

## CHAPTER-VIII

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# Inclusion complexation of tetrabutylammonium iodide by cyclodextrins

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### VIII.1. INTRODUCTION

In modern field of chemistry and biochemistry, cyclodextrins (CDs) are focused with immense interests due to the unique property of controlled release through the innovation of vast inclusion complex (IC) with guest molecules having hydrophobic cavity [1]. In diverse industries including pharmaceutical, food, textile, pesticides, cosmetics sectors Cyclodextrins have enormous applications [2]. CDs are cyclic oligomer of  $\alpha$ -D-glucose having diverse numeral of glucopyranose units (6 in  $\alpha$ -CD, 7 in  $\beta$ -CD and 8 in  $\gamma$ -CD) hop by  $\alpha$ -(1-4) linkages [3]. CDs are truncated cone shaped with a quite rigid and distinct hydrophobic cavity of varying diameter and two separate rims, all secondary hydroxyl groups containing a wider rim and all the primary hydroxyl groups containing a narrow rim [3]. Hence CD is very proficient in forming stable supramolecular host-guest inclusion complex with variety of molecules for having a hollow-cylindrical shaped fragment [4]. Due to having the special structure and prospective application in the discovery of molecular switches, molecular machines and supramolecular polymers macrocyclic CD molecule always depict the concentration in this field of chemistry [5]. In some case due to micro-encapsulation of guest by CD various changes in physical and chemical properties occur such as very volatile substance fixation, masking the colour, smell and taste of substance etc. [6] In case of drug delivery devices and nano-sensors the molecular recognition of the host for functioning as nano-sensors is owing to conjugation of CD with a variety of nanoparticles [7].

Tetrabutylammonium Iodide ( $\text{but}_4\text{NI}$ ) is mainly quaternary ammonium compounds of a group of ammonium salts in which all the four hydrogen atoms are substituted by four organic radicals (in this compound butyl group) which may be alkyl, aryl and aralkyl.  $\text{but}_4\text{NI}$  is a water soluble strong electrolyte which exhibits a assortment of physical, chemical and biological properties. The ionic solid has immense appliances in various fields such as in chemical reactions it acts as surface-active agents (due to the hydrophobic communications between the butyl groups and water molecules), solvents, Intermediates emulsifying means, pigment disperse and phase transfer catalyst [8,9]. Since  $\text{but}_4\text{NI}$  has the tendency of locating at the interface of two phases (liquid-liquid or solid-liquid) for introducing the continuity between two different phases, so it positively is said as phase transfer catalyst. Due to low cost and low toxicity of  $\text{but}_4\text{NI}$  in recent times it has appeared as a promising substitute as a catalyst for functionalization of C-H bonds [10,11]. In industrial usage  $\text{but}_4\text{NI}$  acts as active ingredient for conditioners, antistatic agent, detergent sanitizers, softener for textiles and paper products etc. In medicinal field it uses as antimicrobials, algacide, slimicidal agents, disinfection agents and sanitizers etc.

In this article the studied ionic solid, viz., tetrabutyl ammonium iodide (scheme VIII.1) is currently of interest in assorted industrial and medicinal aspects. Here we explored the creation of host-guest inclusion complexes (ICs) of the ionic solid with  $\alpha$  and  $\beta$ -CD particularly towards their formation, stabilization, carrying and controlled release without chemical amendment by diverse reliable methods such as  $^1\text{H}$  NMR, FT-IR, surface tension, conductivity, density, viscosity and refractive index measurements.

## **VIII.2. EXPERIMENTAL**

### **VIII.2.1. Source and purity of samples**

The preferred ionic solid and cyclodextrins of puriss grade were bought from Sigma-Aldrich, Germany and used as purchased. The mass fraction purity of  $\text{but}_4\text{NI}$ ,  $\alpha$ -cyclodextrin and  $\beta$ -cyclodextrin were  $\geq 0.99$ , 0.98 and 0.98 respectively.

### VIII.2.2. Apparatus and Procedure

Each stock solutions of Ionic solid,  $\alpha$ -CD and  $\beta$ -CD were prepared by mass (Mettler Toledo AG-285 with uncertainty 0.0001 g) and by mass dilution at 298.15 K the working solutions were obtained. To change molarity of the solutions to the molality of the solutions the density of the solutions was used [34].

Using Bruker ADVANCE 400 MHz instrument at 298.15K the NMR spectra were recorded in D2O at 400 MHz. Signals are cited as  $\delta$  values in ppm using residual protonated solvent signals as internal standard (D2O :  $\delta$  4.79 ppm). As chemical shift all the Data are reported.

With the help of platinum ring detachment technique by a Tensiometer (K9, KRÜSS; Germany) surface tensions (Accuracy  $\pm 0.1$  mN·m<sup>-1</sup>) of the solutions were measured at 298.15 K. Temperature of the system was maintained by circulating thermostated water through a double-wall glass vessel holding the solution.

Conductivities of the solutions were studied by Mettler Toledo Seven Multi conductivity meter having uncertainty 1.0  $\mu$ S·m<sup>-1</sup>. The study was carried out in a thermostated water bath at 298.15K with uncertainty  $\pm 0.01$ K. HPLC grade water was used with specific conductance 6.0  $\mu$ S m<sup>-1</sup>. The conductivity cell was calibrated using 0.01M aqueous KCl solution.

The densities ( $\rho$ ) of the solutions were studied by vibrating U-tube Anton Paar digital density meter (DMA 4500M) having precision  $\pm 0.00005$  g cm<sup>-3</sup> and uncertainty in temperature was  $\pm 0.01$ K. The density meter was calibrated by standard method [30].

Viscosities ( $\eta$ ) were determined by Brookfield DV-III Ultra Programmable Rheometer with spindle size 42. The detail has already been represented in our ealier attempt [16].

Refractive indexes of the solutions were studied with a Digital Refractometer from Mettler Toledo having uncertainty  $\pm 0.0002$  units. The detail has already been described earlier [16].

To prepare both the solid inclusion complexes ([but<sub>4</sub>NI] +  $\alpha$ -CD and [but<sub>4</sub>NI] +  $\beta$ -CD) 1:1 molar ratio of the ionic solid and cyclodextrin were taken. In both the cases 1.0 mmol cyclodextrin was dissolved in 20 mL water and 1.0 mmol ionic solid was

dissolved in 20 mL ethanol and stirred separately for 3 hrs. Then the ethanol solution of the ionic solid was added drop by drop to the aqueous CD solution. The mixture was then allowed to stir for 48 hrs at 50–55°C. It was filtered at this temperature, then cooled to 5°C and kept for 12 hrs. The resulting suspension was filtered and the white polycrystalline powder was found, which was washed with ethanol and dried in air.

Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer FT-IR spectrometer according to the KBr disk technique. Samples were prepared as KBr disks with 1 mg complex and 100 mg KBr. The FTIR spectroscopy measurements were performed in the scanning range of 4000–400  $\text{cm}^{-1}$  at room temperature.

### VIII.3. RESULTS AND DISCUSSION

#### VIII. 3.1. $^1\text{H}$ NMR study establishes inclusion

The inclusion phenomena of the guest ionic solid inside the host CD molecule are ascertained by the most imperative device NMR study. In this work we have studied the interactions of an ionic solid ( $\text{but}_4\text{NI}$ ) with  $\alpha$  and  $\beta$ -CD by  $^1\text{H}$  NMR study taking 1:1 molar ratio of ionic solid and CD in  $\text{D}_2\text{O}$  at 298.15K (Figure VIII1). Table S1 shows the  $^1\text{H}$  NMR data of the ionic solid, two CDs and two ICs. Due to the incorporation of guest ionic solid into the hydrophobic cavity of CD the protons of the CD molecule show considerable chemical shift [12]. In the structure of CD, the H1, H2 and H4 protons are found at the periphery of CD molecule while the H3 and H5 are located within the cavity, more specifically the location of H3 and H5 protons are near the wider rim and narrower rim respectively [13,14]. The H3 and H5 protons of CD show upfield chemical shift as a result of interaction with the guest during the insertion of guest ionic solid molecule inside the cavity of CD. It confirms the formation of host-guest inclusion complexes. The H3 protons located near the wider rim show higher shift than the H5 protons which are present near the narrower rim at the interior of CD due to insertion of guest ionic solid molecule inside the cavity of host CD through the wider rim (scheme S1). Due to the exterior protons upfield chemical shift is also observed but to trivial extent. The interacting protons of the studied ionic solid also show upfield chemical

shift. The shifts of four protons present in each butyl groups give four shifts which exemplifies the insertion mechanism. Moreover, the extent of shift of butyl protons are more in  $\beta$ -CD comparison to that in  $\alpha$ -CD, signifying binding affinity of the former is higher compared to the latter.

### VIII. 3.2. Surface tension study supports inclusion

Surface tension ( $\gamma$ ) is an important consideration which furthermore recommends the inclusion complex formation of the considered ionic solid with both  $\alpha$  and  $\beta$ -CD [15]. There shows no any considerable change to the surface tension of water when CD is added to pure water. This phenomenon indicates that both  $\alpha$  and  $\beta$ -CD are almost surface inactive compounds [16]. In our present work the  $\gamma$  values of aqueous ionic solid have been determined with addition of  $\alpha$  and  $\beta$ -CD at 298.15K (Table S4-S5). With increasing concentration of CDs the  $\gamma$  values substantially increase for this ionic solid but<sub>4</sub>Ni. This is due to the removal of surface active ionic solid molecules from surface of the solution, i.e.,  $\alpha$  and  $\beta$ -CD form the host guest inclusion complexes after entering the hydrophobic tail of ionic solid into the hydrophobic cavity of  $\alpha$  and  $\beta$ -CD [17,18] Figure VIII.2 and Table VIII.1 show the formation of 1:1 inclusion complex of ionic solid and CDs, since both the curves show a single break point and after that point the  $\gamma$  value becomes approximately steady. Inclusion complex formation with complex stoichiometry such as 1:2, 2:1, 2:2 etc occur if the surface tension curve shows more break points (scheme S2) [19,20]. Table VIII.1 shows the values of  $\gamma$  and corresponding concentration of CDs and ILs at each break. The breaks have been originated in certain concentration of ILs and CDs where their concentration ratio in the solution was almost 1:1. Hence this study proves the formation of 1:1 inclusion complex. In this case the  $\gamma$  value at the break point is higher for  $\beta$ -CD than that of  $\alpha$ -CD which suggests that the former is superior to encapsulate the guests than the afterward.

### VIII. 3.3. Conductivity study notifies inclusion

Conductivity ( $\kappa$ ) study validates the construction of host-guest inclusion complex vp along with it also provides the stoichiometry of the assembly [21,22]. We have

measured the conductivity of the aqueous solution of the studied ionic solid having  $10\text{mmolL}^{-1}$  concentration with successive addition of  $\alpha$  and  $\beta$ -CD at 298.15K (table S4-S5). It has been found that the conductivity of the ionic solid decreases on a usual basis with escalating concentration of CDs (Figure VIII.3). Since the guest ionic solid molecules are inserted inside the cavity of the CD molecule, the number of free ions per unit volume reduces. Consequently the conductivity of the solution decreases. This surveillance is in concurrence with the development of inclusion complex. Perusal of Figure VIII.3 and Table VIII.2 show analogous result with surface tension study, each having a perceptible break, signifying the formation of Ionic salt-CD inclusion complex having stoichiometry 1:1. Table VIII.2 shows the values of  $\kappa$  and corresponding concentration of the ionic salt and CDs at each break point.

### VIII. 3.4. Density study: interaction between host and guest

In our current study several expensive informations about the inclusion phenomenon between the ionic solid and CD molecules have been obtained applying density measurement. Apparent molar volume ( $\phi_v$ ) and limiting apparent molar volume ( $\phi_v^0$ ) are the two major parameters used for this intention. Apparent molar volume ( $\phi_v$ ) mainly describes the summation of the geometric volume of the central solute molecule and changes in the solvent volume as a result of interface with the solute around the co-sphere (here, solute =  $\text{but}_4\text{NI}$  and co-solvent = CD) [23]. For this system (ternary phase of Ionic solid + aqueous CD system) solute-solvent interaction is conveyed by limiting apparent molar volume. For this study  $\phi_v$  have been calculated from the density of solution systems by means of equation (5) as revealed in SI at 298.15 K (Table S6). Least square method is employed to the plots of  $\phi_v$  versus  $\sqrt{m}$  using the Masson equation (SI, equation 6, Table S7) for obtaining  $\phi_v^0$  value [24]. It is found that  $\phi_v$  values repeatedly reduce and  $\phi_v^0$  values continually enhance for this studied ionic salt with increasing concentration of both the CDs. It is manifest from this fact that for  $\text{but}_4\text{NI}$ , in both the cases of  $\alpha$  and  $\beta$ -CD the ion-hydrophilic group interactions are more efficient than ion-hydrophobic group interactions. The inspection of figure VIII.4 illustrates that the values of  $\phi_v^0$  increases with increasing mass fractions of both CDs and also found

grater for  $\beta$ -CD than  $\alpha$ -CD, signifying the earlier interacts more with the ionic solid than the later. This may be explained as in case of  $\text{but}_4\text{NI}$ , two hydrophobic butyl group can be encapsulated into the cavity of CD and the single positively charged N atom show higher ion-hydrophilic interaction with the  $-\text{OH}$  groups of CD. The larger diameter of  $\beta$ -CD helps in making more compact inclusion complex with the Ionic solid than  $\alpha$ -CD with relatively smaller cavity size showing less hydrophobic interactions with this Ionic solid.

### VIII. 3.5. Viscosity study: order of interactions

Viscosity study is also fruitful for the interpretation of interface between ILs and CDs [25]. In the present ternary system ( $\text{but}_4\text{NI}$  + aqueous CD), (table S3) the viscosity of the solutions show an escalating trend with increasing concentrations of the Ionic solid. The size and shape of the solute molecule recommend the solute-solvent interactions (here, solute =  $\text{but}_4\text{NI}$  and co-solvent = CD) which is designated as viscosity  $B$ -coefficients (table S7) [26]. All the viscosity  $B$ -coefficient values are found to be positive and depicted in figure VIII.5. Perhaps due to higher solvation and also greater Ionic solid-CD interaction the viscosity  $B$  values increase with increasing concentration of CDs [17]. Since the viscosity  $B$  values is again larger for  $\beta$ -CD than that of  $\alpha$ -CD for the Ionic solid it suggest that inclusion is more constructive in case of former than the latter. The structural feature of the Ionic solid and CDs as explained earlier for which these trends of interactions have been acquired due to the relative consequence of viscosity  $B$ -coefficient of the Ionic solid and CDs has been found analogous as for the density study.

### VIII. 3.6. Refractive index shows the compactness of the inclusion complexes

To establish the molecular interaction in the above mentioned ternary solution systems refractive index is one more important parameter to ascertain the molecular interaction [15]. Using the suitable equation (Table S3 and S6) refractive index ( $n_D$ ) and molar refraction ( $R_M$ ) values of the solutions have been estimated. The compactness

and density of the medium is determined by the greater values of  $R_M$  and the limiting molar refraction ( $R_M^0$ ) (Table S7) [16,17]. In case of Ionic solid in both  $\alpha$  and  $\beta$ -CD the  $R_M^0$  values show an increasing trend with increasing concentrations of both CDs, which suggest that the IC of but<sub>4</sub>NI with both the CDs are more closely packed perhaps due to greater hydrophobic as well as ion-hydrophilic interactions between the guest and host as described earlier. The  $R_M^0$  values designate that  $\beta$ -CD is more competent than  $\alpha$ -CD in case of formation of the ICs (Figure VIII.6). The earlier density and viscosity studies are in concurrence with the observations obtained from refractive index data.

### VIII. 3.7. FT-IR Spectra of solid inclusion complexes

The inclusion phenomena in the solid inclusion complex are nicely proved by FT-IR spectrum [27-29]. Table S8 refers the characteristic IR frequencies of  $\alpha$ -CD,  $\beta$ -CD, but<sub>4</sub>NI and solid ICs. Characteristic broad peaks of -OH at about 3412.10  $\text{cm}^{-1}$  and 3349.84  $\text{cm}^{-1}$  are here in the spectrum for  $\alpha$  and  $\beta$ -CD respectively. The characteristic FT-IR Spectra of but<sub>4</sub>NI is showed due to the presence of peaks for -N-C-H-, -C-H (stretching), -C-H (bending for -CH<sub>3</sub> group), -C-H (bending for -CH<sub>2</sub> group) etc. bonds (Figure VIII.8 and Table S8). Yet, there are either absent or shifted several peaks of the Ionic solid due to the change in atmosphere of the guest after inclusion in the CD cavities. The -C-H bending bands for -CH<sub>3</sub> and -CH<sub>2</sub> of both the Ionic solid are shifted in the spectrum of the inclusion complex. The -O-H stretching of  $\alpha$ -CD is shifted to lower frequency in the spectrum of the IC probably due to involvement of the -O-H groups of the host molecules in hydrogen bonding with the guest molecule. On the other hand the -O-H stretching of  $\beta$ -CD is shifted to higher frequency in the spectrum of the IC probably due to involvement of the -O-H groups of the host molecules in hydrogen bonding with the guest molecule. In the spectrum of the ICs the peak for the C-N group of the guest molecules are present. It is an indication of the fact that the hydrophobic side chains present on one side of the polar N atom of the guest molecules are encapsulated in the hydrophobic cavity of both the CDs.

### VIII. 3.8. Binding constants: non-linear isotherms determined by conductivity method

1:1 host-guest inclusion complex formation of the ionic solid with  $\alpha$  and  $\beta$ -CD can be articulated by this equilibrium



The corresponding equilibrium constant,  $K_f$  is given by

$$K_f = \frac{[IC]}{[IS][CD]} \times \frac{f(IC)}{f(IS)f(CD)} \quad (2)$$

where  $[IC]$ ,  $[IS]$ ,  $[CD]$  and  $f$  represent the equilibrium molar concentrations of the inclusion complex, Ionic solid, CDs and the activity coefficients of the species respectively. Using the dilute solution system, the activity coefficient of uncharged macrocycle,  $f(C)$ , can be reasonably assumed as unity. The employ of Debye-Hückel limiting law, [30] conclude that  $f(IS) \sim f(CD)$ , so the activity coefficients in Equation (2) are cancelled. The complex formation constant in terms of the molar conductance,  $\Lambda$ , can be expressed as [31]

$$K_f = \frac{[IC]}{[IS][CD]} = \frac{(\Lambda_{IS} - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{IC})[CD]} \quad (3)$$

Where

$$[CD] = CD_{ad} - \frac{IS_{ad}(\Lambda_{IS} - \Lambda_{obs})}{(\Lambda_{IS} - \Lambda_{IC})} \quad (4)$$

Here,  $\Lambda_{IS}$  represents molar conductance of the ionic solid before the addition of CD,  $\Lambda_{IC}$  the molar conductance of the inclusion complex,  $\Lambda_{obs}$  the molar conductance of the solution during titration,  $CD_{ad}$  the concentration of added cyclodextrin and  $[IS]$  concentration of the ionic solid. The complex formation constant,  $K_f$  and the molar conductance of the complex,  $\Lambda_{IC}$ , were evaluated by using Equations (3) and (4). Therefore, through the application of a non-linear programme the  $K_f$  values (Table VIII.3) for the ICs were assessed from the binding isotherm.

$K_f$  values indicate that the ionic solid has higher binding constant in  $\beta$ -CD than that of in  $\alpha$ -CD. This fact may be occurring due to the larger cavity dimension of  $\beta$ -CD than that of in  $\alpha$ -CD. So, inclusion complex formation is highly feasible in  $\beta$ -CD than in  $\alpha$ -CD.

### VIII. 3.9. Structural influence of cyclodextrin in inclusion complex formation

Size of the guest molecules and also on the cavity diameter of host, the formation of host-guest ICs between the Ionic solid and CDs is exclusively dependent. Between the two CDs  $\beta$ -CD has the higher cavity diameter (6.0-6.5Å) than that of  $\alpha$ -CD (cavity diameter is 4.7-5.3Å). In view of the compatible size of the taken Ionic solid with  $\beta$ -CD, It is found that  $\beta$ -CD is more apt to form ICs than that of  $\alpha$ -CD with the Ionic solid is possibly due to higher surface interaction, escalating the hydrophobic attractions, which is in concurrence with spectroscopic and physicochemical interpretations [1]. In case of ICs formation no covalent bonds are formed or broken; only the hydrophobic alkyl chains of the Ionic solid are encapsulated into the hydrophobic cavity of CD molecules. This is a very important factor in case of IC formation that the hydrophobic cavity of CD is engaged by polar water molecule, but it is unfavourable, so the water molecules are effortlessly replaced by more hydrophobic alkyl tails of Ionic solid. Furthermore due to release of the trapped water molecules in bulk of the solution entropy of the solution system is enhanced and the IC formation procedure becomes spontaneous. Due to the spontaneity of this procedure the system becomes very low energetic and stable. So, the ring strain of CD molecule becomes very low. Due to the difficulty of the trapping of another Ionic solid by CD molecule probably 1:1 host-guest inclusion complex formation occurs. The stability of the IC can be ascribed by structural feature such that the N atom present in the Ionic solid form H-bonds with the -OH groups present at the rim of CD.

### IV.4. CONCLUSION

The above revealed various physicochemical studies help us to conclude that the ionic solid form host-guest ICs with both  $\alpha$  and  $\beta$ -CD both in solution and solid state. With the help of  $^1\text{H}$  NMR study it may be substantiated that inclusion occurs in the apolar cavity of both CD molecules, even as surface tension and conductivity data suggest 1:1 stoichiometry. Volumetric, viscometric and refractometric measurements are also in excellent concord with another study and furthermore suggested the

interactions between ionic solid and CD. The solid state of ICs have been characterised by FT-IR, confirming their creations also in solid state. In this study the inclusion phenomenon of ionic solid has been originated extra ensnared in case of  $\beta$ -CD than  $\alpha$ -CD. The binding constants, evaluated using a non-linear programme by the conductivity method also supports the trend of IC formation. As a consequence, the exclusivity of our present research work is diverse appliances in the field of bio-chemistry such as drug delivery tools, recycling extraction agents and nano-sensors and so on.

**TABLES:****Table VIII.1:** Values of surface tension ( $\gamma$ ) at the break point with corresponding concentrations of cyclodextrins and but<sub>4</sub>NI at 298.15 K<sup>a</sup>.

Name of the Host	but <sub>4</sub> NI		$\gamma^a / \text{mN}\cdot\text{m}^{-1}$
	Conc. of Host/mM	Conc of ionic Solid/mM	
$\alpha$ -CD	4.89	5.10	72.67
$\beta$ -CD	4.77	5.23	73.52

**Table VIII.2:** Values of conductivity ( $\kappa$ ) at the break point with corresponding concentrations of cyclodextrins and but<sub>4</sub>NI at 298.15 K<sup>a</sup>.

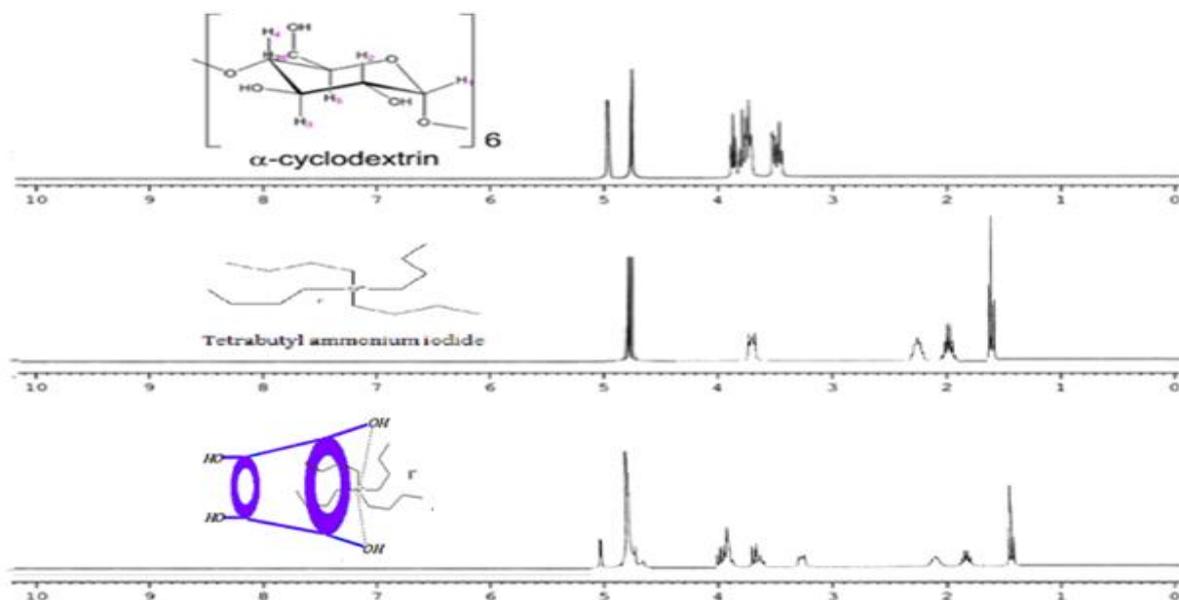
Name of the Host	but <sub>4</sub> NI		$\kappa^a / \text{mS}\cdot\text{m}^{-1}$
	Conc. of Host/mM	Conc of ionic Solid/mM	
$\alpha$ -CD	5.91	4.09	0.40
$\beta$ -CD	5.44	4.56	0.47

**Table VIII.3:** Formation constants of ionic solid-cyclodextrin inclusion complexes.

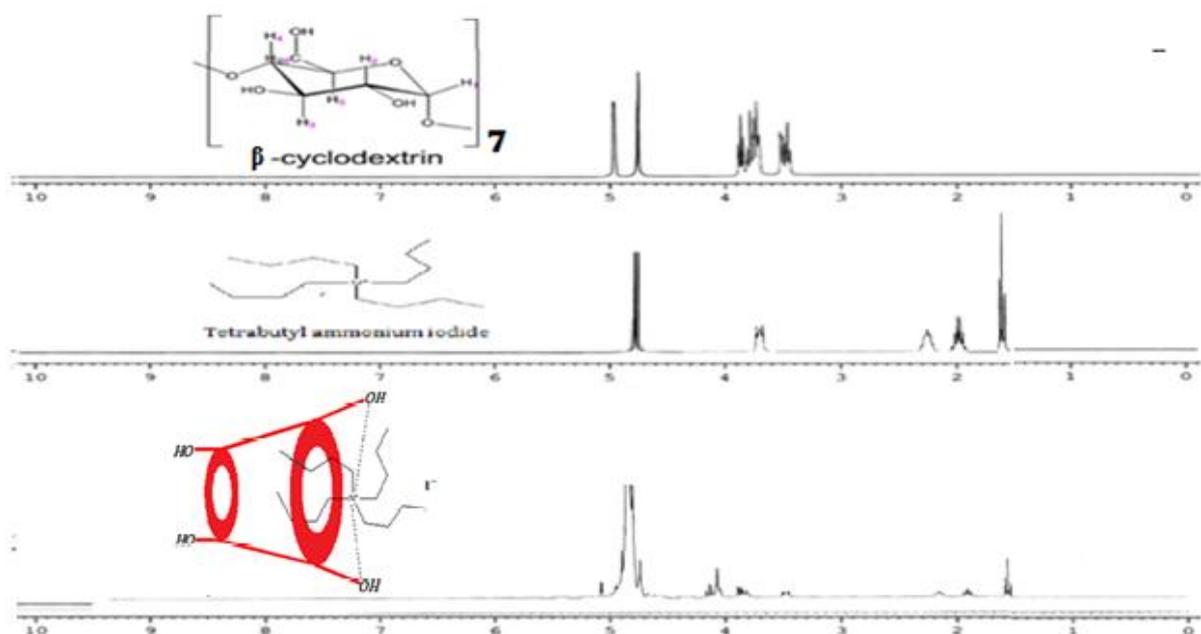
Cyclodextrin	$\log K_f^b (\text{M}^{-1})$		
	298.15 K <sup>a</sup>	303.15 K <sup>a</sup>	308.15 K <sup>a</sup>
$\alpha$ -CD	3.12	2.95	2.78
$\beta$ -CD	3.38	3.15	2.99

<sup>a</sup>Standard uncertainties in temperature are:  $u(T) = \pm 0.01 \text{K}$ . <sup>b</sup>Mean errors in  $K_b = \pm 0.01 \times 10^{-3} \text{M}^{-1}$

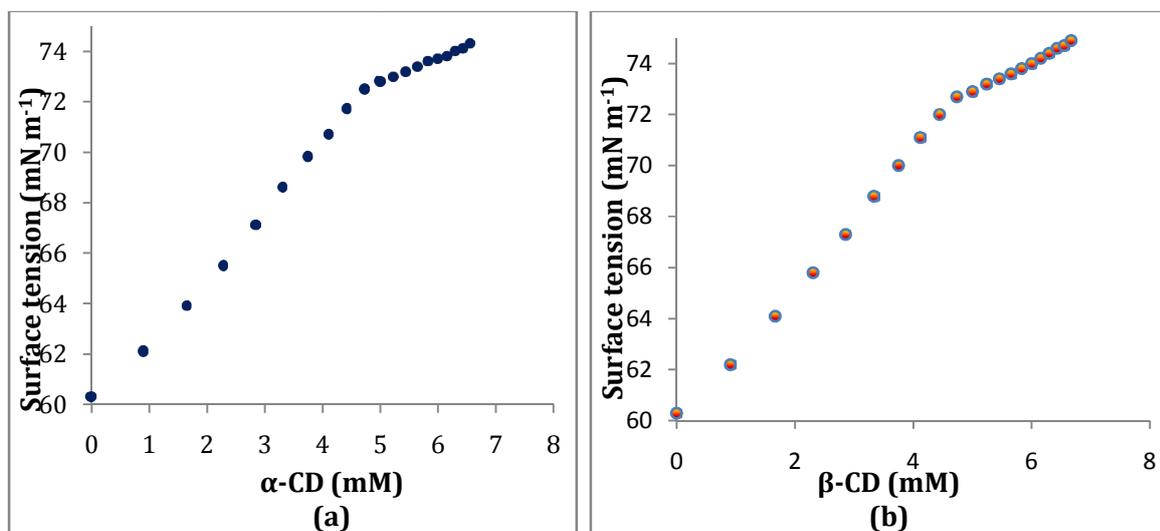
## FIGURES



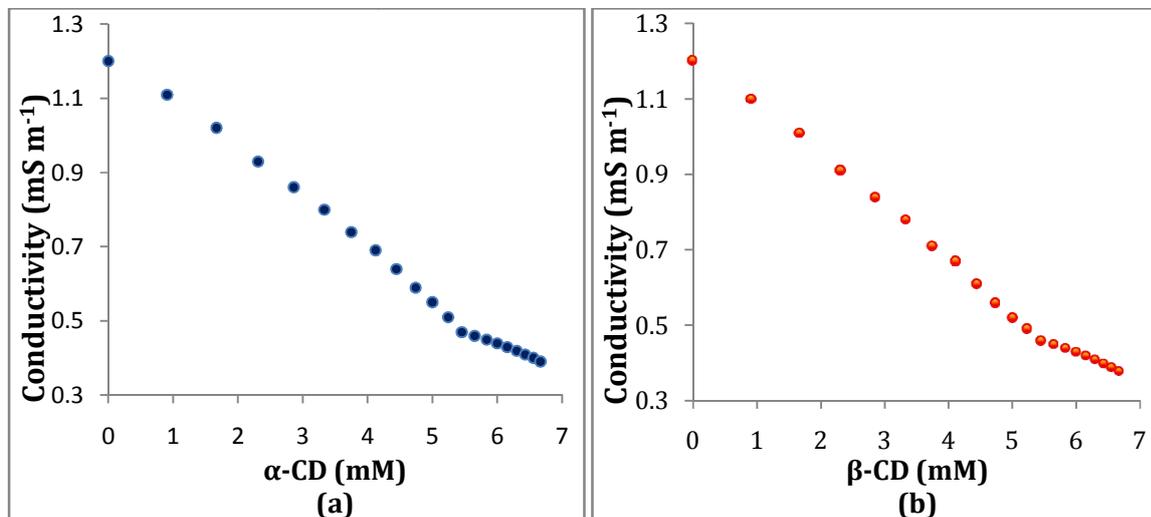
**Figure VIII.1(a).**  $^1\text{H}$  NMR Spectra of  $\alpha$ -CD, Tetrabutyl ammonium iodide and 1:1 molar ratio of  $\alpha$ -CD + Ionic Solid in  $\text{D}_2\text{O}$  in 298.15 K.



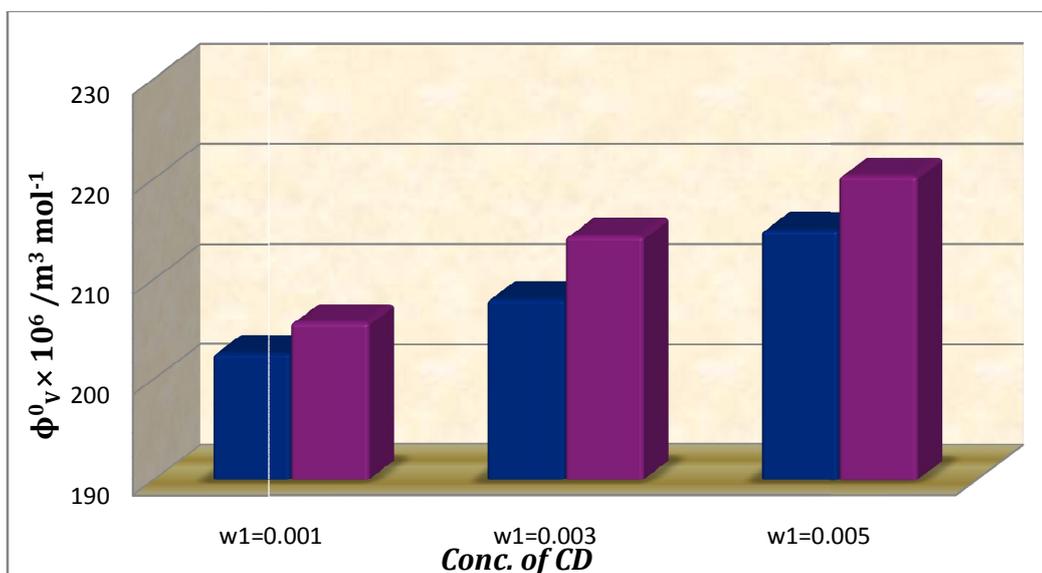
**Figure VIII.1(b).**  $^1\text{H}$  NMR Spectra of  $\beta$ -CD, Tetrabutyl ammonium iodide and 1:1 molar ratio of  $\beta$ -CD + Ionic Solid in  $\text{D}_2\text{O}$  in 298.15 K.



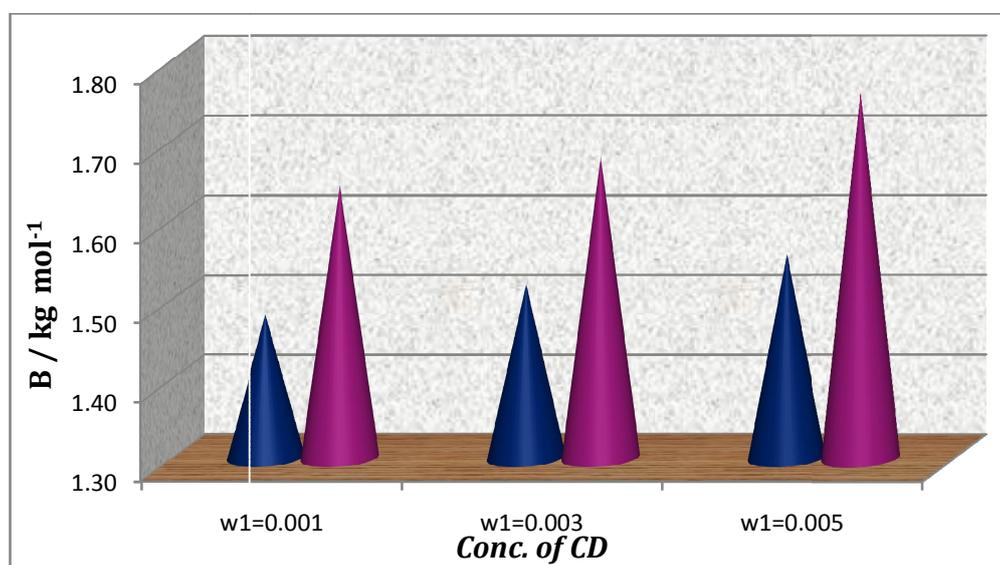
**Figure VIII.2.** Variation of surface tension of aqueous (a) but<sub>4</sub>NI-α-CD and (b) but<sub>4</sub>NI-β-CD systems respectively at 298.15 K.



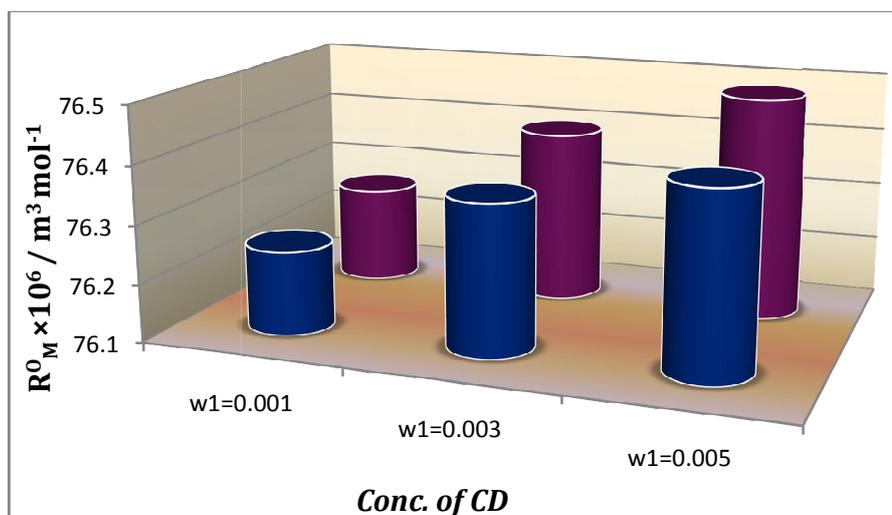
**Figure VIII.3.** Variation of conductivity of aqueous (a) but<sub>4</sub>NI-α-CD and (b) but<sub>4</sub>NI-β-CD systems respectively at 298.15 K.



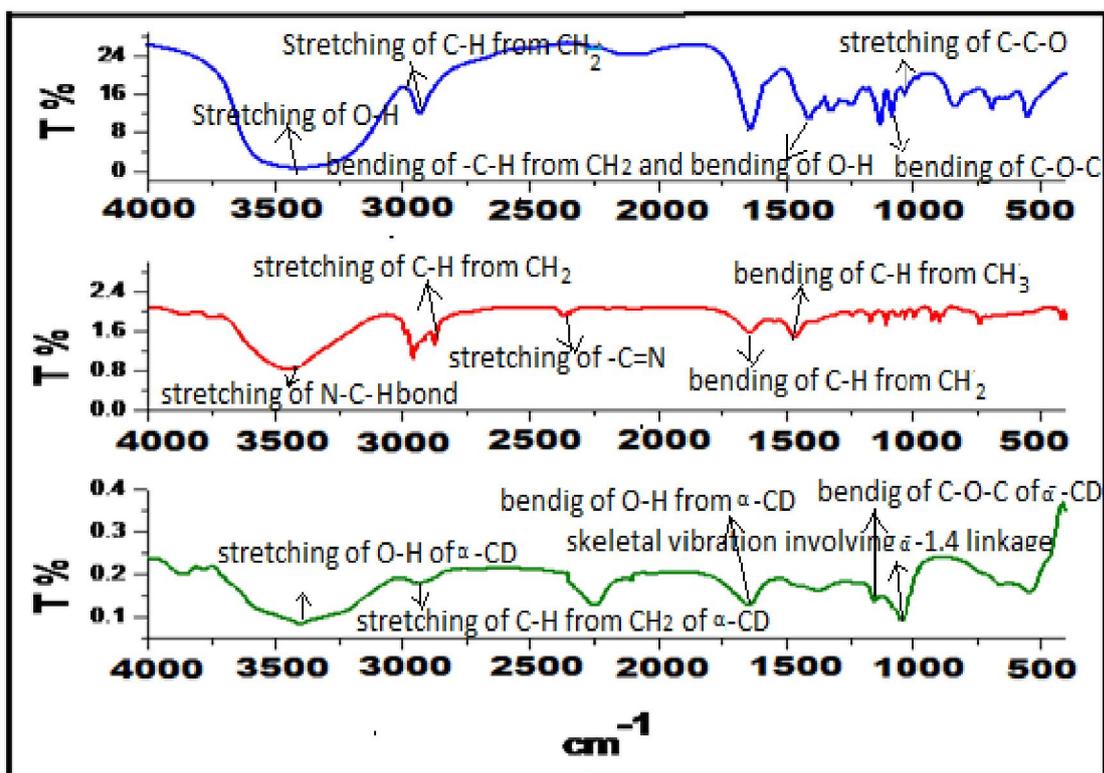
**Figure VIII.4.** Plot of limiting molar volume ( $\phi_v^0$ ) against mass fraction ( $w$ ) of aqueous  $\alpha$ -CD (blue) and aqueous  $\beta$ -CD (purple) for but<sub>4</sub>NI at 298.15 K.



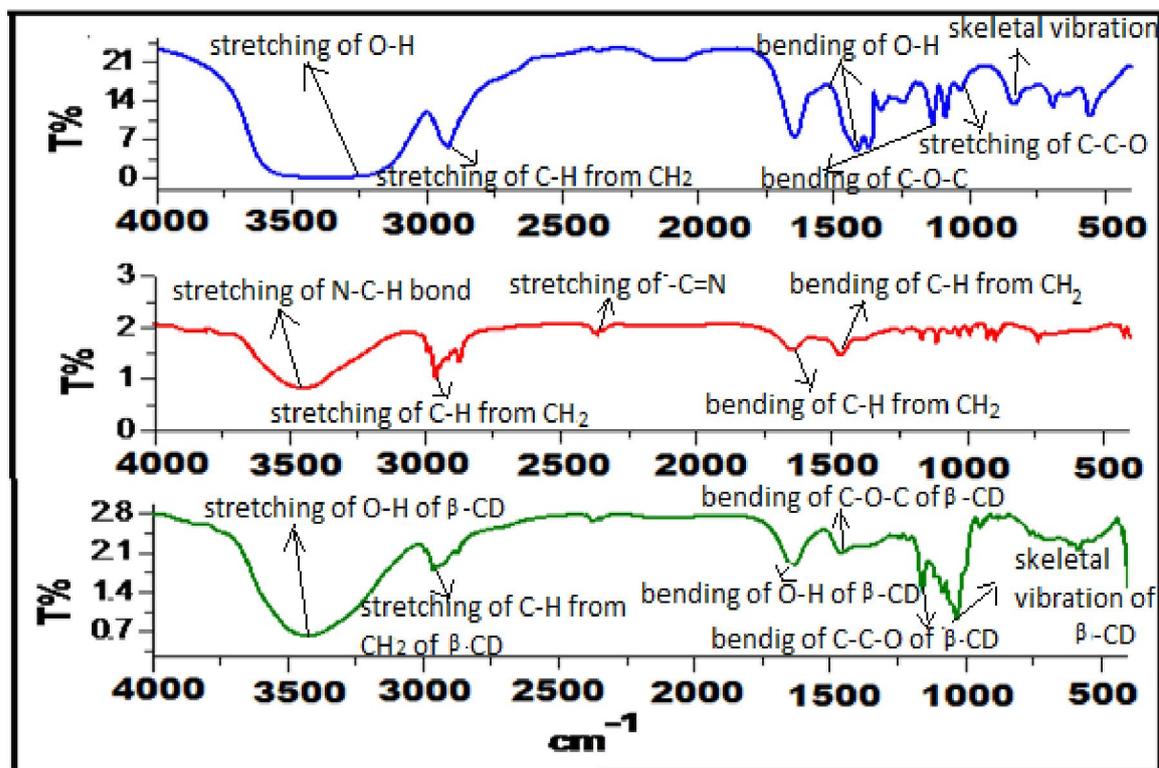
**Figure VIII.5.** Plot of viscosity B-coefficient against mass fraction ( $w$ ) of aqueous  $\alpha$ -CD (blue) and aqueous  $\beta$ -CD (purple) for but<sub>4</sub>NI at 298.15 K.



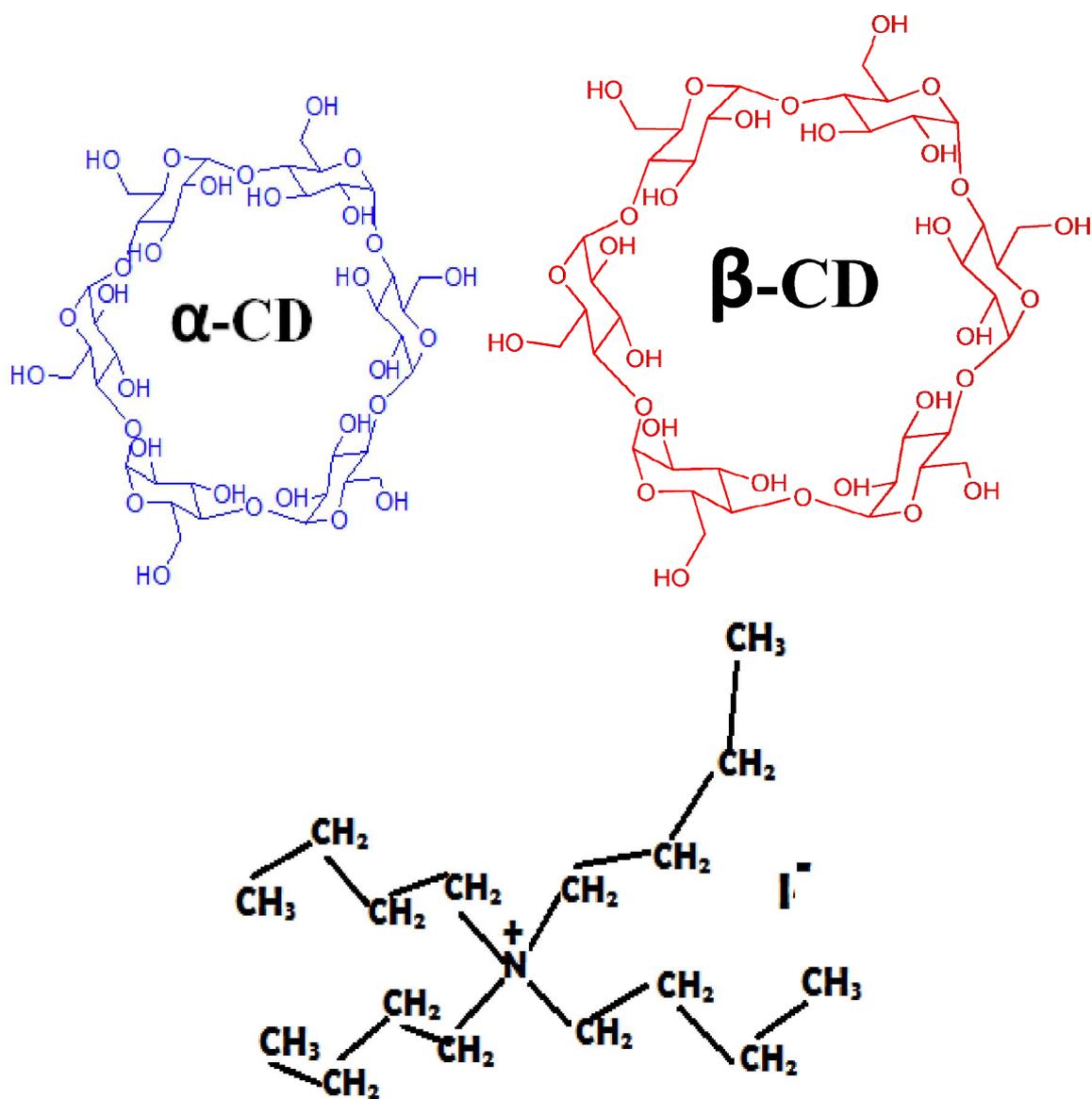
**Figure VIII.6.** Plot of limiting molar refraction ( $R_M^0$ ) for but<sub>4</sub>NI in different mass fractions ( $w$ ) of aqueous  $\alpha$ -CD (blue) and aqueous  $\beta$ -CD (purple) respectively at 298.15 K.



**Figure VIII.7(a).** FTIR spectra of  $\alpha$ -CD (top), but<sub>4</sub>NI (middle) and but<sub>4</sub>NI- $\alpha$ -CD inclusion complex (bottom).



**Figure VIII.7(b).** FTIR spectra of  $\beta$ -CD (top),  $\text{but}_4\text{NI}$  (middle) and  $\text{but}_4\text{NI}$ - $\beta$ -CD inclusion complex (bottom).

**SCHEMES**

**Scheme VIII.1.** Molecular structure of cyclodextrin molecules and tetrabutylammonium iodide.