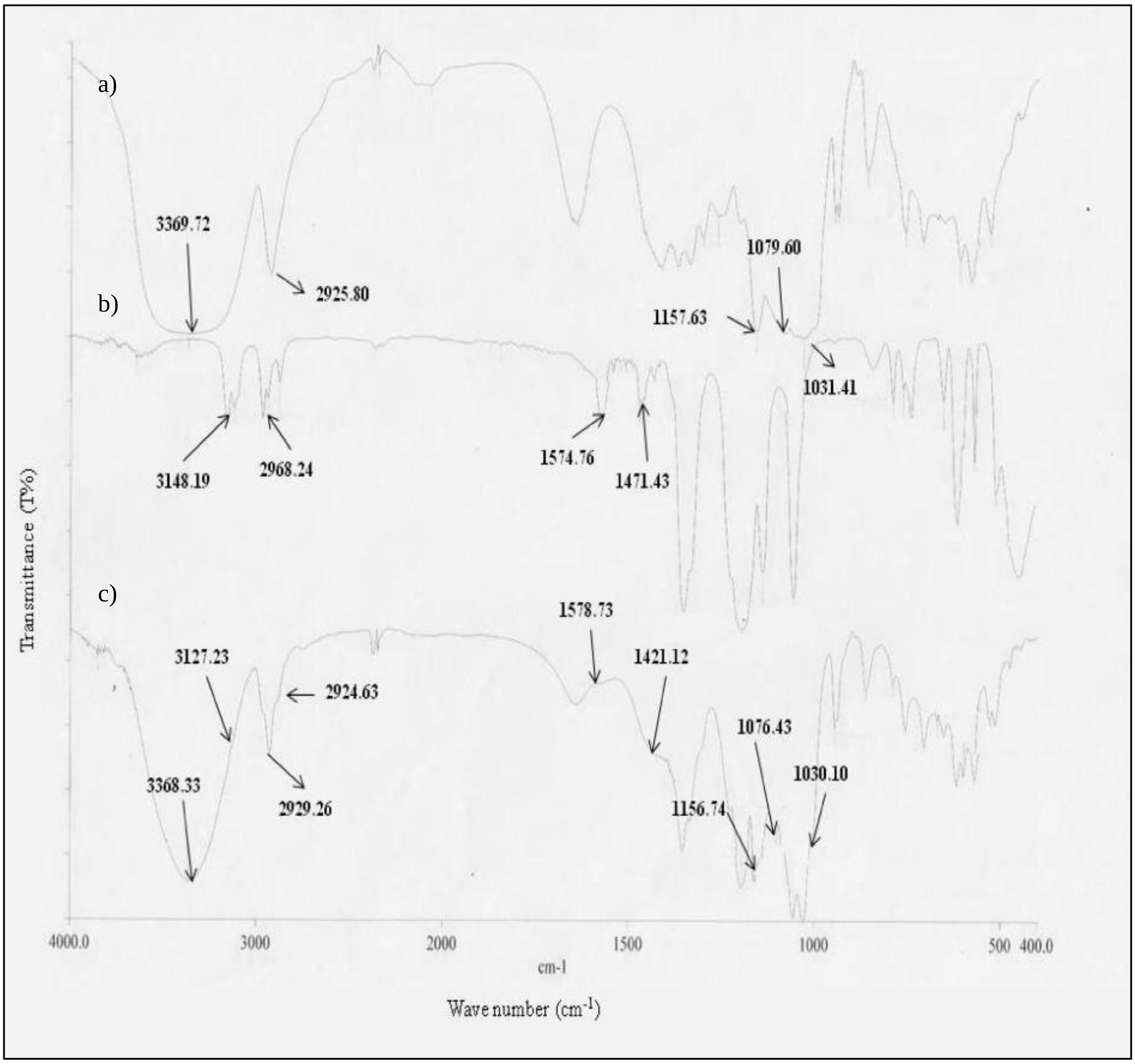


Figure 4.1FT-IR spectra of a) β-CD, b) [bmim][BF_4] and c) β-CD-[bmim][BF_4] respectively.

As referred to the spectra, the FT-IR spectrum for β-CD-[bmim][BF_4] is similar to the pure β-CD. This is a major characteristic of formation host-guest system in CD inclusion complex. For instances, the broad hydroxyl band of β-CD at wavenumber 3369 cm^{-1} narrow in the spectrum of the inclusion complexes which further confirmed the formation of complexes. Similar finding was reported by Li et al. (2006) in their work synthesizing inclusion complex between β-CD with $C_{12}mimPF_6$ guest molecules.

The presence of inclusion complex can be confirmed through bands of CH imidazolium ring stretch, CH_3(N) stretch, imidazolium ring bend and CH_2 bend of β-CD-[bmim][BF_4] as observed in FT-IR spectrum of β-CD-[bmim][BF_4] in Figure 4.1. Table 4.2 summarize these band shift of β-CD-[bmim][BF_4] as compared to the pure β-CD and [bmim][BF_4]. In addition the FT-IR curves in the bands regions below than 1300cm^{-1}, confirmed that the β-CD-[bmim][BF_4] is different from the original β-CD and [bmim][BF_4] as they exhibit different spectroscopic signals. Further confirmation of inclusion complex formation has been carried out through ^{1}H NMR spectroscopy.

Wavenumber (cm^{-1})in 400-4000 cm^{-1} region		
Mode	**[bmim][BF_4]**	**β-CD-[bmim][BF_4]**
CH imidazolium ring stretch	3148.19	3127.23
CH3(N)stretch	2968.24	2924.63
Imidazolium ring bend	1574.76	1578.73
CH2 bend of [bmim][BF4]	1471.43	1421.12

Table 4.2 Wavenumber of FT-IR bands of [bmim][BF_4] and β-CD-[bmim][BF_4].

4.1.2 ^{1}H NMR Spectroscopy

The solution structure of the inclusion complex of β-CD and [bmim][BF$_4$] was further characterize through ^{1}H NMR spectroscopy. ^{1}H NMR spectroscopy provides direct evidence for the formation of inclusion complex (Schneider et al., 1998). In addition, ^{1}H NMR spectroscopy provides information of the stoichiometry, stability and structure of CD complexes (Chen et al., 2006).

Figure 4.2 shows the NMR spectrum of β-CD, [bmim][BF$_4$] and β-CD-[bmim][BF$_4$] inclusion complex. While Table 4.3 shows chemical shifts (δ) of pure β-CD, ionic liquid, [bmim][BF$_4$] and β-CD-[bmim][BF$_4$] inclusion complex.

Proton	**β-CD**	**[bmim][BF$_4$]**	**β-CD-[bmim][BF$_4$]**	
	δ	**δ**	**δ**	**Δδ**
H1	4.820		4.81	-0.01
H2	3.306		3.2807	-0.0253
H3	3.634		3.5953	-0.0387
H4	3.356		3.327	-0.0290
H5	3.598		3.5357	-0.0543
H6	3.646		3.6213	-0.0247
Ha		0.9090	0.8888	-0.0202
Hb		1.2605	1.2354	-0.0251
Hc		1.7718	1.7474	-0.0244
Hd		4.1638	4.1412	-0.0226
He		7.7407	7.6354	-0.1053
Hf		7.8614	7.7489	-0.1125
Hg		3.8337	3.8317	-0.0020
Hh		9.3721	9.0941	-0.2780

Table 4.3 Chemical shifts (δ) of β-CD, [bmim][BF$_4$] and β-CD-[bmim][BF$_4$].

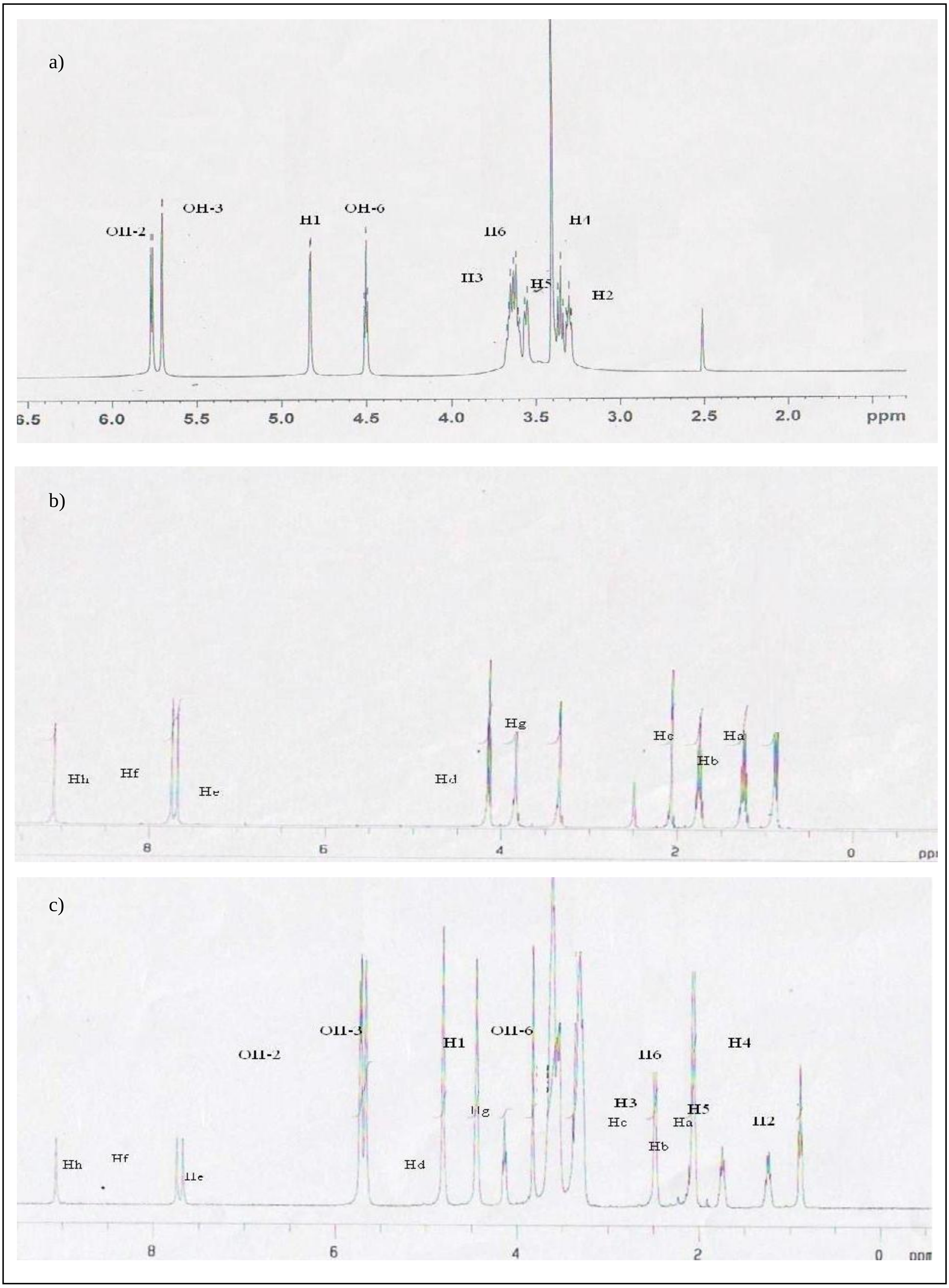


Figure 4.2 NMR spectrum of a) β-CD, b) [bmim][BF$_4$] and c) β-CD-[bmim][BF$_4$] inclusion complex.

The NMR spectra confirmed the inclusion complex due to significant differences of the signals for each compound. H3 and H5 proton of β-CD molecules contribute to the β-CD torus shape conformation and both protons are located inside of the cavity. While H2 and H4 protons are situated at the exterior of the structure. H6 proton of the primary alcohol group is located on the narrow side of the β-CD and H1is in the glycosidic bond plane of β-CD. Thus from Table 4.3 the significant up field shift occurred for both H3 and H5 protons can be observed.

The changes of chemical shift for H3, H5 and H6 suggested that [bmim][BF_4] ionic liquid had enter the hydrophobic inner cavity of the β-CD structure (Chen et al., 2006). Since H3 proton is located at the secondary hydroxyl group and away from the symmetrical axis of the β-CD, the interaction is not that obvious which resulting in the narrow shift compared to H5 proton chemical shift. Assume that the imidazolium ring inserted into the β-CD central cavity from the wide secondary hydroxyl groups which have close contact with the atoms on the inner surface of the primary hydroxyl group region. While the butyl tail positioned near the center of the cavity along the molecular axis of β-CD did not make contact with H3 protons. This finding is supported by similar phenomenon observed by Goa et al., (2005).the chemical shifts of H1, H2 and H4 of β-CD which located on the outer surface region of β-CD experienced only minor chemical shifts by [bmim][BF_4].

Other than that, He, Hf and Hh (as label in Figure 4.2) imidazolium ring of [bmim][BF_4] shows significant up field shift. The great up field shifts of imidazolium ring protons indicate that the guest molecule has strong interaction with β-CD protons. Based on this chemical shifts the [bmim][BF_4] molecule is highly suggested to be incorporated into the β-CD central cavity structure. The incorporation of [bmim][BF_4] into the hydrophobic cavity of β-CD had cause changes to the micro environment of [bmim][BF_4] protons which cause upfield shift of the protons. In addition, the proton signal of [bmim][BF_4] did not broaden clearly indicating that the molecule fit loosely into the cavity (Ishizu et al., 1999). The ratio of [bmim][BF_4] to β-CD was determined using integration of inclusion complex which confirms the inclusion complex ratio of 1:1 (Goa et al., 2006; Chen et al., 2006)

4.1.3 Differential Scanning Calorimetry (DSC)

DSC has been one of the most widely used calorimetric techniques for the characterization of solid-state interaction between guest molecule and cyclodextrin (Li et al., 2005). In this work, DSC was conducted to evaluate the interaction between β-CD and [bmim][BF_4] in the solid state.

DSC thermograms for β-CD, [bmim][BF_4] and β-CD-[bmim][BF_4] inclusion complex is shown in Figure 4.3. As shown in this Figure 4.3, the curve of β-CD displays a wide and strong endothermic effect in the 80°C-100°C interval at peak maximum temperature of 70.67°C. This may be due to elimination of high-energy water molecules in the cavity of β-CD. Decomposition of β-CD occurs in 280°C-350°C where the peak maximum temperature is at 310.70°C. The DSC curve of [bmim][BF_4] shows an endothermic peak at 284.60°C, which correspond to ionic liquid melting point. The DSC scan of the β-CD-[bmim][BF_4] inclusion complex does not exhibit endothermic peak assigned to [bmim][BF_4] at 284.60°C. The maximum peak temperature of the β-CD-[bmim][BF_4] is at 302.52°C. This suggest that inclusion complex between [bmim][BF_4] and β-CD had been form.

New peaks in β-CD-[bmim][BF_4] inclusion complex thermogram also suggesting the formation of inclusion complex. The presence of such peaks provides further evaluation on the present of inclusion complex (Cwiertnia et al., 1999). Moreover, the melting point of inclusion complex was higher than the original β-CD and [bmim][BF_4].

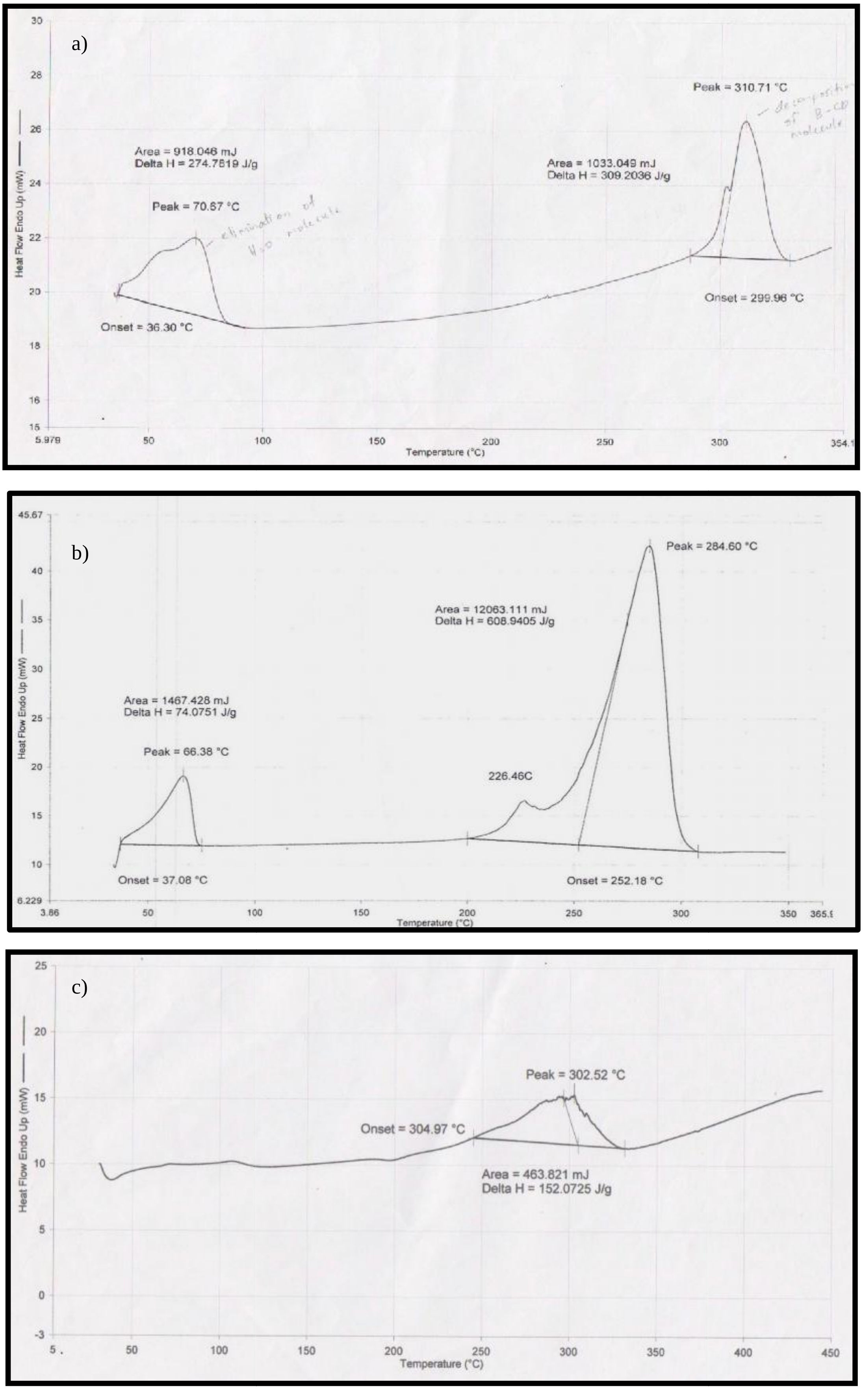


Figure 4.3 DSC curves of a) β-CD, b) [bmim][BF4] and β-CD-[bmim][BF4] inclusion complex

4.1.4 Thermogravimetric Analysis (TGA)

The thermal stability of β-CD-[bmim][BF_4] inclusion complex is further studied through TGA. The thermal stability of the inclusion complex was compared to the β-CD and [bmim][BF_4].

TGA was performed at a heating rate of 20°C/min in an atmosphere of nitrogen. Figure 4.4 shows the weight loss curve for β-CD-[bmim][BF_4] inclusion complex as well as β-CD and [bmim][BF_4]. From the figure, β-CD exhibit two weight loss steps which is at 50°C-100°C and 350°C-375°C. The first weight loss curve is due to the evaporation of water that had been absorbed by β-CD molecule. The second weight loss curve is due to decomposition of β-CD. The ionic liquid [bmim][BF_4], exhibit a single weight loss curve at 100°C-340°C which is due to evaporation and/or decomposition of [bmim][BF_4]. While the inclusion complex exhibited three step of weight loss – 50°C-100°C, 300°-350°C-200°C and 370°C-480°C. The weight loss steps is in parallel to the increase in temperature which is similar to the profiles of β-CD and [bmim][BF_4].

In particular, β-CD-[bmim][BF_4] inclusion complex have lower initial decomposition temperature compared to the pure compounds. Normally, the initial decomposition temperature of inclusion complexes is higher than those of pure β-CD and the inclusion complexation is believed to contribute to the better stability of CDs (Gao et al., 2005; Subramaniam et al., 2010). Hence, the findings of TGA results are unusual. This result probably due to the unique molecular structure and properties [bmim][BF_4] compare to the organic compounds and polymers. The steric congestion and geometry distortion of the components may make β-CD-[bmim][BF_4] inclusion complex unstable. Other than that, the detachment of ion pairs of [bmim][BF_4] upon inclusion complexation may reduce the thermal stability of β-CD-[bmim][BF_4] complex. Similar phenomenon had been observed in several studies of inclusion complex between β-CD with ionic liquids (Gao et al., 2005; Subramaniam et al., 2010).

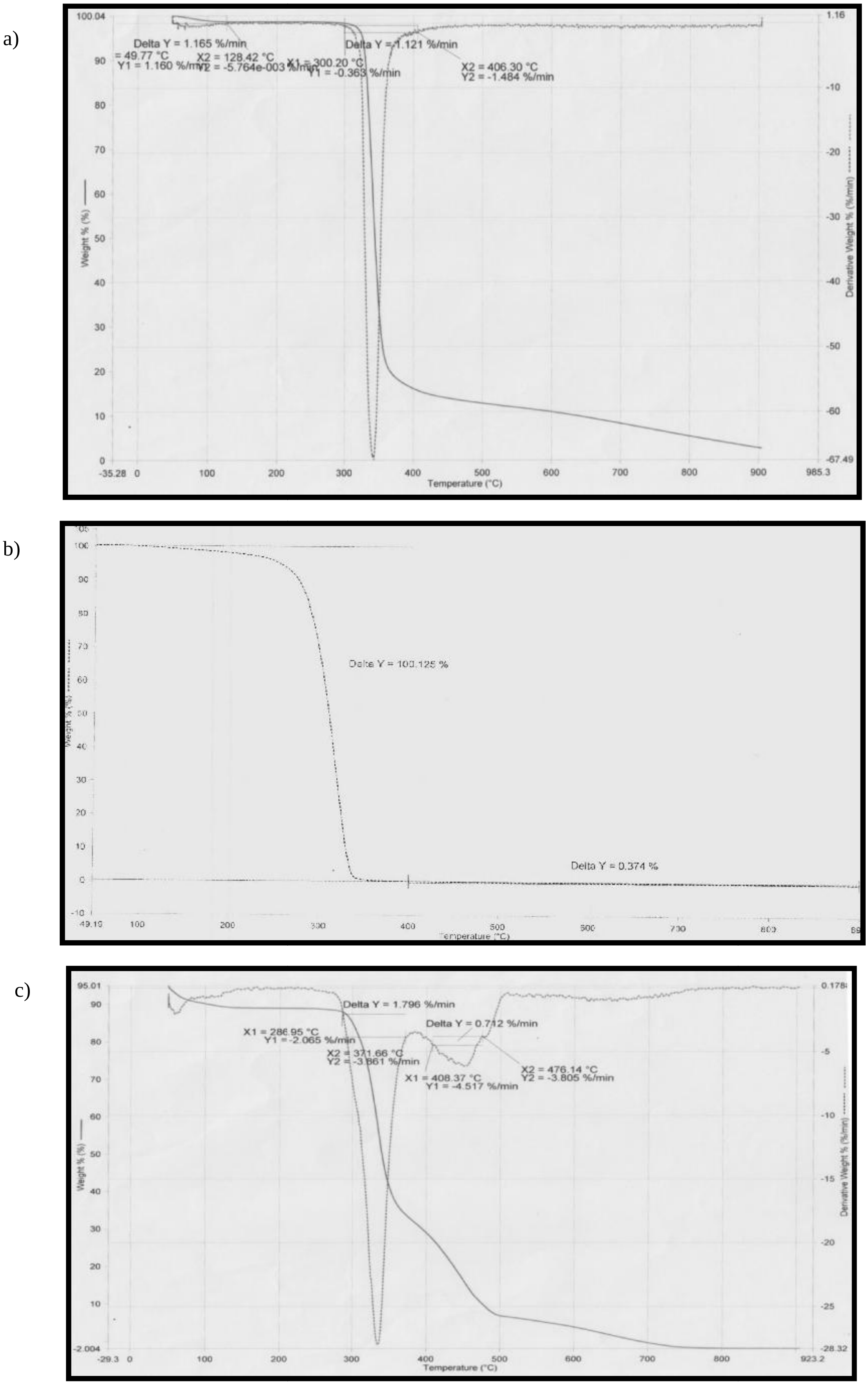


Figure 4.4 TGA the weight loss curve of a) β-CD, b) [bmim][BF4] and c) β-CD-[bmim][BF4]

4.2 Proposed mechanism of Inclusion Complex

The host molecule, β-CD reacts with guest molecule, [bmim][BF_4] to form 1:1 host-guest complex. The mechanism of inclusion complexation between these two compounds is show in Figure 4.5 below.

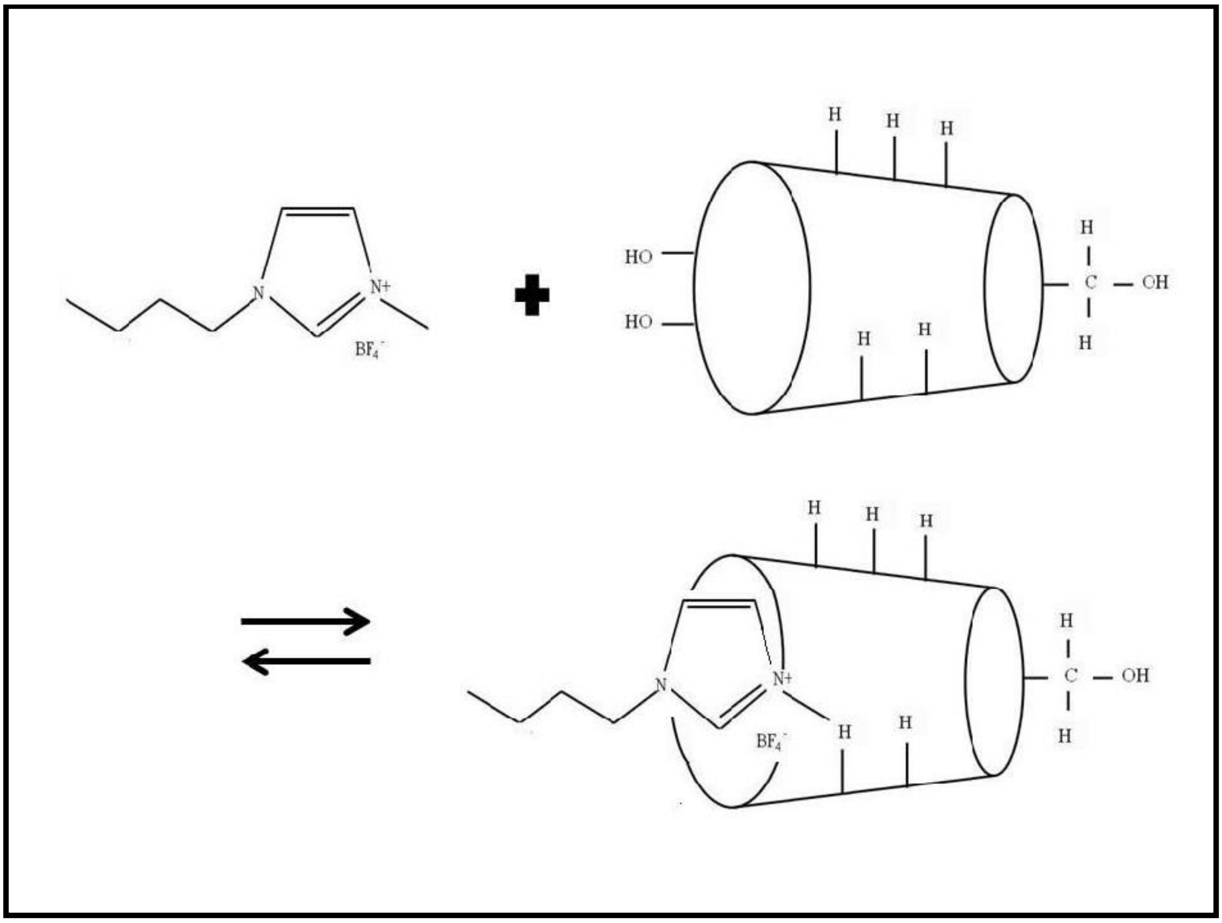


Figure 4.5 Inclusion mechanism of β-CD reacts with [bmim][BF_4]

CHAPTER 5

CONCLUSION

An inclusion complex was formed between the β-CD and [bmim][BF_4] with the ratio of 1:1. The inclusion complex behavior had been studied through Fourier Transfer-Infra Red (FTIR) spectra, H1-NMR spectra, Differential Scanning Calorimetry (DSC) and Termogravimetric Analysis (TGA) confirmed the presence of new product, with properties different from those of originating host and guest molecules. The results obtained by different characterization techniques clearly indicate that kneading method leads to formation of complex between β-CD and [bmim][BF_4]. FT-IR analysis shows that band shifts had occurred for the inclusion complex when compared to the original compound. While through NMR analysis the results had exhibit chemical shifts in inclusion complex NMR spectrum. Other than that, through DSC and TGA the thermal stability of inclusion complex is lower than its two precursors. For future work, Scanning electron microscope (SEM), X-Ray Diffusion (XRD) and UV-Vis Spectroscopy analysis should be conducted to further characterize the formation of inclusion complex between β-CD and [bmim][BF_4].

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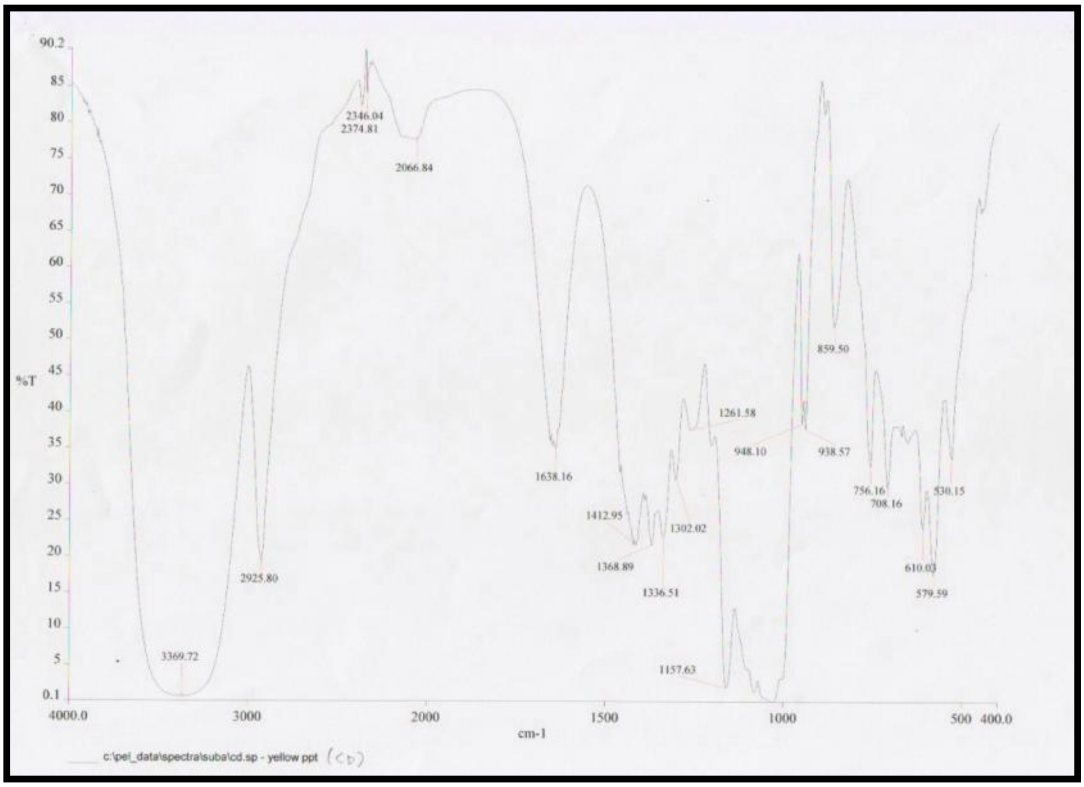
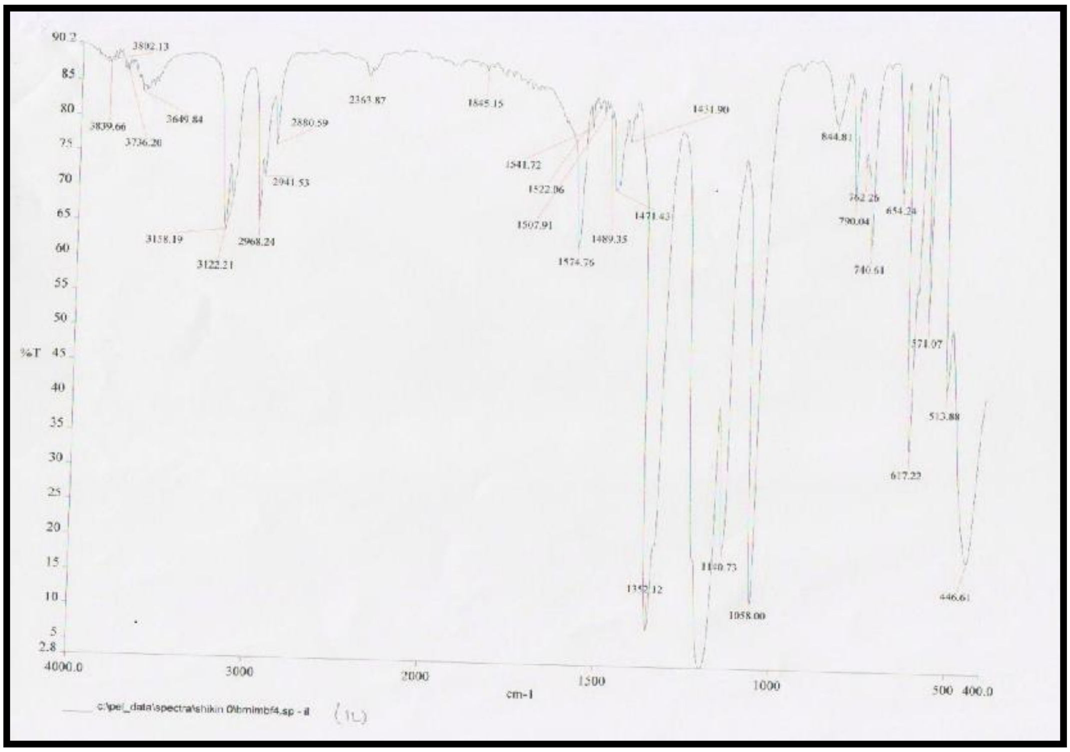
APPENDIX A

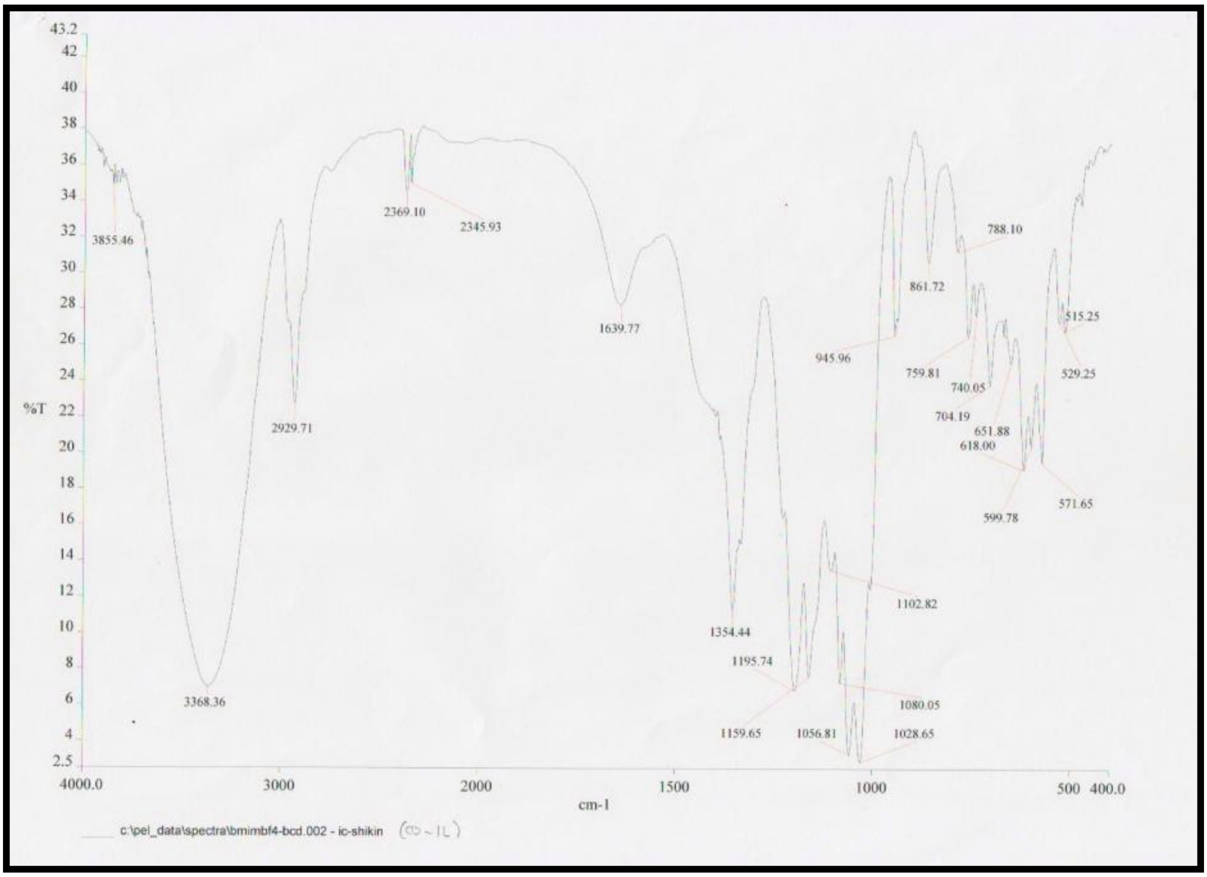
Fourier Transform Infrared Spectroscopy (FTIR)



β-CD



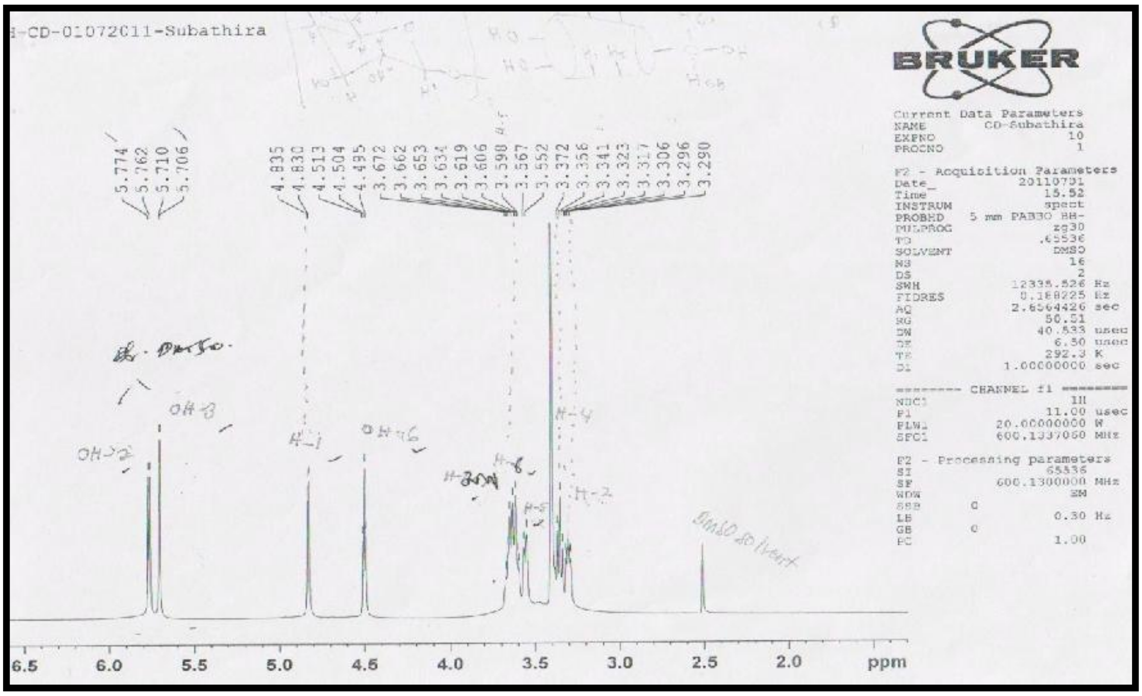
[bmim][BF_4]



β-CD-[bmim][BF4] inclusion complex

APPENDIX B

^{1}H NMR Spectroscopy



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PROCNO                   1

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PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                      16
DS                       2
SWH              12335.526 Hz
FIDRES            0.188225 Hz
AQ               2.6564426 sec
RG                   50.51
DW                  40.533 usec
DE                    6.50 usec
TE                   292.3 K
D1              1.00000000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.00 usec
PLW1           20.00000000 W
SFO1           600.1337060 MHz

F2 - Processing parameters
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SSB      0
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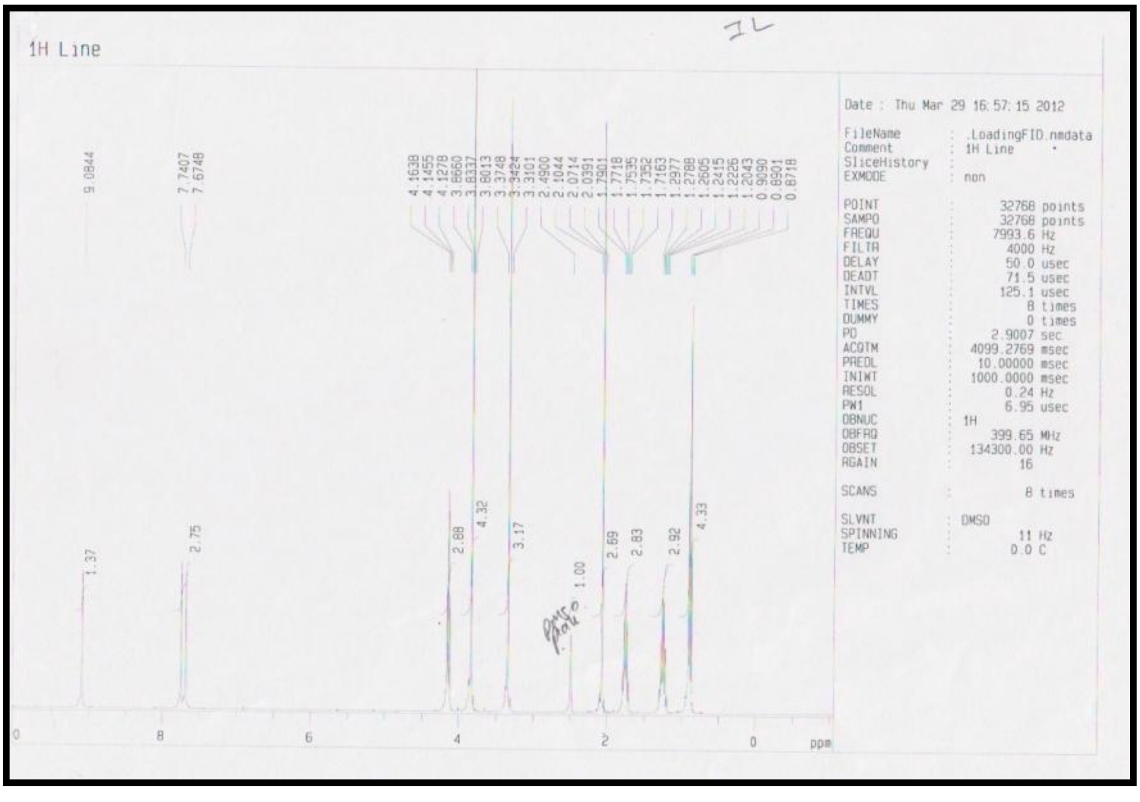
β-CD



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INTVL         :      125.1 usec
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DUMMY         :          0 times
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ACQTM         :  4099.2769 msec
PREDL         :   10.00000 msec
ININT         :  1000.0000 msec
RESOL         :       0.24 Hz
PW1           :       6.95 usec
OBNUC         : 1H
OBFRQ         :     399.65 MHz
OBSET         :  134300.00 Hz
RGAIN         :         16

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SLVNT         : DMSO
SPINNING      :         11 Hz
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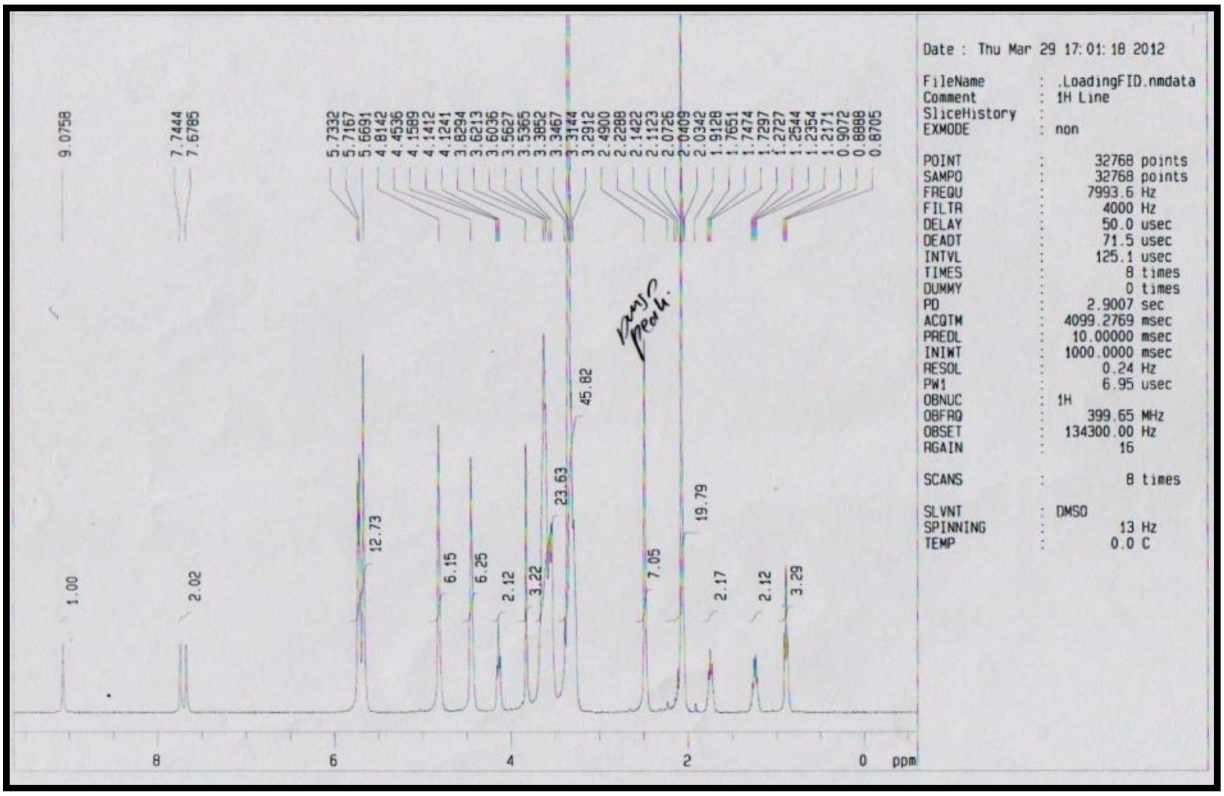
[bmim][BF$_4$]



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POINT           :       32768 points
SAMPO           :       32768 points
FREQU           :      7993.6 Hz
FILTR           :        4000 Hz
DELAY           :        50.0 usec
DEADT           :        71.5 usec
INTVL           :       125.1 usec
TIMES           :           8 times
DUMMY           :           0 times
PD              :      2.9007 sec
ACQTM           :   4099.2769 msec
PREDL           :    10.00000 msec
INIWT           :   1000.0000 msec
RESOL           :        0.24 Hz
PW1             :        6.95 usec
OBNUC           : 1H
OBFRQ           :      399.65 MHz
OBSET           :   134300.00 Hz
RGAIN           :          16

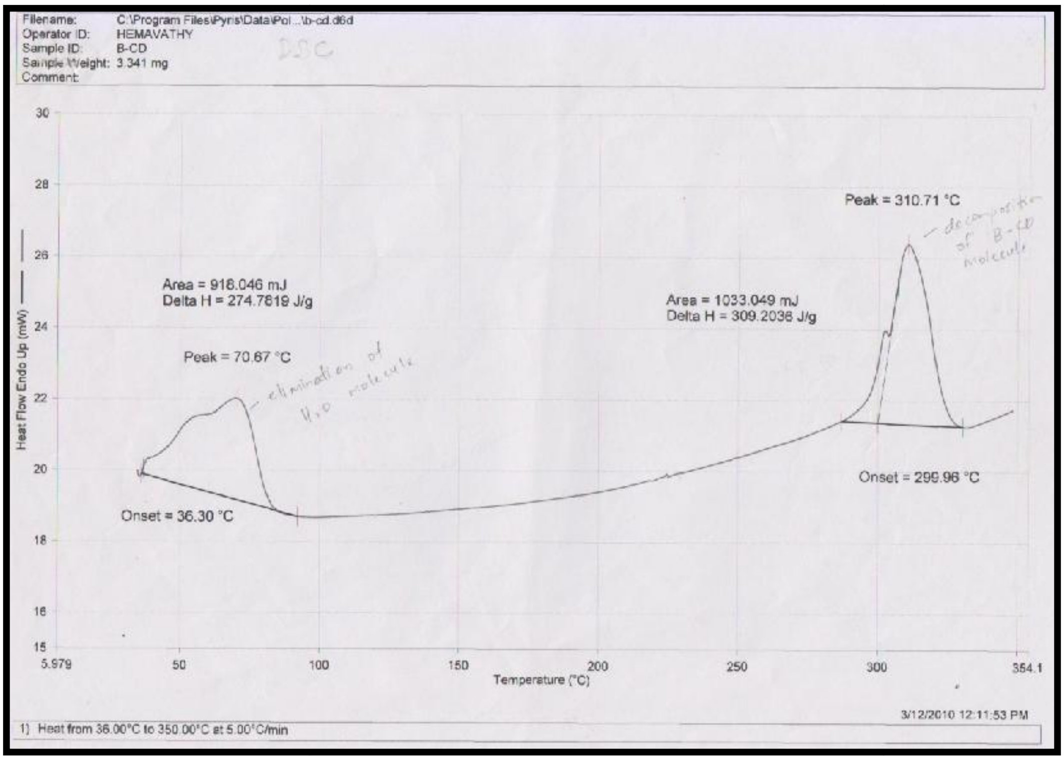
SCANS           :           8 times

SLVNT           : DMSO
SPINNING        :          13 Hz
TEMP            :         0.0 C
```

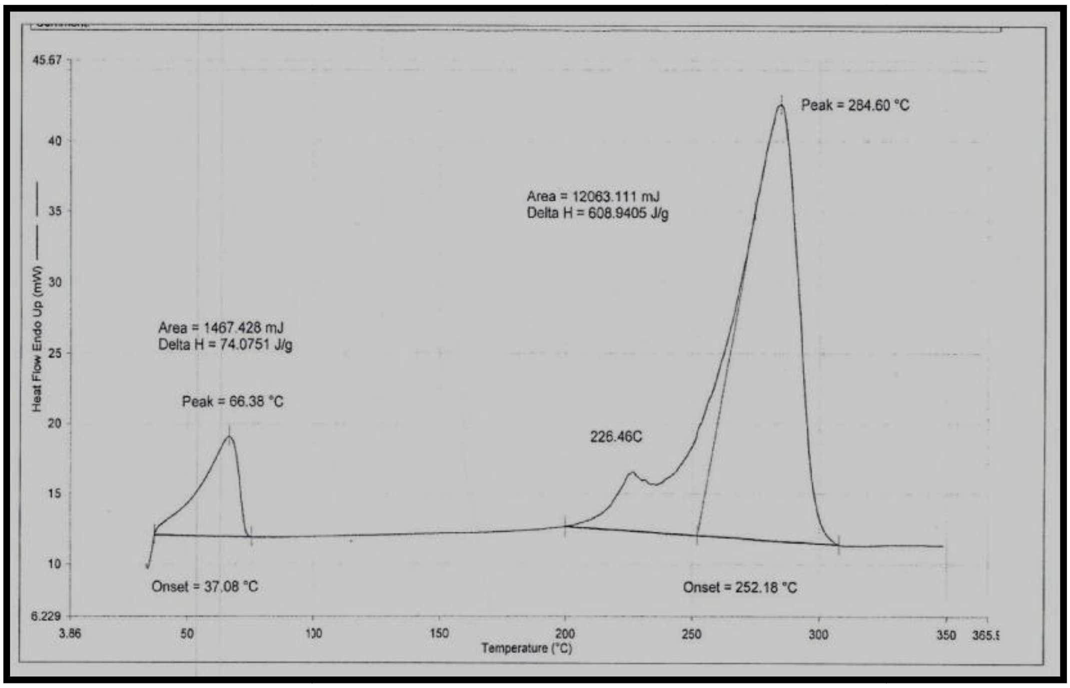
β-CD-[bmim][BF4] inclusion complex

APPENDIX C

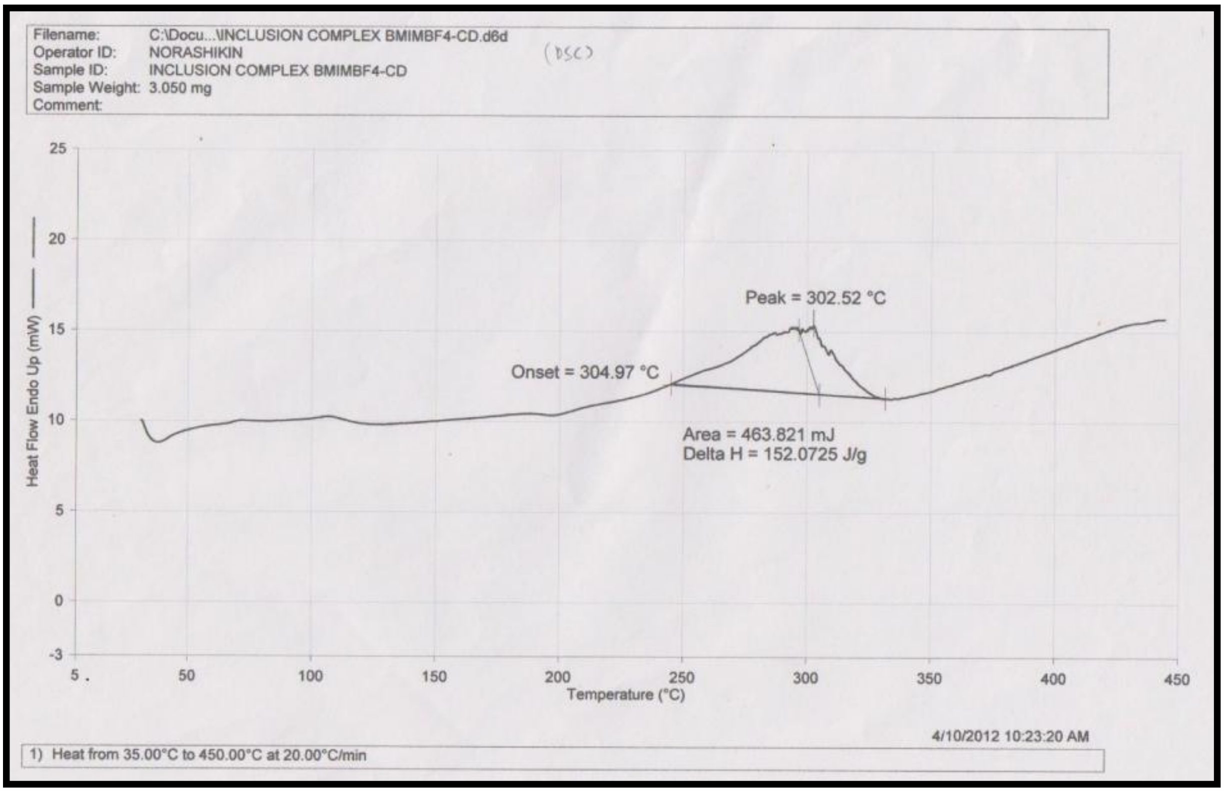
Differential Scanning Calorimetry (DSC)



β-CD



[bmim][BF_4]



Filename: C:\Docu...\INCLUSION COMPLEX BMIMBF4-CD.d6d
Operator ID: NORASHIKIN
Sample ID: INCLUSION COMPLEX BMIMBF4-CD
Sample Weight: 3.050 mg
Comment:

(DSC)

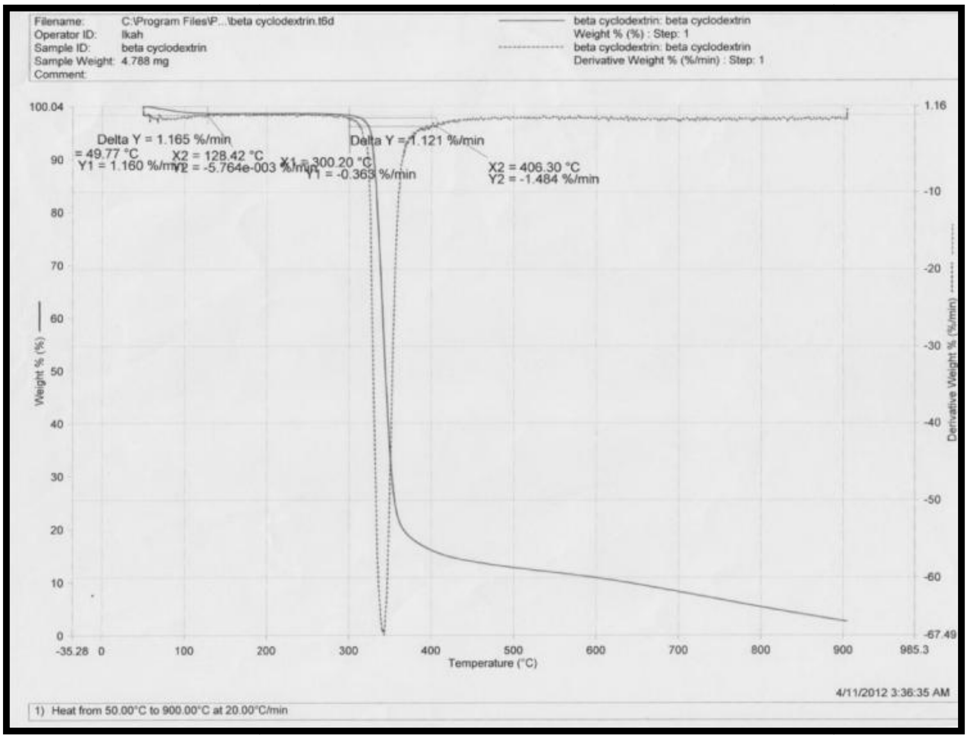
4/10/2012 10:23:20 AM

1) Heat from 35.00°C to 450.00°C at 20.00°C/min

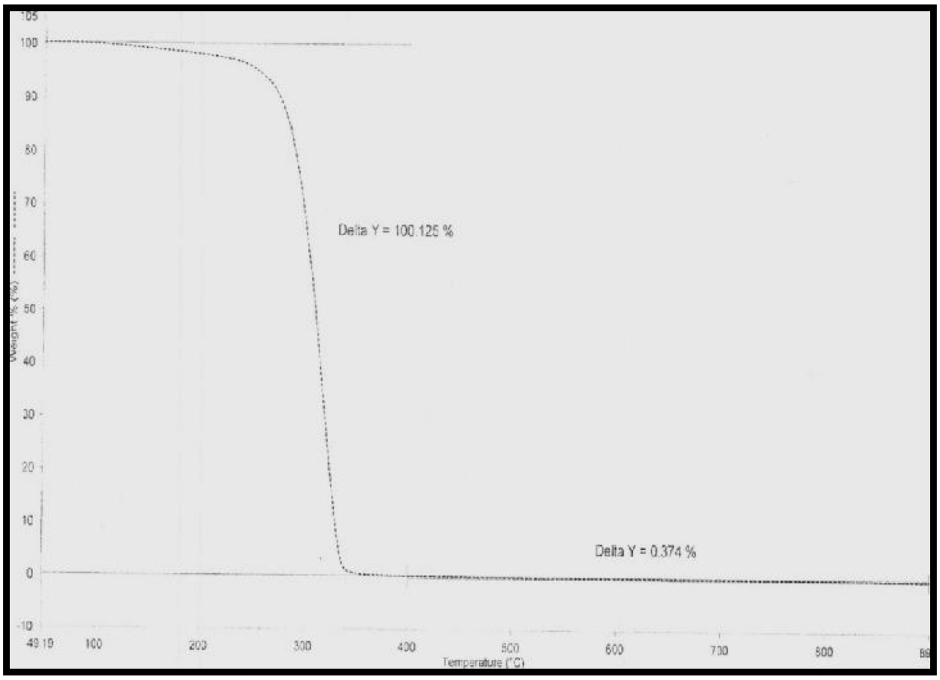
β-CD-[bmim][BF4] inclusion complex

APPENDIX D

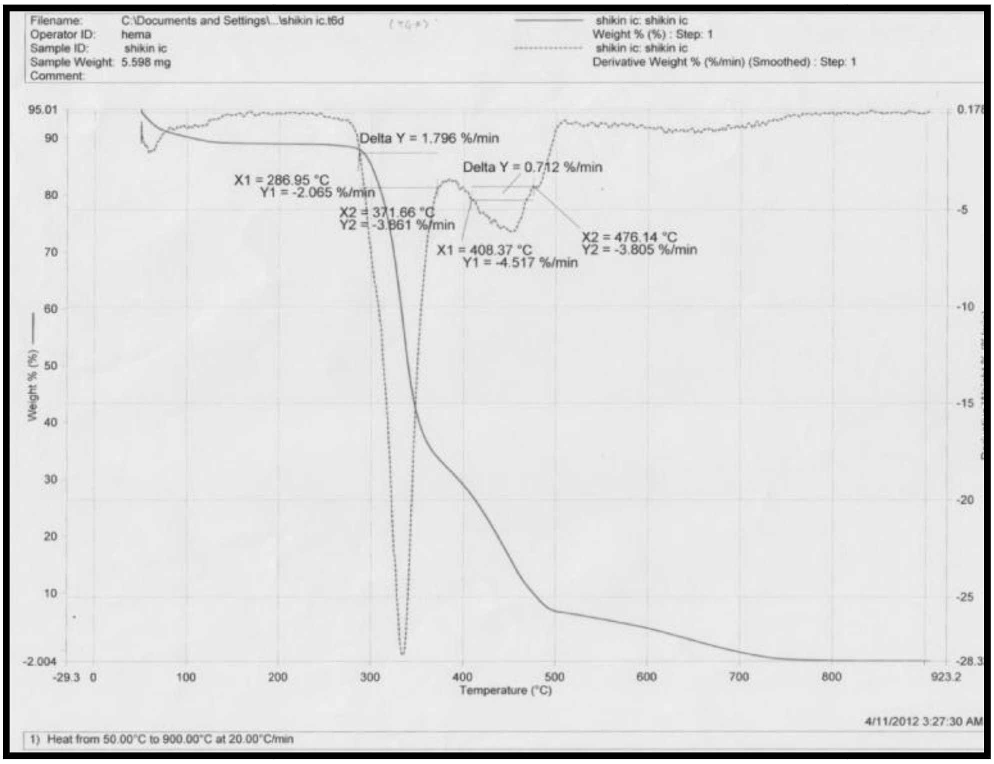
Thermogravimetric Analysis (TGA)



β-CD



[bmim][BF_4]



Filename: C:\Documents and Settings\...\shikin ic.t6d

Operator ID: hema

Sample ID: shikin ic

Sample Weight: 5.598 mg

Comment:

1) Heat from 50.00°C to 900.00°C at 20.00°C/min

4/11/2012 3:27:30 AM

β-CD-[bmim][BF4] inclusion complex

APPENDIX E

Equipment & Chemical

1. Beaker
2. KBr pellets
3. Micro pipette
4. Mortar and paste
5. Magnetic stirrer
6. NMR tube
7. Quartz cell
8. Scale
9. Ultrasonic generator
10. Distilled water
11. Volumetric flask
12. B-Cyclodextrins
13. Ionic liquid, [bmim][BF_4]
14. Dimethyl Sulfur Oxide, DMSO
15. Ethanol