CHAPTER-VII

Inclusion Complexation between Tetrabutylphosphonium Methanesulfonate as Guest and α- and β-Cyclodextrin as Hosts Investigated by Physicochemical Methodology

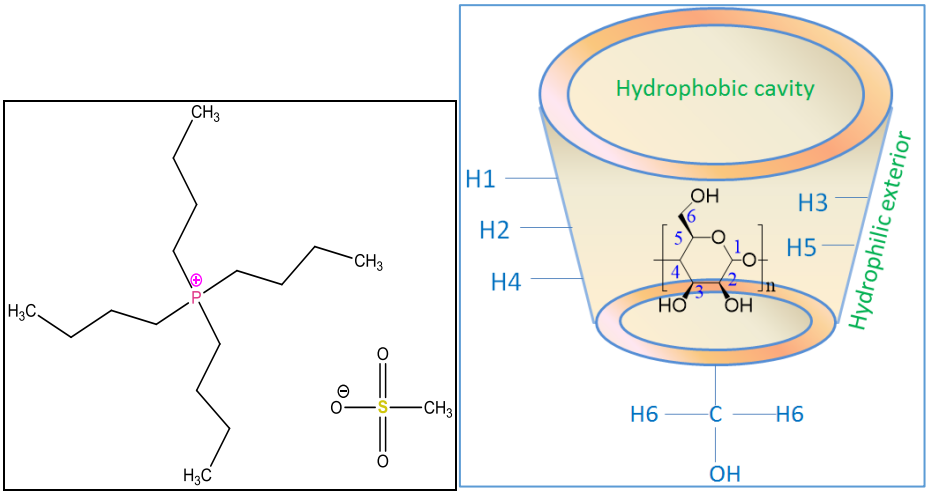
1. Introduction

Molecular recognition and self-assembly of macrocyclic compounds now days are being widely studied due to their vast range of applications in various fields such as drug delivery, nanotechnology, separation techniques [1] [2] [3]. Cyclodextrin (CD) belongs to a family of compounds made up with glucopyranose units. Six, seven and eight glucopyranose units are bound together by means of 1,4-glycosidic linkage to form cyclic oligosaccharides named as α-Cyclodextrin (α-CD), β-Cyclodextrin (β-CD) and γ-Cyclodextrin(γ-CD) respectively [4]. These CDs have unique hollow cylindrical structures which can easily encapsulate various molecules inside it to form supramolecular host–guest inclusion complexes. CDs draw enormous attention because of having ability to form inclusion complexes (ICs) in aqueous medium. More over, CDs and their complexes are commercially available, non-hazardous and water soluble, which make them suitable for numerous applications in the pharmaceutical industry, pesticides, foodstuffs, toilet articles, and textile processing. In addition CDs have applications in the field of molecular recognition and self-assembly, molecular encapsulation, selectivity, chemical stabilization and intermolecular interactions [5-9]. The hollow truncated cone shaped CDs with a hydrophobic void and a hydrophilic outer surface help them to act as better host molecules.

In aqueous medium, the apolar void of CD is occupied by two [10] water molecules which is energetically unfavourable, and therefore can be readily substituted by appropriate guest molecules having less polarity than water. Several attraction forces facilitate the encapsulation of the guest molecule into the hollow cavity of CDs during the formation of the ICs. Extensive studies have been made on the host-guest inclusion phenomenon considering CDs as host molecules. A number of organometallic compounds and their derivatives have been with cyclodextrins to investigate the probability of IC formation. In this work, we have discussed the nature of interactions between the host and guest molecules and characteristics of ICs formed.[11-17].

Ionic Solids (ISs) are important to the modern science because they possess various unusual and interesting properties such as high thermal stability, low vapour pressure and chemical stability. Moreover, they have easily tuneable properties and have marked tendency of solvation towards various organic, inorganic and complex salts, biopolymers and non-flammable materials. Thus ionic solids are accepted as environmentally benign solvents[18][19]. ISs are being widely used in chemical industries due to their green nature leading to the production of less hazardous by-products during their usage. ISs having phosphonium ion in the cationic part are being used widely because of their less toxicity compared to the ammonium ion based ionic liquids or ionic solids[20][21]. Tetrabutylphosphonium methanesulfonate (TBPMS) [Fig.1] is an ionic solid (IS) with molecular formula $C_{16}H_{36}P.CH_3SO_3$, which is taken as the guest molecule in this work. ISs have extensive applications in separation of various dyes from aqueous media and as additives in the hydro-distillation process of separating oils [22].

Here, inclusion of TBPMS inside the cavity of α-CD and *β*-CD was investigated in both the solution and solid phase. Various physicochemical studies were carried out to confirm the encapsulation of TBPMS. Stoichiometric ratios of the complexes formed were determined by means of the titrimetric method. Binding constants and thermodynamic parameters of complexation were again elucidated based upon conductivity studies. All of the above experimental results were further verified by the spectroscopic evaluation of the solid ICs.



(a) **(b)**

Fig.1: Molecular structures of (a) tetrabutylphosphonium methanesulfonate and (b) cyclodextrin molecule with interior and exterior protons (n = 6, 7 for α-CD and β-CD respectively).

2. Experimental Section

2. 1. Reagents

Tetrabutylphosphonium methanesulfonate, *α*-cyclodextrin and *β*-cyclodextrin of high purity grade were purchased from Sigma-Aldrich and used as received. Purity of Tetrabutylphosphonium methanesulfonate, *α*-cyclodextrin and *β*-cyclodextrin were ≥98.0%, ≥98.0% and ≥97.0% respectively.

2.2. Instrumentations

The surface tension experiments were studied by platinum ring detachment technique using digital tensiometer K9, KRÜSS, Germany at the experimental temperature. Accuracy in the measurement was ±0.1 mNm^{-1}. Temperature was maintained at 298.15 K using circulating water through auto-thermostated double-walled glass vessel containing the solution.

Conductivities of the experimental solutions were measured by Mettler Toledo Seven Multi conductivity meter having uncertainty of ±1.0 $\mu S\ m^{-1}$. Again the experiment was done in an auto-thermostat water bath at 298.15 K and using HPLC grade water with specific conductivity 6.0μSm^{-1}. The cell was calibrated using a 0.01M aqueous KCl solution.

FT-IR spectra were recorded by Perkin Elmer FT-IR spectrometer using KBr disk method. KBr disks were prepared in 1:100 ratios of sample and KBr. FT-IR studies were performed in the scanning range of 4000−400 cm^{-1} at room temperature.

The Mass Spectroscopic analyses were done using JEOL GC MATE II quadruple double focusing mass analyzer instrument by electron impact ionization.

^{1}H-NMR spectra were recorded in D_2O at 400 MHz using Bruker ADVANCE 400 MHz instrument at 298 K. Signals were recorded in ppm using residual protonated solvent signals as internal standard at 4.79 ppm). Data were reported as chemical shift.

2.3 Preparation of TBPMS-α-CD and TBPMS -β-CD inclusion complexes

The two inclusion complexes of the ionic solid TBPMS with both CD molecules (TBPMS + α-CD, TBPMS + β-CD) were prepared in 1:1 molar ratio. 1.0 mmol of α-CD was dissolved in 30 mL of water and 1.0 mmol of TBPMS was dissolved in 15mL of ethanol.

Both the solutions were separately stirred for 4 hours. After the completion of stirring, the ethanolic solution of the TBPMS was added drop wise to the aqueous α-CD solution. The mixture was again stirred for 72 hours at about 60°C followed by the filtration and then allowed to cool upto 10 °C. It was kept for 12 hours followed by the filtration of the suspension. The white crystalline powder obtained was washed with ethanol and dried in air. IC of β-CD was prepared following the same procedure.

3. Result and discussion

3.1. 1H-NMR and 2D-ROESY:

The Structure of the CD molecule is suitable for the host guest inclusion complextation and the presence of the –C-H inside the CD cavity is significant for the 1H-NMR and 2D-ROESY experiments. Fig.1 clearly depicts the presence of the H3 and H5 protons inside the cavity while H1, H2 and H4 are present on the outer surface[23]. Now, if guest molecule enters into the hydrophobic cavity of the host molecule, the protons inside the cavity of the CD may experience interactions with the guest leading to the change of the chemical environment and consequently the Shift of the peaks in 1H-NMR signal.

The spectra clearly show (Table1, TableS1, Fig.2, Fig.S1) that there are changes of the chemical shifts of H3 and H5 protons in the inclusion complexes compared to the pure one. Also, the protons of guest molecules were found to appear at the downfield position compared to the pure one. Thus, this leads to the conclusion that there are some mutual shielding through space among the protons of host and the guest molecules and which is only possible if guest enters inside the host [24][25][26][27][28]. The diamagnetic shielding of the protons of CD leads to the up-field shift of the signals of the same[25]. The change of the chemical shift of H6 protons was not observed. Moreover, the up-field shift of the H3 proton (0.23 ppm) has greater value compared to the H5 proton (0.10 ppm). The difference in values signifies the guest molecule enters through the wider rim instead of the narrower rim of the CD molecule [29]. Again, experiment justified the fact of more effective inclusion of TBPMS with α-CD compared to the β-CD as shift of the H3 proton is comparatively higher for TBPMS + α-CD complex than TBPMS + β-CD complex.

The special proximity (0.5 nm range) of the atoms of the host and the guest molecules can create Nuclear Overhauser Effect (NOE) cross-correlation in NOE spectroscopy (NOESY) or rotating-frame NOE spectroscopy (ROESY)[30-33]. Due to the

structural speciality of the CD molecules, discussed above, the ROSEY experiment can produce a strong evidence of encapsulation [34]. Fig.3 shows NOE cross peaks of H3 and H5 of CD with the protons of TBPMS. The 1:1 complexes of TBPMS with both the CDs give cross peaks due to the proximity of H-4' proton of TBPMS and H5 proton of CD and also H-1' proton of TBPMS and H3 proton of CD. Thus, these signals are the indications of the interactions of the atoms of host and guest and which is only possible if there is encapsulation of host inside the guest [35]. The guest TBPMS enters through the wider rim of CD which is evident from the absence of the signal due to H6 proton of CD and protons of guest.

Table1. Change in chemical shifts (ppm) of the H3 and H5 protons of cyclodextrin molecules in two different host-guest complexes in D2O at 298.15 K[a].

Protons of CD	TBPMS+α-CD	TBPMS+β-CD
H3	0.23	0.21
H5	0.10	0.10

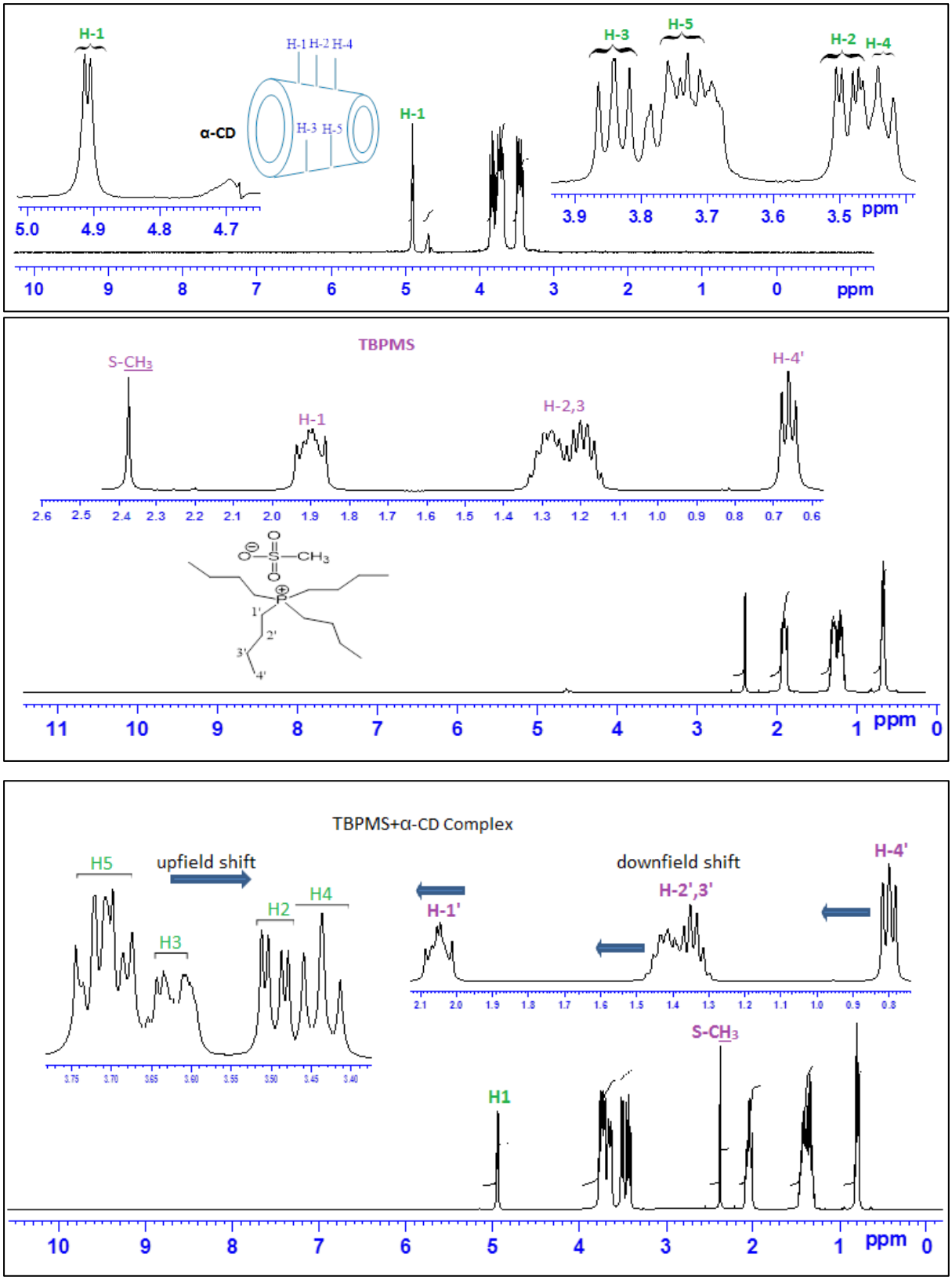
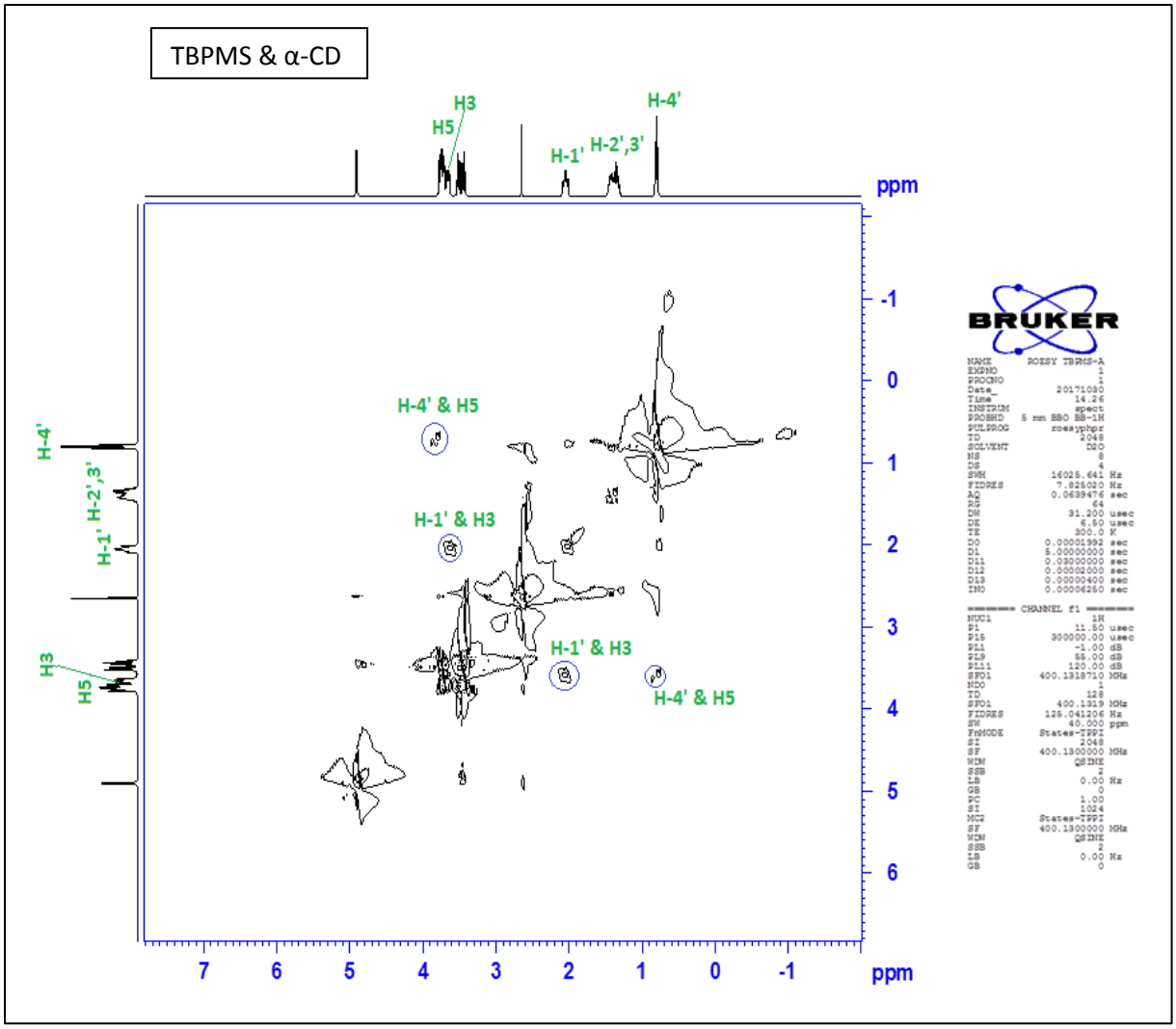


Fig.2. ^{1}H-NMR spectra of (**a**) pure TBPMS (b) pure α–CD and (c) α–CD & TBPMS complex


TBPMS & α-CD
H3
H5
H-1'
H-2',3'
H-4'
ppm
H-4' & H5
H-1' & H3
H-1' & H3
H-4' & H5
H-4'
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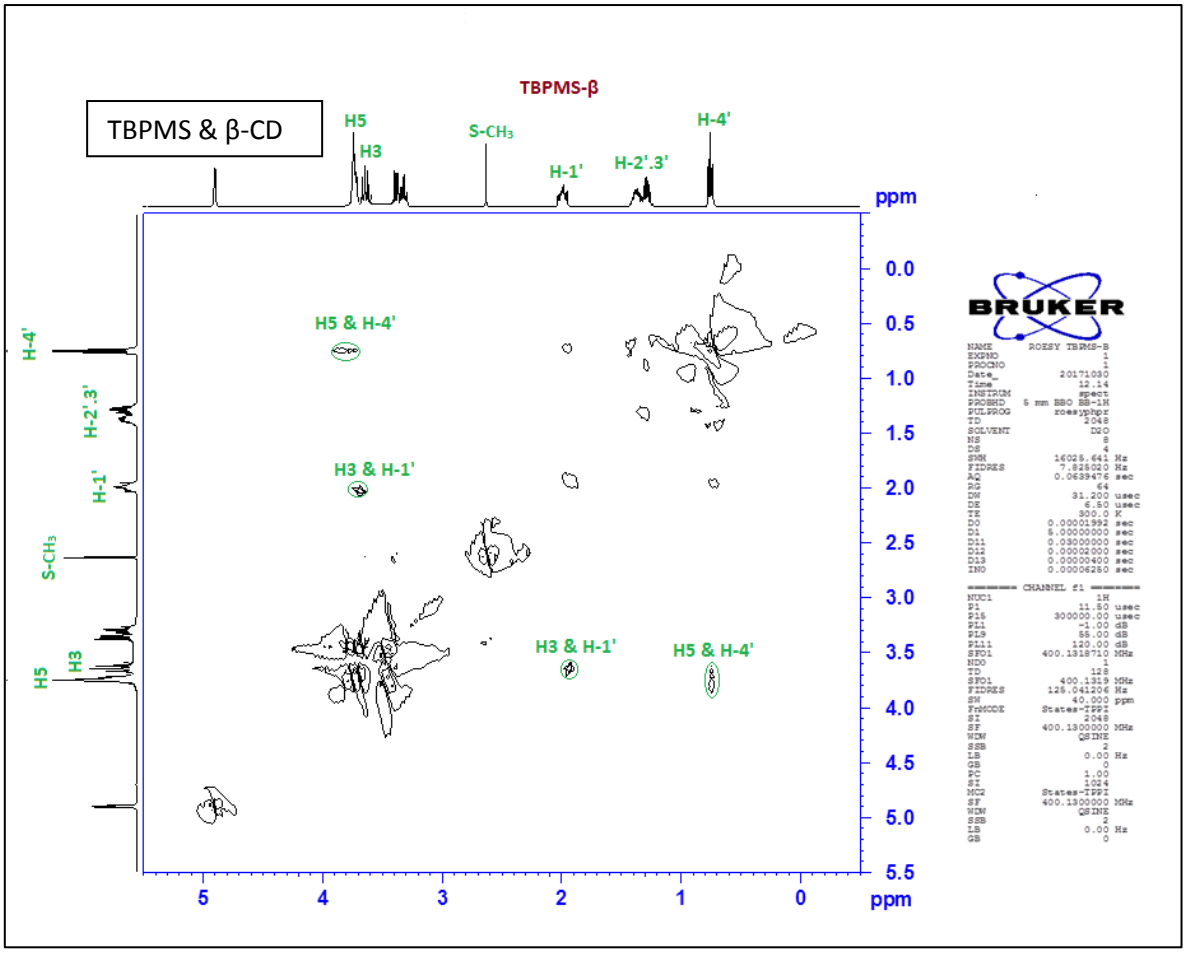


Fig.3. 2D ROESY spectra of solid inclusion complex of 1:1 molar ratio of TBPMS+ α -CD complex and TBPMS + β-CD complex in D_2O (correlation signals are marked by green borders).

3.1. Surface tension study illustrates the inclusion and its stoichiometric ratio

The surface tension study helps us to interpret the formation and stoichiometry of the inclusion complexes. The addition of CD to water does not show any change of surface tension (γ), therefore CD might be classified as surface inactive compound [19][11]. The ionic solid TBPMS contains four long hydrocarbon chains and acts as surface active agent. The γ value of TBPMS is much lower than pure water. Here, the γ values of the solutions of TBPMS with continuous addition of α-CD and β-CD were recorded at 298.15 K. The γ values were found to be increased with the increasing concentration of both CD molecules. This fact can be explained in terms of IC formation[36][16]. The availability of the surface active IS in the solution decreases due to the insertion of the hydrocarbon part of the IS into the hydrophobic cavity of the CD molecule and hence there is the

increment of the surface tension value. The plot of surface tension against concentration shows single distinguishable break in each case of α-CD and β-CD (Fig.4), suggests the formation of IC. The concentrations of TBPMS and the CD molecules at the break point (Table2) is approximately 1:1 (near 5mM concentration), which further confirms the stoichiometry of the two ICs as 1:1. The number of break point more than one is the indication of the inclusion complexation of the complex stoichiometry such as 1:2, 2:1, 2:2 etc. The surface tension at the break point is slightly higher for α-CD indicating that it acts as better host compared to β-CD.

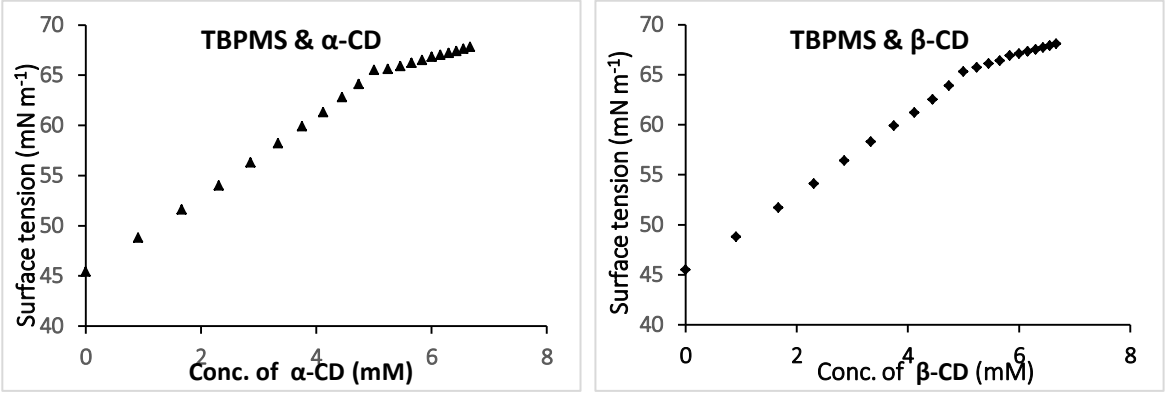


Fig.4. Variation of surface tension of aqueous TBPMS with increasing concentration of aqueous α-CD and β-CD solution respectively at 298.15 K.

Table2. Values of surface tension (γ) at the break point with corresponding concentrations of TBPMS and CD at 298.15 K[a]

	Conc. of CD/mM	γa/mN.m-1
α-CD	5.08	65.3
β-CD	5.23	65.7

[a] Standard uncertainties: temperature:(T) = ±0.01 K, surface tension: ±0.1 mN·m^{-1}

3.2. Conductivity study demonstrates inclusion process and the stoichiometry

The ionic solid TBPMS showed considerable conductivity in its aqueous solution due to the charged structure. The continuous addition of the aqueous solution of CD in the aqueous solution of TBPMS at 298.15K led to regular decrease of the conductivity and at a certain concentration of the CD the regularity broke and then became almost parallel to the abscissa. Such decreasing trend of the conductivity may be due to the complexation with the CD molecule. Here, the encapsulation of the hydrocarbon chain of TBPMS molecule inside the hydrophobic cavity of CD decreases the availability of the ionic moieties in the solution which leads to the decrease of the conductivity value[37]. Further, at a certain concentration all the guest molecules get encapsulated leading to the break of the regular decrease of the conductivity values. A dynamic equilibrium is maintained between the ionic solid and CD molecules.

$$\text{Ionic solid} + \text{Cyclodextrin} \leftrightharpoons \text{Inclusion Complex}$$

At the break point all the guest molecules are encapsulated by the host molecules, after that the concentration of CD increases gradually exceeding the concentration of TBPMS. Thus the equilibrium shifts towards right hand side.

As CD molecules showed negligible conductivity, addition of the CD solution after the break point, led to hardly any change of the conductivity. The values of *k* at the corresponding concentrations of the host molecules have been listed in the Table 3. The break point at nearly 5mM concentration of CD indicates the formation of the IC of 1:1 stoichiometry [38,39, 40].

Table3: Values of conductivity (κ) at the break point with corresponding concentrations of TBPMS and CD at 298.15 K[a]

Temperature (K)	Concentration of α-CD (mM)	κ^a/mS.cm^{-1}	Concentration of β-CD (mM)	κ^a/mS.cm^{-1}
293.15	4.98	0.29	5.22	0.28
303.15	5.08	0.48	5.29	0.47
313.15	5.08	0.79	5.32	0.77

[a] Standard uncertainties in temperature:± 0.01K, conductivity: ±0.001 mS·m^{-1}

3. 3 FT-IR Spectra of solid inclusion complexes

The inclusion of TBPMS in the hydrophobic cavity of guest has been established from FT-IR spectroscopy [41]. Some of the bands resulted due to the inserted part of TBPMS have been found shifted and others have been found absent or their intensities are changed. Fig.5, Fig.S3 and TableS4 represent the FT-IR spectra of TBPMS, α-CD, β-CD and their inclusion complexes. The FT-IR spectrum of the ionic solid are categorized by key absorption bands at 2958.81 cm^{-1} (symmetrical stretching of –C–H from CH3), 2926.10 cm^{-1} (symmetrical stretching of –C–H from –CH2), 750.32 cm^{-1} (stretching of P–CH2–) etc. The characteristic peak due to –O-H of α-CD and β-CD has been observed at 3410.27 cm^{-1} and 3407.16 cm^{-1} respectively. The –O–H frequency in the ICs was found shifted to lower region i.e.; 3389.23 and 3382.36 cm^{-1} for α-CD and β-CD respectively. This may be due to the interaction of the phosphonium ion with the lone pair of the oxygen of –O–H groups of both the CDs. Moreover, the peaks due to –P–CH2, –CH3, –CH2– of the hydrocarbon chains of the ionic solid have been found shifted in case of both the IC's.

It may be the restricted vibration of the guest molecule inside the CD which shifts the IR-bands in the complex. Some peaks are absent but the complexes did not show any additional peak. This fact indicates the presence of only non-covalent interactions [42].

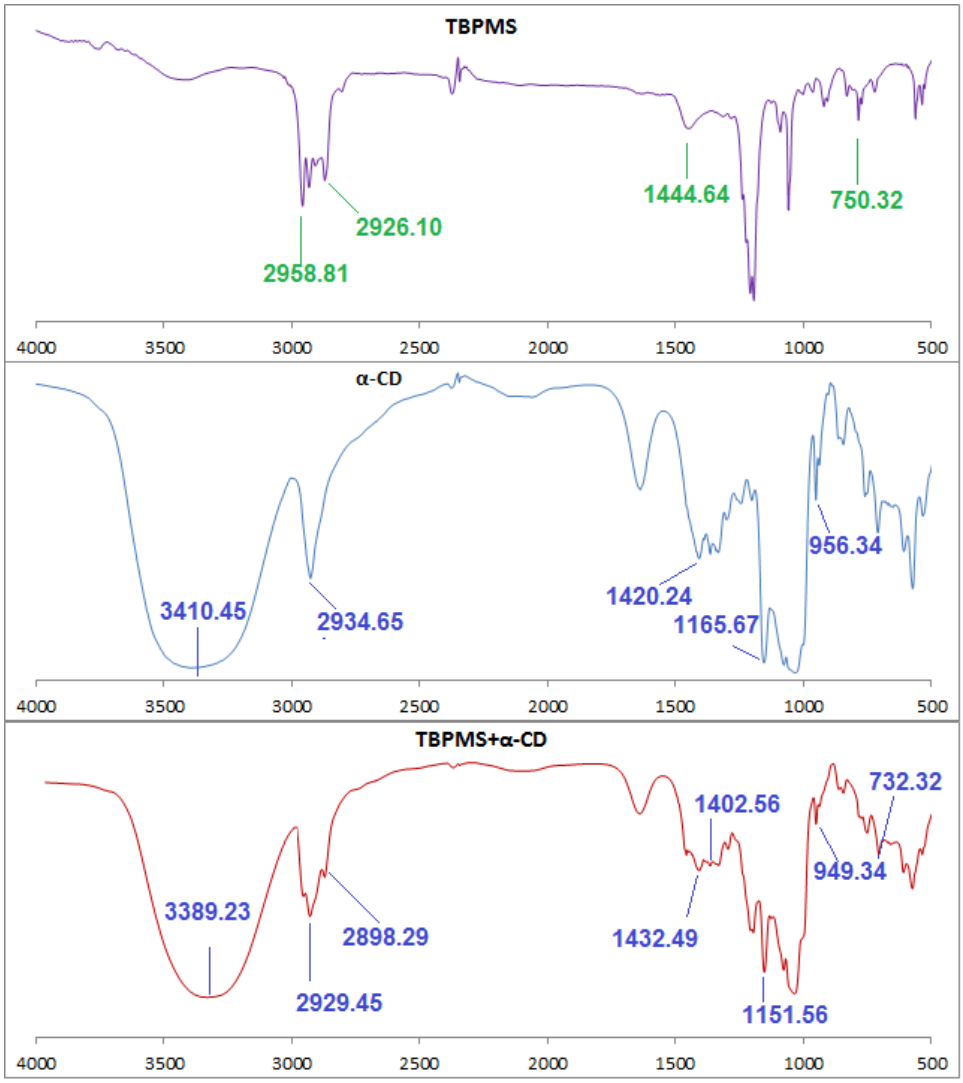


Fig.5: FTIR spectra of free α-CD, TBPMS and their 1:1 inclusion complex (TBPMS:α-CD).

3.4 ESI-mass spectrometric analysis of inclusion complexes

The inclusion complex contains both the host and the guest molecules and hence the mass of that system is equal to the combination of the molecular masses of the two. Thus, from the molecular peak the formation of the IC as well as the stoichiometry can be interpreted. The molecular ion peaks have been obtained for TBPMS and CD complexes (Table4, Fig.S4). The IC in the solid form TBPMS+α-CD, TBPMS+β-CD gave the molecular ion peaks at 1328.39 and 1490.48 respectively, which are the proton adduct of TBPMS+α-CD IC and TBPMS+β-CD IC. Beyond these peaks no other significant peak has been observed. This confirms the formation of the IC and only one guest molecule is occupied by the host molecule i.e., 1:1 IC has been formed [43][4].

Table4. The observed peaks at different m/z with corresponding ions for the solid inclusion complexes

TBPMS:α-CD inclusion complex		TBPMS:β-CD inclusion complex	
m/z	Ion	m/z	Ion
355.72	$[TBPMS+H]^+$	355.68	$[TBPMS+H]^+$
973.93	$[\alpha\text{-}CD+H]^+$	1135.86	$[\beta\text{-}CD+H]^+$
1328.39	$[TBPMS+\alpha\text{-}CD+H]^+$	1490.48	$[TBPMS+\beta\text{-}CD+H]^+$

3.8. Binding constants

The formation IC of 1:1 stoichiometry of TBPMS with α-CD and β-CD can be represented as follows:

$$TBPMS + CD \xleftrightarrow{K_f} IC \quad (1)$$

The corresponding equilibrium constant, K_f is given by

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

Where, [IC], [TBPMS] and [CD] denote the molar concentrations of the ICs, ionic solid and CDs at equilibrium respectively and *f* denote the activity coefficients of the species indicated. The activity coefficient of uncharged macrocycle, f(CD), has been assumed to be unity [39], as the system was dilute. From Debye-Hückel limiting law [40], f(TBPMS) ~ f(IC), Equation (2) becomes

$$K_f = \frac{[IC]}{[TBPMS][CD]} \quad (3)$$

In relations of the molar conductance, Λ, the formation constant of the complex is given as [37,39].

$$K_f = \frac{[IC]}{[TMPMS][CD]} = \frac{(\Lambda_{TBPMS} - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{IC})[CD]} \quad (4)$$

$$\text{Where} \quad [CD] = CD_{ad} - \frac{TBPMS_{ad}\,(\Lambda_{TBPMS} - \Lambda_{obs})}{(\Lambda_{TBPMS} - \Lambda_{IC})} \quad (5)$$

Here, Λ_{TBPMS} is the molar conductance of the ionic solid TBPMS before addition of CD, Λ_{IC} is the molar conductance of the inclusion complex, Λ_{obs} the molar conductance of the mixture, CD_{ad} the analytical concentration of CD added and C_{TBPMS} is the analytical concentration of the IS. The formation constant of the complex, K_f, and the molar

conductance of the inclusion complex, Λ_{IC}, were determined by using Equations (4) and (5). The K_f values (Table 4.) reveal that the TBPMS has higher binding efficiency with α-CD than β-CD. This can be explained in terms of the fitting capability of the guest inside the host. The hydrophobic interaction plays the key role to bind the IS more effectively with the α-CD than β-CD, which leads to the formation of more stable IC.

From the binding constant values the change in the enthalpy (ΔH^0) and entropy (ΔS^0) can be obtained by plotting $\log K_f$ values against 1/T according to Van't Hoff equation (6) (Fig.6) the values of ΔH^0 and ΔS^0 have been determined and tabulated in the table5. From the change of enthalpy and entropy values, the change in the Gibb's free energy has also been calculated for both the systems.

$$2.303 \log K_f = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (6)$$

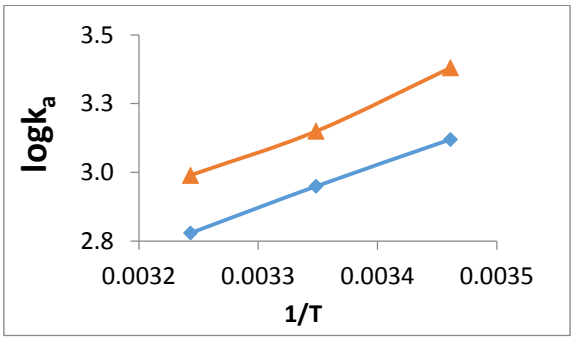


Fig.6. Linear relationships of $\log K_f$ vs. 1/T for the interaction of TBPMS+α-CD (▲), TBPMS+β-CD (♦)

Table5. Association constants (K_a), Gibb's free energy, enthalpy and entropy of various ionic liquid-cyclodextrin systems.

IL & CD systems	$\log K_f$ (M^{-1})			ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1})
	293.15 K	303.15 K	313.15K			
TBPMS & α-CD	3.74	3.37	3.06	-49.96	-34.30	-52.52
TBPMS & β-CD	3.81	3.47	3.14	-42.39	-29.84	-42.08

[a]Standard uncertainties in temperature: ±0.01 K.

Table5 shows that the values of change in entropy are negative, which is due to the association of the host and guest molecules. Again ΔG^0 for both the cases were found to be negative, which is a clear indication of the feasible formation of the IC. Again,(the higher value of) ΔG^0 for TBPMS & α-CD system is attributed to the higher feasibility of the formation of the TBPMS & α-CD IC compared to the other.

3. 9 Structural influence of cyclodextrin in inclusion complex formation

The inclusion complex formation between host and the guest is largely dependent on the structural combination of the host and the guest molecule. Here, it is clear that guest molecule will only enter inside the host molecule in the solution if the non-covalent interactions between the host and guest molecules overcome other interactions which prevent formation of IC. β-CD has the large cavity diameter (6.0–6.5 Å) than α-CD (4.7–5.3Å) and hence it can provide more space to the guest compared to the α-CD. Again hydrophobic interaction between two species increases as the proximity increases; possibly due to higher surface proximity the interaction is a bit higher in α-CD. In the process of inclusion complexation no covalent bond formation or breaking process takes place, only the hydrophobic alkyl chains of TBPMS are encapsulated in the hydrophobic cavity of CD molecules. One important factor is that the hydrophobic cavity of Cyclodextrin is engaged by water molecules which is unfavourable, and hence TBPMS can easily replace the water molecules by its apolar part. The exclusion of the water molecules increases the entropy of the system to some extent which helps again the formation of the ICs. The better combination between host and guest fits the guest inside the host by lowering the ring strain of the CD and consequently the energy is lowered. Thus the complex gains stability.

After encapsulation of one guest molecule, the host becomes sterically blocked which prevents another molecule to enter inside the host. This phenomenon explains the formation of 1:1 complex. Another stabilising effect is the interaction between the phosphonium ion of the guest and the lone pair of the oxygen of the –OH group present at the rim of CD (Fig.7).

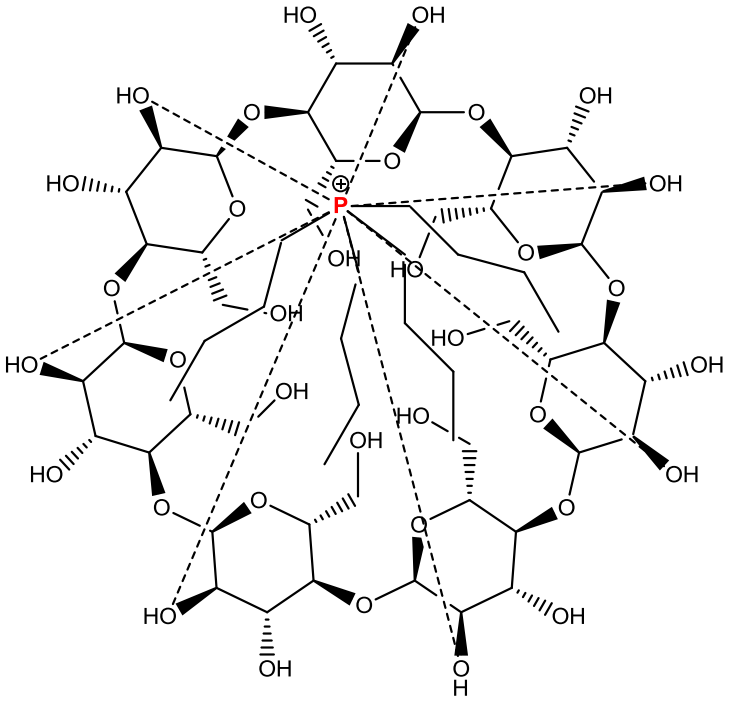


Fig.7 Schematic representation of plausible interactions taking place in the inclusion complex.

4. Conclusion

The attempt of encapsulation of TBPMS inside CDs in aqueous medium was successful. Solidification of the IC was again found successful, which was confirmed by analysing the result obtained from 1H-NMR, 2D ROESY, FT-IR and ESI-MS. In aqueous media the formation of the ICs was confirmed by means of Surface tension and conductivity study. Again 1:1 stoichiometry of the IC in the aqueous medium was confirmed by surface tension and conductivity study and in solid state by EI-MS analysis. The binding constant of the ICs was calculated and the thermodynamic parameters obtained by calculation confirmed the higher stability of the ICs formed. A schematic representation of the inclusion was depicted on the basis of all the experimental observations explained above. These types of ICs being environmentally non-hazardous are of great interest now days in various industrial processes

Supplementary data

Table:

TableS1. 1H-NMR spectra of TBPMS, α-CD, β-CD and TBPMS+α-CD, TBPMS+β-CD complexes.

α-Cyclodextrin (400 MHz, Solvated in D2O) δ /ppm	β-Cyclodextrin (400 MHz, Solvated in D2O) δ /ppm
3.41-3.46 (6H, t, J= 9.00 Hz), 3.48-3.52 (6H, dd, J= 10.00, 3.00 Hz), 3.73-3.89 (18H, m), 3.81-3.87(6H,t, J = 9 Hz), 4.89-4.94 (6H, d, J = 3 Hz)	3.40-3.46 (6H, t, J = 9.2 Hz), 3.48-3.52 (6H, dd, J =9.6, 3.2 Hz), 3.72-3.77 (18H, m), 3.79-3.86 (6H,t,J=9.2 Hz), 4.89-4.94 (6H, d, J = 3.6 Hz).
TBPMS	
0.49-0.53 (12H, t, J=7.2Hz); 1.01-1.16 (16H, m), 1.71-1.79 (8H, m); 2.39 (3H,s)	
TBPMS +α-CD[a]	TBPMS +β-CD[a]
3.41-3.44 (6H, t, J= 9.00 Hz), 3.45-3.51 (6H, dd, J= 10.00, 3.00 Hz), 3.62-3.67 (18H, m), 3.55-3.61(6H,t, J = 9 Hz), 4.89-4.94 (6H, d, J = 3 Hz); 0.92(3H, s); 0.76-0.85 (12H, t, J=7.2Hz); 1.28-1.48 (16H, m), 1.98-2.11 (8H, m); 2.39 (3H,s)	3.41-3.47 (6H, t, J = 9.2 Hz), 3.48-3.53 (6H, dd, J =9.6, 3.2 Hz), 3.53-3.59 (18H, m), 3.62-3.66 (6H, t, J=9.2 Hz), 5.00-5.01 (6H, d, J = 3.6 Hz). 0.73-0.78 (12H, t, J=7.2Hz); 1.24-1.44 (16H, m), 1.92-2.06 (8H, m); 2.39 (3H,s)

[a]Standard uncertainties in temperature: ± 0.01K, Pressure: ± 10kPa

TableS2. Surface Tension (γ) values of aqueous TBPMS with α-CD and β-CD at 298.15 K[a]

α-CD added (mL)	Total volm (mL)	conc of TBPMS (mM)	conc.of CD (mM)	γ of TBPMS+α-CD ($mN.m^{-1}$)	γ of TBPMS+β-CD ($mN.m^{-1}$)
0	10	10.000	0.000	45.5	45.5
1	11	9.091	0.909	48.4	48.8
2	12	8.333	1.667	51.3	51.7
3	13	7.692	2.308	53.6	54.1

4	14	7.143	2.857	55.9	56.4
5	15	6.667	3.333	57.7	58.3
6	16	6.250	3.750	59.5	59.9
7	17	5.882	4.118	60.8	61.2
8	18	5.556	4.444	62.1	62.5
9	19	5.263	4.737	63.5	63.9
10	20	5.000	5.000	65	65.3
11	21	4.762	5.238	65.4	65.7
12	22	4.545	5.455	65.9	66.1
13	23	4.348	5.652	66.2	66.4
14	24	4.167	5.833	66.5	66.9
15	25	4.000	6.000	66.8	67.1
16	26	3.846	6.154	67	67.3
17	27	3.704	6.296	67.2	67.5
18	28	3.571	6.429	67.4	67.7
19	29	3.448	6.552	67.6	67.9
20	30	3.333	6.667	67.8	68.1

[a]Standard uncertainties in temperature: ± 0.01K,
Pressure: ± 10kPa, Surface tension: ±0.01 mNm^{-1}

Table S3. Data for the conductivity study of aqueous TBPMS+α-CD and TBPMS+β-CD system (concentration of stock solution of TBPMS = 10mM, concentration of stock solution of CD = 10mM) at 293.15K[a], 303.15K[a], 313.15K[a]

conc of TBPMS (mM)	conc of CD (mM)	293.15 K		303.15 K		313.15 K	
		α-CD & TBPMS Complex	β-CD & TBPMS Complex	α-CD & TBPMS Complex	β-CD & TBPMS Complex	α-CD & TBPMS Complex	β-CD & TBPMS Complex
10.000	0.000	1.10	1.10	1.30	1.30	1.60	1.60
9.091	0.909	0.95	0.90	1.13	1.15	1.46	1.43
8.333	1.667	0.82	0.80	1.02	1.03	1.33	1.32
7.692	2.308	0.72	0.71	0.92	0.92	1.23	1.22
7.143	2.857	0.62	0.64	0.85	0.83	1.14	1.15

6.667	3.333	0.55	0.57	0.77	0.76	1.07	1.07
6.250	3.750	0.49	0.51	0.71	0.70	1.00	1.01
5.882	4.118	0.42	0.45	0.66	0.64	0.94	0.96
5.556	4.444	0.37	0.41	0.61	0.58	0.88	0.91
5.263	4.737	0.33	0.35	0.55	0.54	0.84	0.85
5.000	5.000	0.30	0.30	0.52	0.51	0.80	0.81
4.762	5.238	0.28	0.28	0.48	0.48	0.79	0.78
4.545	5.455	0.27	0.27	0.46	0.47	0.77	0.76
4.348	5.652	0.27	0.26	0.45	0.47	0.76	0.75
4.167	5.833	0.26	0.25	0.45	0.46	0.75	0.74
4.000	6.000	0.25	0.24	0.44	0.45	0.75	0.73
3.846	6.154	0.25	0.23	0.43	0.45	0.74	0.73
3.704	6.296	0.24	0.23	0.42	0.44	0.74	0.72
3.571	6.429	0.24	0.22	0.42	0.44	0.73	0.72
3.448	6.552	0.23	0.22	0.41	0.43	0.73	0.71
3.333	6.667	0.23	0.22	0.41	0.43	0.73	0.71

[α]Standard uncertainties in temperature: ± 0.01K
conductivity: ± 0.02 mS $m^{-1.}$ Pressure: ± 10kPa

TableS4. Data obtained from FT-IR spectroscopic study of α-CD, β-CD, TBPMS and the complexes of α-CD & TBPMS, β-CD & TBPMS.

TBPMS			
Group	**Wavenumber (cm^{-1})**	**Group**	**Wavenumber (cm^{-1})**
stretching of –C-H from $–CH_2$	2926.10	bending of –C-H from $–CH_2$	1444.64
stretching of –C-H from $–CH_3$	2958.81	stretching of P-C	750.32

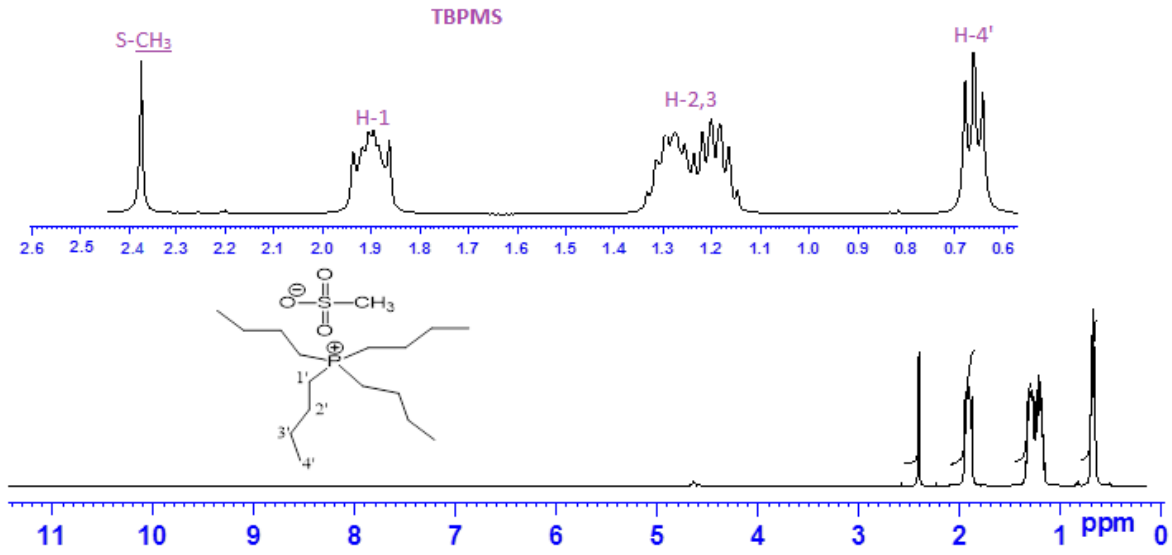
α-Cyclodextrin		**β-Cyclodextrin**	
Wavenumber	**Group**	**Wavenumber**	**Group**

(cm^{-1})		(cm^{-1})	
3410.27	stretching of O-H	3407.16	stretching of O-H
2932.10	stretching of –C-H from $–CH_2$	2940.56	stretching of –C-H from $–CH_2$
1420.16	bending of –C-H from $–CH_2$ and bending of O-H	1403.72	bending of –C-H from $–CH_2$ and bending of O-H
1160.61	bending of C-O-C	1160.37	bending of C-O-C
954.12	vibration involving α-1,4 linkage	954.13	skeletal vibration involving α-1,4 linkage

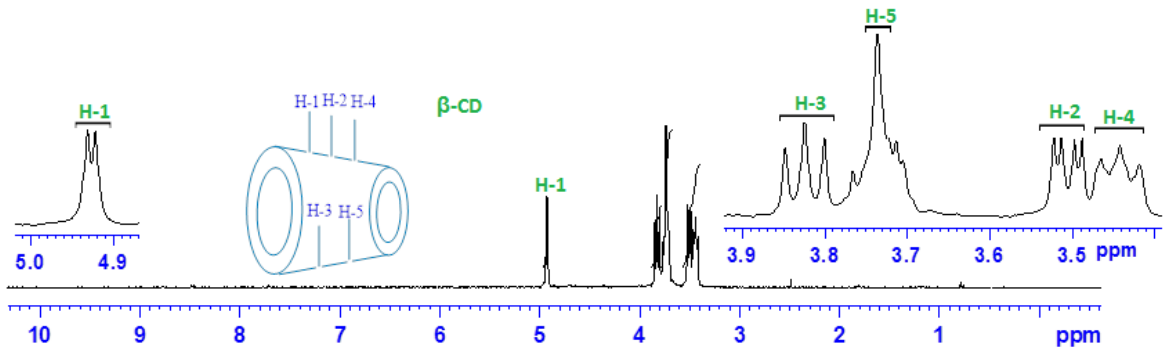
TBPMS-α-CD inclusion complex		**TBPMS-β-CD inclusion complex**	
Group	**wave number/ cm^{-1}**	**Group**	**wave number/ cm^{-1}**
stretching of O-H of α-CD	3389.23	stretching of O-H of β-CD	3382.36
stretching of –C-H from $–CH_2$ of α-CD	2929.45	stretching of –C-H from $–CH_2$ of β-CD	2929.32
bending of –C-H from $–CH_2$ and bending of O-H of α-CD	1402.56	bending of–C-H from $–CH_2$ and bending of O-H of β-CD	1392.16
bending of C-O-C of α-CD	1151.56	bending of C-O-C β-CD	1154.77
skeletal vibration involving α-1,4 linkage	949.34	skeletal vibration involving β-1,4 linkage	943.52
stretching of –C-H from $–CH_2$	2888.29	stretching of –C-H from $–CH_2$	2882.32
stretching of –C-H from $–CH_3$	2929.45	stretching of –C-H from $–CH_3$	2929.17

bending of –C-H from $–CH_2$	1432.49	bending of –C-H from $–CH_2$	1431.48
stretching of P-C	732.32	stretching of P-C	739.26

Figures:



(a)



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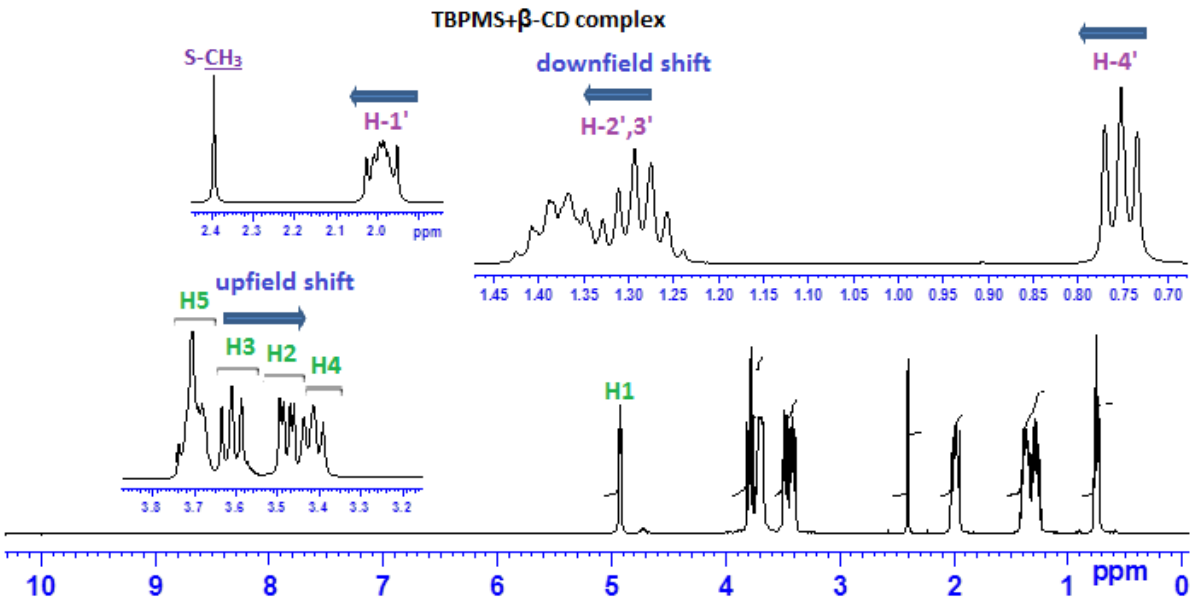
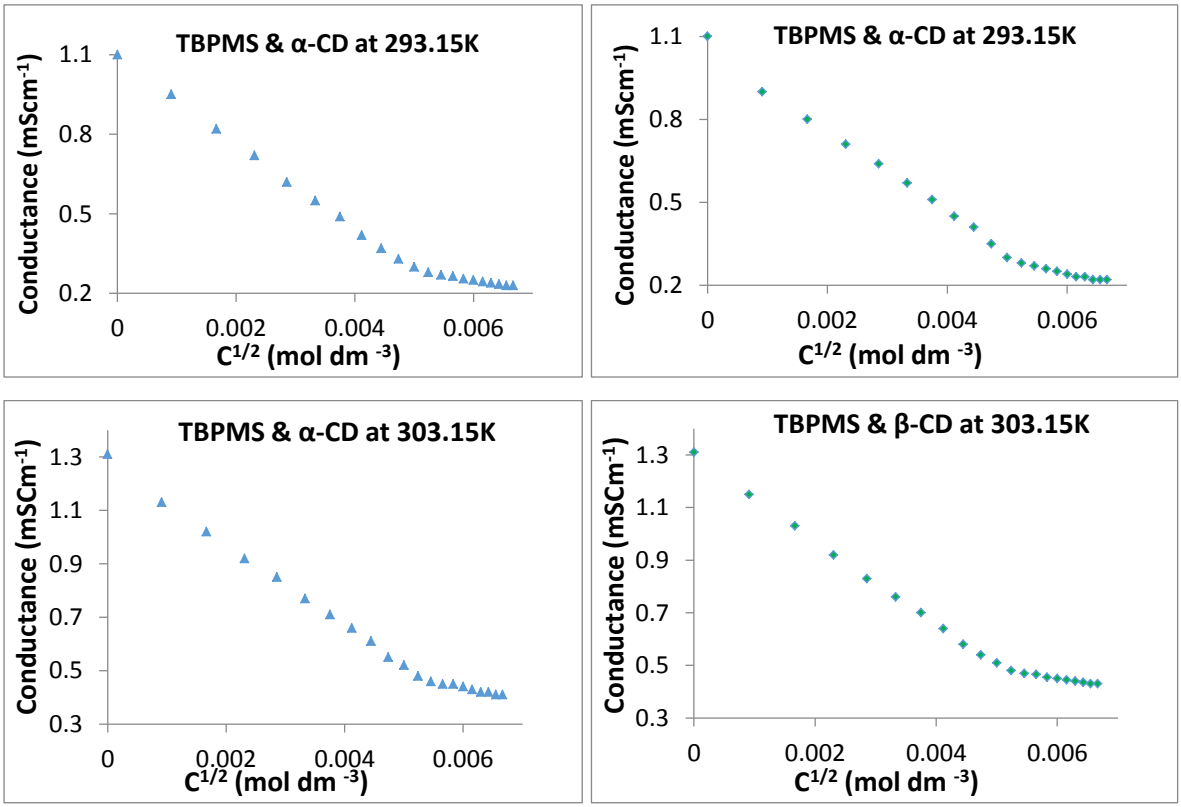


(c)

Fig.S1. ^{1}H NMR spectra of (a) pure TBPMS (b) pure β –CD and (c) β–CD & TBPMS complex.



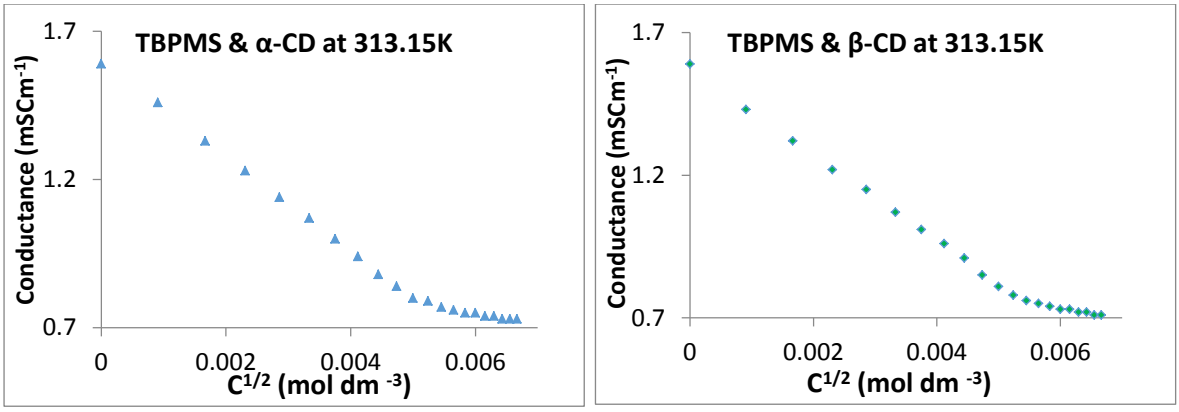


Fig.S2. Plot of conductivity against square root of molar concentration (√C) for TBPMS +α-CD(▲), TBPMS+β-CD(♦) at 293.15 K, 303.15K and 313.15K.

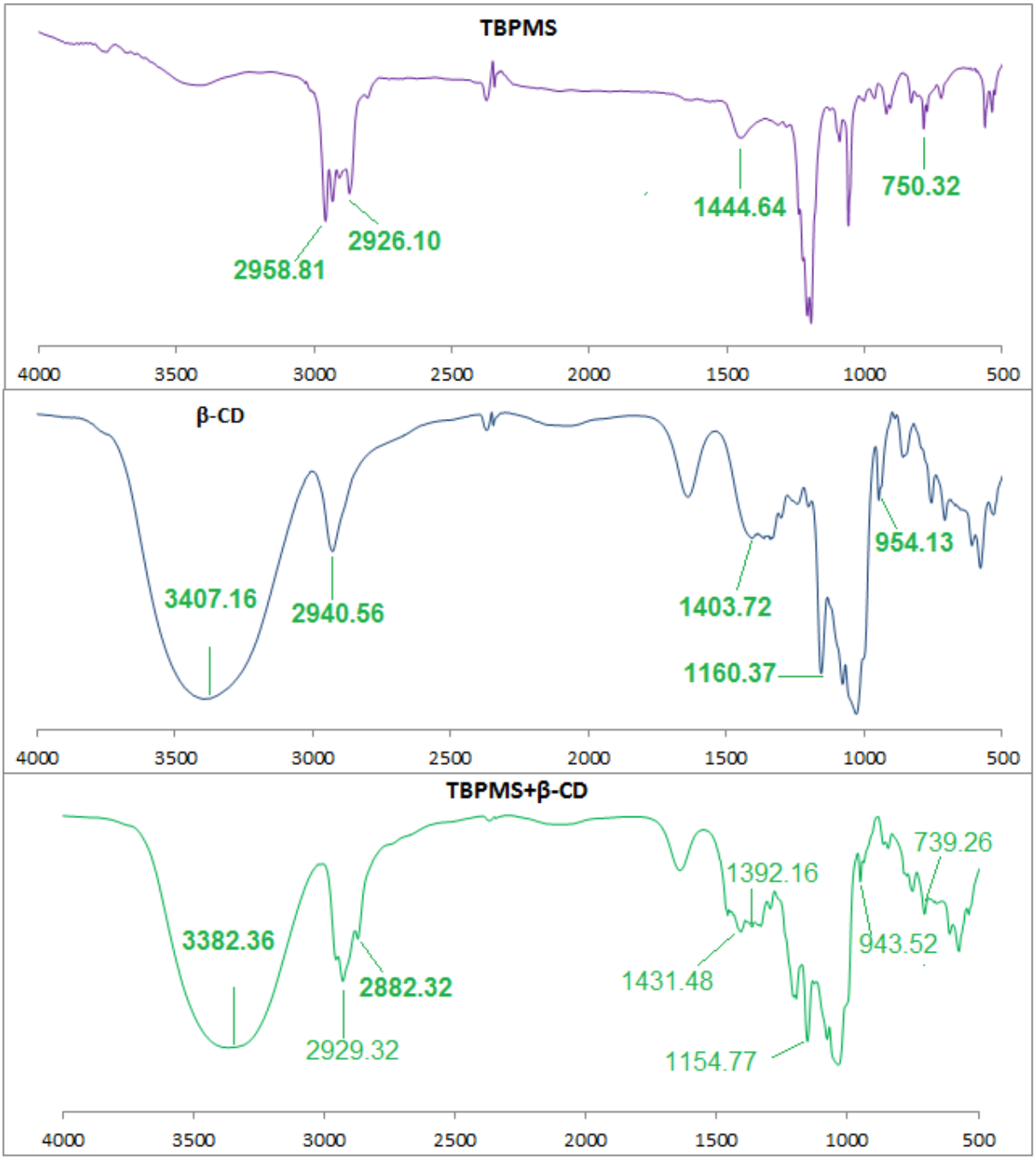


Fig.S3: FT-IR spectra of free β-CD, TBPMS and their 1:1 inclusion complex (TBPMS:β-CD).

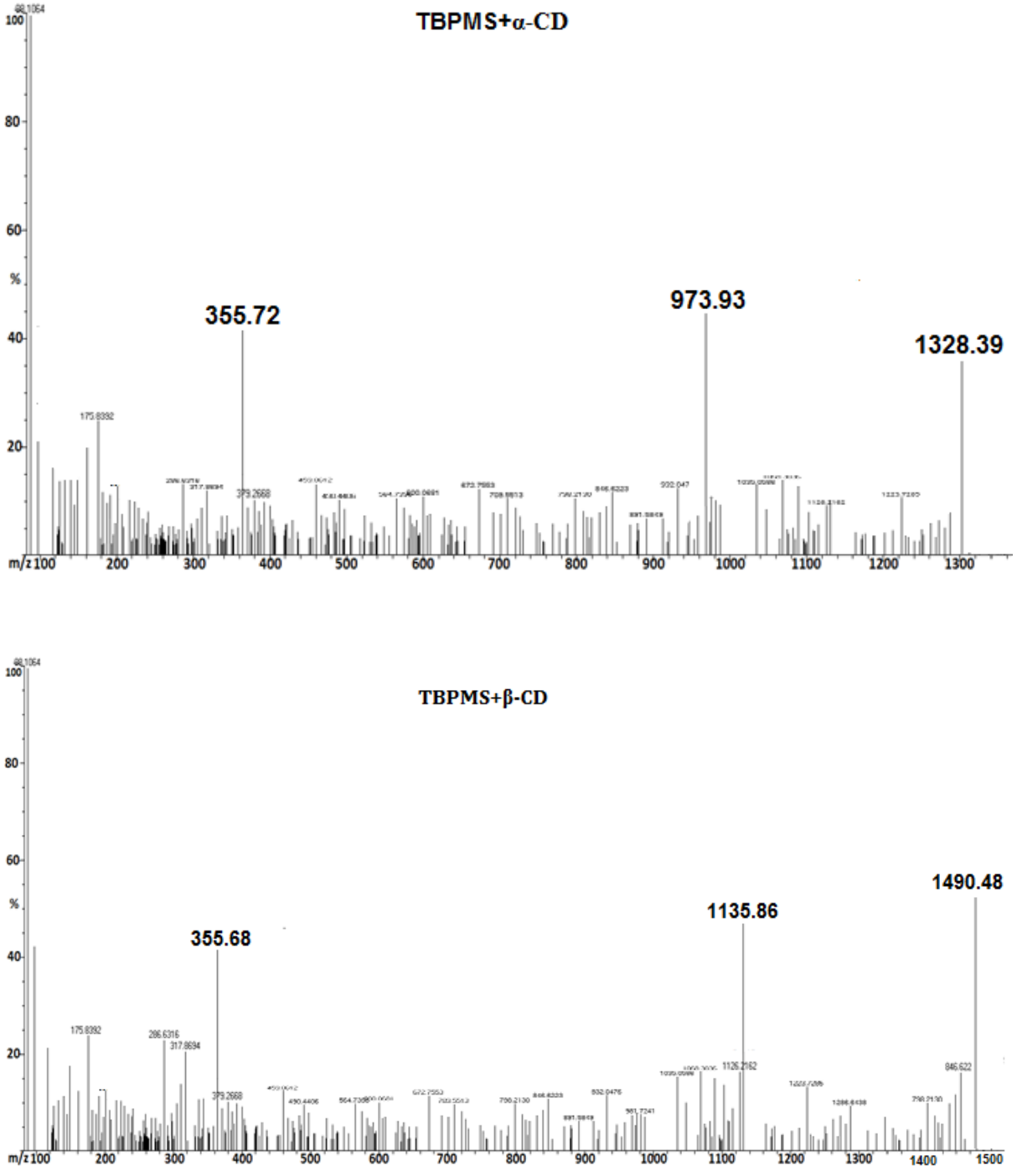


Fig.S4: ESI mass spectra of TBPMS-β-CD inclusion complex and TBPMS-β-CD inclusion complex.