CHAPTER V

Cage to cage study of Ionic liquid and cyclic oligosachharides to form inclusion complexes

The inclusion complexation behaviour, charecterization and binding ability of Trihexyltetradecylphosphonium chloride with α and β -Cyclodextrin have been investigated both in aqueous and solid state by means of ¹H-NMR, surface tension, conductivity, density, viscosity,refractive index, FT-IR,HRMS study. The shifts in the NMR spectra reveals that part of the ionic liquid is inserted in the cyclodextrin molecules. Surface tension and conductivity study approves the 1:1 stoichiometry of the inclusion complex while density,viscosity and refractive index shows the interaction of the ionic liquid with host molecules. FT-IR and HRMS confirms the inclusion phenomenon. Binding constants have been evaluated using a non linear programme indicating a higher degree of encapsulation in case of β -cyclodextrin compared to α -cyclodextrin.



V. 1. Introduction

The field of Ionic liquids draws the attention of modern chemists because of their unusual properties such as low vapour pressure, high thermal and chemical stability, large liquid temperature range and high solvation ability towards inorganic, organic, complex salts and biopolymers.[1] These properties make them completely different from molecular liquids. Ionic liquids are generally constituted with a large organic cataion and a small anion.[2] They have vast applications in various chemical industries because of their green nature. They produce less hazardous compounds during their use.[3] Phosphonium based ionic liquids are less toxic and more thermally stable than nitrogen based ionic liquids.¹ In this research article the phosphonium based hydrophobic ionic liquid Trihexyltetradecylphosphonium chloride(TTP)(Scheme 1)has been used. This ionic liquid is highly used in separation of different dyes including methylene blue from aqueous media. This has also application as additives to improve the yield of essential oils in the hydrodistillation process.[4]

Cyclodextrin(CD), a cyclic oligosachharide, is well known in supramolecular chemistry as molecular host because of their ability of inclusion of a range of guest molecules through non covalent interaction in their hydrophobic cavity.[5] α , β and γ cyclodextrins consists of 6,7 and 8 glucose units respectively linked by α -1,4 glucosidic linkage.[6] They can be described as a shallow truncated cone having primary and secondary hydroxyl groups in the rims (Scheme 2).[5] They can form stable inclusion complex with drugs,vitamins,ionic liquids, amino acids, neurotransmitters etc guest molecules.⁷ The weak intermolecular forces acting between the guest and host includes Vanderwaal's force, dipole-dipole interaction, electrostatic and hydrogen bonding interactions.[8] CD's are non-toxic and considered safe to humans. Formation of inclusion complex is the best method to improve the physicochemical properties of the guest molecule. Due to the enormous application of the inclusion complexes formed by them they are used in cosmetic, food and pharmaceutical industeries.[9]

In the present study we attempt to ascertain the formation and nature of IC of α and β -CD with TTP in aqueous environment by spectroscopic and physicochemical studies. Our aim is to explore the formation, carrying and controlled release of this ionic liquid by forming IC with CD without any chemical and biological modification of the guest molecule. Thus it will find better utility in the dye industry and also in the hydrodistillation process of oils. To the best of our knowledge no theoretical investigations concerning inclusion complex formation between α and β -CD and TTP have been perform so far.

V. 2. Experimental Section

V.2.1. Source and Purity of Samples

Trihexyltetradecylphosphoniumchloride, α -cyclodextrin and β -cyclodextrin of puriss grade were bought from SigmaAldrich, Germany. The chemicals are used in the experiment in the same condition as purchased. The mass fraction purity of TTP, α -cyclodextrin and β -cyclodextrin ≥ 0.98 , ≥ 0.99 and ≥ 0.98 respectively.

V.2.2. Apparatus and Procedure

The above mentioned ionic liquid trihexyltetradecylphosphonium chloride and the two CDs are freely soluble in triply distilled, deionized and degassed water. The stock solutions of TTP and aqueous CD were prepared by mass at 298.15 K. Mettler Toledo AG-285(uncertainty 0.0001 g) was used for weighing.

 ^1H NMR spectra were taken in D_2O at 300 MHz with help of Bruker Advance instrument at

298.15 K. Signals are mentioned as δ values in ppm. The internal standard is D₂O (protonated signal at 4.79ppm). Data are cited as chemical shift.

The surface tension study was performed with platinum ring detachment technique using a Tensiometer (K9, KRSS; Germany). The temperature is maintained at 298.15 K by circulation of thermostated water through a double

wall glass vessel containing the solution. The accuracy of the instrument is about ± 0.1 mN m⁻¹.

The conductivity study was carried out using a Mettler Toledo Seven Multi conductivity meter (uncertainty $\pm 1.0 \ \mu \text{Sm}^{-1}$) in a thermostated waterbath at 298.15 K. HPLC grade water was used with a specific conductance of 6.0mSm⁻¹. Calibration of the conductivity cell was done with 0.01 M aqueous KCl solution. Uncertainty of temperature was ± 0.01 K.

The densities (r) of the series of solutions were measured by vibrating U-tube Anton Paar digital density meter (DMA 4500 M) (precision ± 0.00005 g cm⁻³). Calibration of the density meter was carried out by standard method. Uncertainty of temperature was ± 0.01 K.

The viscosities (η) of the solutions are measured with Brookfield DV-III Ultra Programmable Rheometer(spindle size 42). Other informations have already mentioned.

Digital Refractometer from Mettler Toledo has been used to measure the refractive index of the solutions (uncertainty ± 0.0002 units). Other informations have already mentioned.

The two inclusion complexes of the ionic liquid TTP with both CD molecules (TTP+ α -CD, TTP+ β -CD) have been prepared in 1:1 molar ratio. 1.0mmol α -CD and 1.0mmol TTP were separately dissolved in 30 ml water. The two solutions were separately stirred for 4 hours. Then the aqueous solution of the TTP was dropwise added to aqueous α -CD solution. The mixture is stirred for 72 hours at about 60° c. The solution is filtered at 60° c and allowed to cool to 10° c. It was kept for 12 hours. After that the suspension was filtered and white crystalline powder was found. It was washed with ethanol and dried in air.

The solid inclusion complexes are dissolved in methanol. HRMS spectra were recorded with a Q-TOF high resolution instrument by positive mode electrospray ionization.

FT-IR spectra were taken by Perkin Elmer FT-IR spectrometer by KBr disk technique. For preparation of KBr disk 1mg of the solid inclusion complex and 100mg KBr were mixed. The scanning range of the spectra is 4000–400 cm⁻¹ at room temperature.

V. 3. Result and discussion

V.3.1. ¹H-NMR spectra

¹H-NMR study confirms the formation of inclusion complex of TTP with α and β -CD.[9,10] Insertion of ionic liquid molecule into the hydrophobic cavity of CD molecules consequences the chemical shift of both the guest and host molecule. The TTP molecule results dimagnetic shielding of the protons as a result of interaction with the CD protons after inclusion. The position of different protons in the CD molecules are shown in scheme 3. The H3 and H5 protons are situated inside the cavity near the wider rim and narrower rim respectively. The other protons H1,H2 and H4 are situated outside the CD molecule.[11,12] The respective δ values of the ionic liquid TTP, α -CD, β -CD and inclusion complexes are reported in table V.1. The protons of CD and TTP show considerable upfield shift in 1:1 inclusion complex of the ionic liquid and CD (Figure 1,2). It can be concluded from chemical shift that the protons of the hydrocarbon chain of TTP interacts more with the H3 protons than H5 suggesting the TTP molecule enters in the hydrophobic cavity from wider end. The shift in δ value of both the CD perhaps due to change of environment after inclusion complex formation. The H6 proton of α and β -CD remain uneffected after inclusion which again supports the fact that the guest molecule inserts from wider end.

V.3.2. Surface Tension Study

The formation and stoichiometry of the inclusion complexes can be interpreted with surface tension study.[13,14] Adding CD to water does not change the surface tension (γ)of water as it is hydrophobic in nature. This fact also illustrates that CD is surface inactive compounds.[15] The ionic liquid TTP

contains many long hydrocarbon chains and acts as strong surface active agent. The γ value of TTP is lower than pure water. Here the γ value of a series of solutions of TTP with increasing concentration of α -CD and β -CD have been measured at 298.15K (Table V.2-V.3). The γ value is found to increase for both the CD molecules. This is probably due to insertion of the hydrocarbon chain of the ionic liquid from the solution to the hydrophobic cavity of the host CD molecules. A single distinguisable break appears in the two surface tension plots depicted in figure V.3 which suggests the formation of IC.[16,17] The concentrations of TTP and the CD molecules at the break point (Table V.4) is approximately 1:1 which further confirms the stoichiometric ratio of the two ICs as 1:1. More number of breaks in the plot suggests complex stoichiometry of the complex such as 1:2,2:1,2:2 etc. the surface tension at the break point is slightly higher for β -CD indicating it a better host compared to α -CD.

V.3.3. Conductivity Study

Conductivity study also supports the formation and stoichiometry of the two inclusion complexes formed.[18,19] The aqueous solution of the ionic liquid TTP shows considarable conductivity as it exsists as a charged structure. In this study the conductivity of a series of solutions of TTP with increasing concentration of α -CD and β -CD have been measured at 298.15K (Table V.2-V.3). The conductivity value shows regular decrease and after a sharp break point the conductivity value almost becomes constant. Similar results obtained in case of both host CD molecules. The decrease in the κ value probably due to the encapsulation of the long hydrocarbon chain of the guest TTP molecules in the hydrophobic cavity of CD. The values of κ and corresponding concentration of the host CD molecules are reported in table 1 which suggests that the ratio of concentration of TTP and the CD at the break point is almost 1:1.The appearance of sharp break(Figure V.4) points suggest the formation of inclusion complex and also the stoichiometry as 1:1.[20]

The break point indicates certain concentration where maximum number of TTP molecules are inserted in CD molecule ever before. [11]A dynamic equilibrium exsists between the guest ionic liquid and host CD molecules.

Ionic liquid + cyclodextrin Inclusion complex

Maximum inclusion takes place at break point, after it the concentration of CD is higher than the concentration of TTP and the equilibrium shifts more towards the formation of IC.

V.3.4. Density study: illustrates the interaction

The interaction between the ionic liquid and the host molecules can be nicely explained with the help of density study. The apparent molar volume (φ_v) and limiting aparent molar volume (φ_v°) have been calculated to explain the interaction. φ_v can be defined as the summation of volume of the central solute molecule and changes in the solvent volume as a result of interaction of the solute around its co-sphere.^[21] The TTP forms a ternary solution system with aqueous CD molecules. Here TTP acts as solute and the CD plays the role of cosolvent. φ_{v} illustrates the interaction between them in the following system. φ_{v} values have been determined from the solvent density (measured at 298.15K) (Table V.6) using Masson Equation (Table V.7). φ_v° values were calculated by applying least square treatments to the plots of φ_v versus \sqrt{m} with the help of Masson Eqn. [22,23] The limiting aparent molar volumes are depicted in figure V.5. φ_v and φ_v° values shows decreasing and increasing trend respectively for TTP with the increase of concentration of CD molecules. This trend clearly indicates that for this ionic liquid the ion-hydrophilic group interactions are more than ion –hydrophobic interactions. The limiting aparent molar volume increases regularly with increasing mass fraction of CD molecules. The value is slightly higher for β -CD indicating that it is a better host for TTP. The probable reason behind the assumption is that the hydrocarbon chains are encapsulated in the hydrophobic cavity of host CD and the positively charged P atoms interacts with the hydrophilic –OH groups of the CD present in the rim.

The larger cavity of β -CD helps to form more stable inclusion complexes with TTP as it contains more number of polar –OH groups.

V.3.5. Viscosity

The inclusion of of the ionic liquid TTP in the CD molecule can be also explained with the help of viscosity study.[24,25] The viscosity of the solution increases with the increase of the molarity of TTP in this ternary system due to structure making contribution of CD with water molecules (Table V.6). The viscosity B coefficient have been determined (table V.7) which explains the solute solvent interactions based upon the size and shape of solvent molecules. This parameter is found to be positive and depicted in the figure 6. The rising value of B signifies the increasing interaction of TTP with CD and higher solvation.[21] The long hydrophobic decyl chain is encapsulated in the CD cavity. Again the B value is higher for β -CD than α -CD as the former is better host due to larger diameter than the latter. The viscosity result shows similarity with that of density study and it can be concluded that the structure of CDs and TTP are responsible for this kind of interaction.

V.3.6. Refractive Index

The refractive index(η_D) also explains the interaction between the ionic liquid TTP with CD molecules.[20,21] It also supports the data obtained from density and viscosity data. The η_D values for a series of solutions are measured(Table V.6) with increasing molarity of TTP. The molar refraction (R_M) and limiting molar refraction (R_M °) of the solutions were also determined (V.7 and V.8). The plot (Figure V.7) shows that the R_M ° value increases with the increase of mass fraction of TTP. The increasing values of both R_M and R_M ° signify the ternary solution becomes more compact and dense. This means the inclusion complex of TTP with both the CD molecules are closely packed than TTP probably due to greater hydrophobic and ion-hydrophilic interactions. The higher R_M ° value for β -CD illustrates that it can better accommodate the ionic liquid in comparison to α -CD.

V.3.7. FT-IR spectra

The encapsulation of TTP in the hydrophobic cavity of CD was confirmed from FT-IR spectroscopy as the band resulted from the inserted part of TTP showed a shift or their intensities are changed. [26,27] FT-IR spectra of TTP, α -CD, β -CD and the inclusion complexes were represented in figure V.8 and V.9. The various frequencies of the above mentioned compounds are reported in table V.8. The IR spectrum of the ionic liquid can be characterized by principal absorption peaks at 3372.75(Symmetrical Stretching of -C-H from CH₃), 2941.63(Symmetrical Stretching of -C-H from -CH₂), 1454.58(Stretching of P-CH₂-) etc. The broad -O-H stretching frequency for α -CD and β -CD was observed at 3412.10 and 3349.84 cm⁻¹ respectively. In the two IC's the –O-H frequency shifted to lower regeion i.e.; 3378.08 and 3335.76 cm⁻¹ for α -CD and β -CD respectively. The reason behind the fact is the involvement of the –O-H groups of both the CDs in hydrogen bonding with the guest TTP molecule. [28,29] The prominent peaks of the ionic liquid for -P-CH₂, -CH₃,-CH₂, of the hydrocarbon chains are shifted in both the IC's. The changes in the FT-IR spectra of TTP are due to the restriction of the vibration of free TTP molecules as the hydrocarbon chains are inserted in the cavity of CD molecules. No additional peaks are obtained in the spectra of IC's. This fact again suggests that only non covalent interaction exsists between the CDand TTP, only Vanderwaal's interaction are present. [30,31]

V.3.8. Mass Spectra

The charecterisation of the two inclusion complexes can also be done by ESI-MS study.[32,33] Although it is difficult to interpret sometimes but m/z value helps to charecterise the inclusion complexes formed. Figure V.9 and V.10 shows the MS spectra of the two inclusion complexes TTP+ α -CD, TTP+ β -CD respectively. The intense peaks at m/z 1491.80 and 1653.85 indicates the proton adduct of TTP- α -CD IC and TTP- β -CD IC. No other significant peaks are observed at higher values. This study confirms the formation of two inclusion complexes with 1:1 stoichiometry. [34, 35]

V.3.9. Binding Constants: Non linear isotherms

Association constants(K_b) of the two inclusion complexes have been determined from conductivity study.[25] The insertion of the ionic liquid molecule into the hydrophobic cavity of the two CD molecule results the change in conductivity of the aqueous solution. A non linear programme was used to determine the binding constants depending upon this fact.[36,37] There exsists an equilibrium between guest TTP and host CD molecules leading to the formation of 1:1 inclusion complex. The equilibrium can be represented as

$$TTP_f + CD_f \stackrel{K_b}{\longrightarrow} IC$$
 (1)

The expression of the binding constant can be obtained from the above equation as

$$K_{b} = \frac{[IC]}{[TTP]_{f}[CD]_{f}}$$
(2)

In the above equation, $[IC],[TTP]_f$ and $[CD]_f$ expresse the equilibrium concentration of the inclusion complex, free TTP and cyclodextrin molecule respectively. The binding constant K_b can be expressed in terms of conductivity κ as

$$K_{b} = \frac{[IC]}{[TTP]_{f}[CD]_{f}} = \frac{(\kappa_{obs} - \kappa_{o})}{(\kappa - \kappa_{obs})[CD]_{f}}$$
(3)

where,
$$[CD]_f = [CD]_{ad} \qquad \frac{[TTP]_{ad}(\kappa_{obs} - \kappa_o)}{(\kappa - \kappa_o)}$$
(4)

Where κ_{o}, κ_{obs} and κ represent the conductivity of TTP initially, during addition of host and final state respectively. [TTP]_{ad} and [CD]_{ad} are the concentrations of IL and the added CD respectively. Application of the non linear programme to the binding isotherms gives the value of K_b (Table V.10). The association constant for TTP is slightly higher in case of β -CD probably due to the reason that it can better accommodate the ionic liquid due to its more larger dimension compared to $\alpha\mbox{-}CD.$

V.4. Conclusion

The present article confirms that the above mentioned ionic liquid Trihexyltetradecylphosphonium chloride forms inclusion complex with both α and β -CD in aqueous medium and in solid state. These two IC's can be used for controlled release of this ionic liquid. ¹H-NMR study confirms the inclusion phenomenon whereas surface tension and conductivity study reveal the 1:1 stoichiometry of the complexes. Density ,viscosity and refractive index study show the interaction between the guest and host CD's. FT-IR spectra and mass spectra also supported the formation of IC. The binding constants for the formation of the two IC's have been evaluated from non linear isotherms using conductivity study. It is found to be higher for β -CD. These two IC's have application in various industrial processes to make them greener.

Tables

Table V.1. ¹H NMR data of TTP, α -CD, β -CD and inclusion complexes

α-Cyclodextrin: (500 MHz, Solv: D₂O) δ=3.48-3.51 (6H, t, *J* = 9.00 Hz), 3.53-3.56 (6H, dd, *J*=10.00, 3.00 Hz), 3.74-3.83 (18H, m), 3.87-3.91 (6H, t, *J* = 9 Hz), 4.96-4.97 (6H, d, *J* = 3 Hz)

β-Cyclodextrin: (500 MHz, Solv: D₂O) δ=3.49-3.54 (6H, t, *J* = 9.2 Hz), 3.57-3.60 (6H, dd, *J* = 9.6, 3.2 Hz), 3.79-3.84 (18H, m), 3.87-3.92 (6H, t, *J* = 9.2 Hz), 5.00-5.01 (6H, d, *J* = 3.6 Hz)

TTP: (400 MHz, Solv: D₂O) δ=0.71-0.77(9H,d,*J*=), 1.0-1.61(48H,m), 2.0-2.07(2H,d,*J*=), 2.29(6H,s)

TTP-α-CD: (1:1 molar ratio, 300 MHz, Solv: D_2O) : δ = 0.90-1.22(54H,m), 3.22-3.26(6H, t, *J*= Hz), 3.30-3.32(6H, dd, J=)3.47-3.57(18H, m), 3.59-3.62(6H, t, *J* = Hz) TTP-β-CD: (1:1 molar ratio, 300 MHz, Solv: D_2O) : 0.88-1.20(54H,m), 1.35-1.37(2H,d, *J*=), 3.18-3.22(6H, t, *J*=), 3.28-3.30(6H, dd, J=), 3.42-3.52(18H, m), 3.52-3.67(6H, t, *J* = Hz)

Table V.2. Data for surface tension and conductivity study of aqueous TTP- α -CD system at 298.15K^a

Volm of α-CD (mL)	Total volm (mL)	Conc of TTP (mM)	Conc of α-CD (mM)	Surface tension (mN m ⁻¹)	Conductuvity (mS m ⁻¹)
0	10	10.000	0.000	25.5	5.81
1	11	9.091	0.909	28.4	5.29
2	12	8.333	1.667	31.3	4.77
3	13	7.692	2.308	33.6	4.34
4	14	7.143	2.857	35.9	3.98
5	15	6.667	3.333	37.7	3.64
6	16	6.250	3.750	39.5	3.35

7	17	5.882	4.118	40.8	3.14
8	18	5.556	4.444	42.1	2.93
9	19	5.263	4.737	43.5	2.75
10	20	5.000	5.000	45.0	2.60
11	21	4.762	5.238	45.4	2.54
12	22	4.545	5.455	45.9	2.51
13	23	4.348	5.652	46.2	2.48
14	24	4.167	5.833	46.5	2.45
15	25	4.000	6.000	46.8	2.43
16	26	3.846	6.154	47.0	2.41
17	27	3.704	6.296	47.2	2.39
18	28	3.571	6.429	47.4	2.37
19	29	3.448	6.552	47.6	2.35
20	30	3.333	6.667	47.8	2.33
^a Stand	lard uncertaii	nties in temperatu	tre u are: $u(T) = \pm 0$	0.01 K.	

Table V.3. Data for surface tension and conductivity of aqueous TTP- β -CD system at 298.15K^{*a*}

Volm of β-CD (mL)	Total volm (mL)	Conc of TTP (mM)	Conc of β-CD (mM)	Surface tension (mN m ⁻¹)	Conductuvity (mS m ⁻¹)
0	10	10.000	0.000	25.5	5.81
1	11	9.091	0.909	28.8	5.27
2	12	8.333	1.667	31.7	4.74
3	13	7.692	2.308	34.1	4.31
4	14	7.143	2.857	36.4	3.95
5	15	6.667	3.333	38.3	3.61
6	16	6.250	3.750	39.9	3.31

7	17	5.882	4.118	41.2	3.10
8	18	5.556	4.444	42.5	2.89
9	19	5.263	4.737	43.9	2.71
10	20	5.000	5.000	45.4	2.56
11	21	4.762	5.238	45.8	2.51
12	22	4.545	5.455	46.2	2.48
13	23	4.348	5.652	46.6	2.45
14	24	4.167	5.833	46.9	2.42
15	25	4.000	6.000	47.2	2.40
16	26	3.846	6.154	47.4	2.38
17	27	3.704	6.296	47.6	2.36
18	28	3.571	6.429	47.8	2.34
19	29	3.448	6.552	48.0	2.32
20	30	3.333	6.667	48.2	2.30

^{*a*} Standard uncertainties in temperature *u* are: $u(T) = \pm 0.01$ K.

Table V.4.Values of Surface Tension (γ) and Conductance (κ) data the break point with corresponding concentration of α and β -CD at 298.15K.

ТТР						
α-CI)	β-CD				
Surface Tension	γ mNm ⁻¹	Surface	Tension	γ mNm ⁻¹		
Concentration(mM) 45.57		Concentr	ation(mM)	45.84		
5.30		5.24				

Conductivity	к mSm ⁻¹	Conductivity	к mSm ⁻¹
Concentration(mM)	2.59	Concentration(mM)	2.56
4.97		4.95	

Table V.5. Experimental values of density (ρ), viscosity (η) and refractive index (n_D) of different mass fractions of aqueous α and β -cyclodextrin mixtures at 298.15 K^{*a*}

Aqueous solvent	0×10-3	п				
mixture	/kg m ⁻³	/mP s	$n_{ m D}$			
	aq. α-CD					
<i>w</i> ₁ = 0.001	0.99735	1.29	1.3329			
<i>w</i> ₁ = 0.003	0.99802	1.30	1.3332			
$w_1 = 0.005$	0.99868	1.31	1.3335			
	aq. β-CD					
$w_2 = 0.001$	0.99755	1.30	1.3328			
<i>w</i> ₂ = 0.003	0.99819	1.31	1.3331			
$w_2 = 0.005$	0.99895	1.32	1.3334			
^{<i>a</i>} Standard uncertainties <i>u</i> are: $u(\rho) = 5 \times 10^{-5}$ g cm ⁻³ , $u(\eta) = 0.003$ mP s, $u(n_D) = 0.0002$, and $u(T) = \pm 0.01$ K.						

Table V.6. Experimental values of density (ρ), viscosity (η) and refractive
index (<i>n</i> D) of selected ionic liquid in different mass fractions of aqueous α
and $meta$ -cyclodextrin mixtures at 298.15 K a

molality /mol kg ^{.1}	ρ×10 ⁻³ /kg m ⁻³	η /mP s	n _D	molality /mol kg ^{.1}	ρ×10 ⁻³ /kg m ⁻³	η /mP s	n _D	
ТТР								
	$W_1 = ($).001 ^b				$w_2 = 0.001^b$		
0.010073	0.99791	1.31	1.3335	0.010073	0.99795	1.33	1.3341	
0.025352	0.99911	1.33	1.3336	0.025361	0.99876	1.35	1.3342	
0.040821	1.00066	1.34	1.3338	0.040859	0.99974	1.37	1.3343	
0.056485	1.00228	1.36	1.3339	0.056567	1.00086	1.39	1.3344	
0.072328	1.00416	1.37	1.3340	0.072482	1.00211	1.41	1.3345	
0.088371	1.00599	1.38	1.3342	0.088605	1.00345	1.43	1.3347	
	$W_1 =$	0.003^{b}				$w_2 = 0.003$	b	
0.010068	0.99841	1.33	1.3346	0.010066	0.99859	1.34	1.3349	
0.025349	0.99921	1.35	1.3347	0.025340	0.99955	1.37	1.3350	
0.040841	1.00017	1.37	1.3348	0.040816	1.00077	1.39	1.3352	
0.056546	1.00122	1.39	1.3349	0.056491	1.00216	1.41	1.3354	
0.072462	1.00237	1.40	1.3350	0.072362	1.00371	1.43	1.3356	
0.088593	1.00358	1.42	1.3351	0.088440	1.00524	1.45	1.3359	
	147-	- 0 005 <i>b</i>				$w_{0} = 0.00$)5 <i>b</i>	
0.010062	0 99902	1 341	1 3353	0.010060	0 99925	1 35	1 3357	
0.025335	0.99975	1.365	1.3354	0.025328	1.00003	1.38	1.3358	
0.040821	1.00065	1.384	1.3355	0.040807	1.00099	1.40	1.3359	
0.056526	1.00156	1.403	1.3356	0.056492	1.00215	1.43	1.3362	
0.072434	1.00275	1.421	1.3358	0.072387	1.00337	1.44	1.3364	
0.088559	1.00395	1.440	1.3360	0.088500	1.00459	1.46	1.3367	

Table V.7. Apparent molar volume (ϕ_V), (η_r -1)/ \sqrt{m} and molar refraction
($R_{\rm M}$) of selected ionic liquid TTP in different mass fractions of aqueous $lpha$
and β -cyclodextrin mixtures at 298.15 K ^a

molality /mol kg ⁻¹	$\phi_V \times 10^6$ / m ³ mol ⁻¹	(η _r - 1)/√m /kg ^{1/2} mol ^{-1/}	$R_{\rm M} \times 10^{6}$ /m ³ mol ⁻¹	molality /mol kg ⁻¹	$\phi_V \times 10^6$ / m ³ mol ⁻	(η _r - 1)/√m /kg ^{1/2} mol ^{-1,}	$R_{\rm M} \times 10^{6}$ /m ³ mol ⁻¹
ТТР							
$w_1 = 0.001^b$						$w_2 = 0.00$	1^b
0.010073	464.54	0.162	106.5855	0.010073	480.49	0.230	107.3600
0.025352	450.10	0.180	107.1893	0.025361	472.07	0.261	107.3020
0.040821	437.72	0.200	107.0897	0.040859	465.70	0.278	107.2260
0.056485	430.82	0.212	106.9820	0.056567	460.26	0.294	107.1350
0.072328	423.15	0.225	106.8381	0.072482	455.28	0.314	107.0304
0.088371	418.77	0.235	106.6671	0.088605	451.00	0.328	106.9455
		w	$v_1 = 0.003^b$			$w_2 = 0.003$	3 ^b
0.010068	481.26	0.222	107.4476	0.010066	480.18	0.251	107.5027
0.025349	472.65	0.246	107.3874	0.025340	465.75	0.293	107.4167
0.040841	466.48	0.259	107.3167	0.040816	455.63	0.310	107.3450
0.056546	462.04	0.278	107.2364	0.056491	447.94	0.331	107.2659
0.072462	458.07	0.294	107.1488	0.072362	441.25	0.346	107.1774
0.088593	454.80	0.305	107.0592	0.088440	437.16	0.359	107.1095
$w_1 = 0.005^b$						$w_2 = 0.00$	5 ^b
0.010062	485.95	0.236	107.5943	0.010060	489.82	0.249	107.6730
0.025335	477.14	0.264	107.5448	0.025328	476.61	0.286	107.6149
0.040821	470.68	0.280	107.4772	0.040807	468.80	0.315	107.5428
0.056526	467.56	0.299	107.4085	0.056492	461.61	0.338	107.5129
0.072434	461.78	0.315	107.3390	0.072387	456.65	0.349	107.4454
0.088559	457.91	0.333	107.2686	0.088500	453.43	0.367	107.4049

^{*a*} Standard uncertainties u are: u(T) = 0.01K.

 $^b\,w_1$ and w_2 are mass fractions of α and β -cyclodextrin in aqueous mixture respectively.

Table V.8. Limiting apparent molar volume (ϕ_{V^o}), experimental slope (S_V^*), viscosity A and B-coefficient and limiting molar refraction (R_{M^o}) of ionic liquid TTP in different mass fractions of aqueous α and β -cyclodextrin mixtures at 298.15 K^a

Aq. solvent	$\phi^{o}{}_{V} imes 10^{6}$	$S_V^* \times 10^6$	В	A	$R_M^O \times 10^6$				
mixture	/ m ³ mol ⁻¹	/m ³ mol ^{- 3/2} kg ^{1/2}	/kg mol ⁻¹	/kg ^{1/2} mol ^{-1/2}	/m ³ mol ⁻¹				
TTP									
$w_1 = 0.001^b$	487.4	-236.5	0.376	0.122	107.59				
$w_1 = 0.003^b$	494.2	-134.3	0.423	0.178	107.68				
$w_1 = 0.005^b$	499.7	-140.2	0.483	0.185	107.79				
TTP									
$w_2 = 0.001^b$	495.7	-149.9	0.492	0.180	107.61				
$w_2 = 0.003^b$	501.3	-221.3	0.540	0.201	107.72				
$w_2 = 0.005^b$	507.1	-186.3	0.596	0.191	107.82				

Table V.9. Frequencies at FTIR spectra of PB, α -CD, β -CD and solid inclusion complexes

	Wave Number / cm ⁻¹	Group
ТТР	3372.75	Symmetrical Stretching of – C-H from CH ₃
	2941.63	Symmetrical Stretching of - C-H from –CH ₂
	1624.43	Bending of -C-H from -CH ₂
	1454.58	Stretching of P-CH ₂ -
	1215.23	Bending of P-CH ₂ -

	1111.34	Weak Stretching of -C-C-
	989.76	Weak bending of -C-C-
α-Cyclodextrin	3412.10	stretching of O-H
	2930.79	stretching of –C-H from – CH ₂
	1406.76	bending of –C-H from – CH ₂ and bending of O-H
	1154.39	bending of C-O-C
	1030.39	stretching of C-C-O
	952.36	skeletal vibration involving α-1,4linkage
	3349.84	stretching of O-H
β-Cyclodextrin	2921.52	stretching of –C-H from – CH ₂
	1412.36	bending of –C-H from – CH ₂ and bending of O-H
	1157.57	bending of C-O-C
	1033.51	stretching of C-C-O
	938.53	skeletal vibration involving α-1,4linkage
TTP+α-CD	3378.08	Stretching of –O-H of α-CD
	2927.03	Stretching of –C-H from – CH ₂ of TTP
	2364.96	Stretching of –C-H from – CH ₂ of TTP
	1626.46	Bendingof –C-H from –CH ₂ of TTP
	1148.51	Bending of –C-O-C of α-CD
	1017.64	Stretching of –C-C-O of α- CD
TTP+β-CD	3335.76	Stretching of -0 -H of β -CD

		Stretching of –C-H from –
	2916.86	CH_2 of TTP
		Bending of –C-H from –CH ₂
	1646.96	of TTP
		Stretching of P-CH ₂ from
	1385.73	TTP
		Bending of –C-O-C- from β-
	1156.87	CD
		Weak stretching of C-C of
	1080.34	TTP
		Stretching of –C-C-O of β-
	1021.32	CD

Table V.10. Binding constants (Kb) of various ionic liquid-cyclodextrininclusion complexes

Binding constant ^b K _b ×10 ⁻³ /M ⁻¹				
Temperature ^a /K	TTP-α-CD	TTP-β-CD		
293.15	2.35	2.47		
298.15	2.14	2.27		
303.15	1.98	2.02		

^a standard uncertainties in temperature u are: u(T)=±0.01K.

 $^{\rm b}$ Mean errors in K_b=±0.01×10^-3M^-1

Figures



Figure V.1. ¹H NMR Spectra of (a) α -CD (b) TTP and (c) 1:1 molar ratio of α -CD + TTP in D₂O in 298.15 K.



Figure V.2. ¹H NMR Spectra of (a) β -CD (b) TTP and (c) 1:1 molar ratio of β -CD + TTP in D₂O in 298.15 K.



Fig V.3. variation of surface tension of aqueous TTP solution with increasing concentration of (a) α -CD (b) β -CD respectively at 298.15K.



Fig V.4. variation of conductivity of aqueous TTPsolution with increasing concentration of (a) α -CD (b) β -CD respectively at 298.15K.



Fig V.5: Plot of limiting molar volume (ϕ_v°) against mass fraction (w) of aqueous α -CD and β -CD for TTP(α -CD Blue, β -CD Brown) at 298.15 K



Fig V.6. Plot of viscosityB-coefficient against mass fraction(w) of aqueous α -CD and aqueous β -CD for TPP(blue and green respectively) at 298.15K



Fig V.7. Plot of limiting molar refraction(R_M°) for TPP in different mass fraction of aqueous α -CD and β -CD at 298.15K



Fig V.8. FTIR spectra of (a) TTP (b) α -CD and (c) TTP- α -CD inclusion complex.



Fig V.9. FTIR spectra of (a) TTP (b) β -CD and (c) TTP- β -CD inclusion complex.



Fig V.10. ESI mass spectra of TTP- α -CD inclusion complex.



Fig V.11: ESI mass spectra of TTP- β -CD inclusion complex.

Schemes



Scheme V.1: Two dimentional molecular structure of the ionic liquid Trihexyltetradecylphosphonium chloride.



Scheme V.2: Structure of (a) α -CD (b) β -CD and (c) cone structure of cyclodextrin molecule



Scheme V.3. Location of different protons in truncated conical structure of α and β -cyclodextrin



Scheme V.4. Plausible mechanism of formation of inclusion complex between TTP and CD molecule.