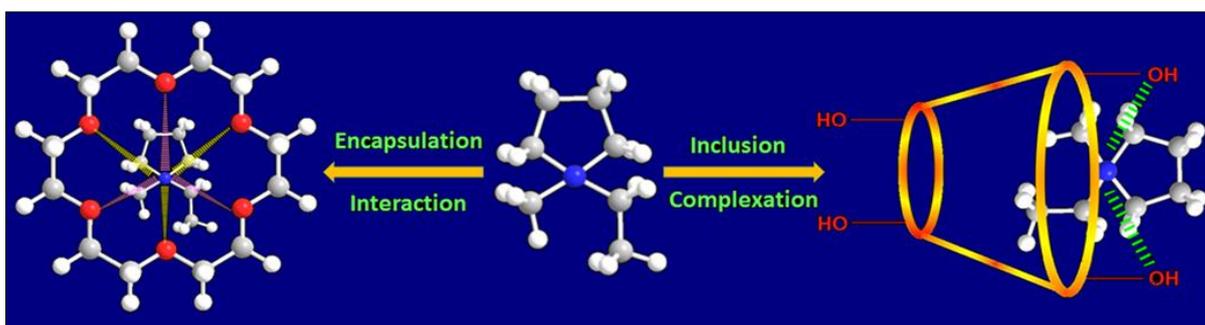


CHAPTER-VI

Evidences for Inclusion and Encapsulation of an Ionic liquid with β -CD and 18 C-6 in Aqueous Environments by Physicochemical Investigation

- **Highlights** \Rightarrow It may be expected that, as innovative applications like those in [chromatography](#), [electron microscopy](#), and biochemistry, become more widely appreciated; by the use of the studied Ionic liquid will become properly recognized. The ability to control and enhance [proton](#)-catalyzed chemical reactions should be another feature of studied protic ionic liquid chemistry; it is a very effective solvent media for optimum output in several applications with minimum possible environment pollution.
- Physicochemical investigation of both inclusion and encapsulation complexes for β -CD and 18-C-6 with Pyrrolidinium based ionic liquid are overviewed in the present work. In the first case ionic liquid combines with α - and β - CD which has interesting variations in thermo chromic behavior of the dye molecules and would be desirable in the near future. On the other hand 18-C-6 including hydrophobic ionic liquid has a vital role in electrochemistry. Such type of inclusion complexes are used in recycling process. This proposed electrochemical process for remediation of extraction solvent preserves the ionic liquid.

Graphical Abstract \Rightarrow



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Theoretical abstract:

The interface between pyrrolidinium-based ionic liquid i.e. 1-ethyl-1-methylpyrrolidinium bromide, with beta-cyclodextrin and 18-crown-6 solution have been compared and explored by means of density, viscosity, refractive index, electrical conductance and surface tension, FTIR, ^1H nuclear magnetic resonance, 2D ROESY NMR, high resolution mass spectroscopy studies. Limiting apparent molar volumes (ϕ_V^0), experimental slopes (S_V^*) interpreted in terms of inclusion and interaction (ion- solvent, ion- ion). Establishment of binding affinity were discussed in molecular terms supported this inclusion complexation and encapsulation interaction process. The result shows that the stability of the resulting complexes of beta-cyclodextrin: [EMPyrr] $^+$, 18-Crown-6: [EMPyrr] $^+$ based on the geometrical and spectrometric data. Host guest chemistry of the five-membered nitrogen containing cation with two different macro cyclic hosts is supported by studying NMR. HRMS has been used to support the complexation process with the proper stoichiometry ratio. The solid complex formations established by Fourier transform infrared study.

1.Introduction

β -Cyclodextrin otherwise known as β -Cycloamylose is of great significance for complexation ability and assorted multiskilled versatile characteristics, continuing to have diverse imperative applications in different areas of novel delivery systems. It is believed that β -cyclodextrin will occupy a very imperative task in these recent physicochemical investigations. β -cyclodextrin, a bottomless bowl shaped (truncated cone) stuffed by hydrogen bonding can operate as a host molecule for assorted guest molecules. In an aqueous solution, the slightly hydrophobic cavity of β - cyclodextrin is occupied by a small quantity of water molecules that are energetically unfavored and therefore can be readily substituted by selective guest moiety that are not as much of polar as compared to water. ¹

In contrast Crown ethers are macro cyclic polyether. The most significant and extraordinary property of the macro cyclic "crown compounds" (used as host, also known as ligand) is their affinity to form complexes with the various category of guest species, for example, metal ions, amino acids, and ionic liquids (IL). Over the past years, they have gripped broad attention due to their unique capacity to form complex with cations. Such complexes are held together in unique structural relationships by electrostatic attraction between cation and negative end of C-O dipoles except those of full covalent bond. The firmness of the

aforesaid crown ether-guest complexes strongly depends on how well the cation moiety fits into the ring of the polyether; influenced by the charge density of the cation, the nature and the number of the heteroatoms.²⁻⁶

Among diverse guest molecules, the IL (1-ethyl-1-methylpyrrolidinium bromide (EMPyrr) Br) has been preferred because of having a vast area of interest for vital reasons associated with their negligible vapor pressure, i.e., they do not evaporate and known as “designer solvents” and “green” due to the criterion for replacement for toxic volatile organic solvent, good ionic mobility, excellent thermal, and chemical stabilities. There is a wide range of industrial applications of ILs due to their unique physicochemical character as ion exchange agents and consumer uses as electrical and electronic products.⁷⁻⁹ nowadays the uses of such ILs increase the interest in the various fields to the development of new ideas and techniques.

Eco-effectiveness and Green chemistry are the foremost tools to promote a transformation from unsustainable development to [sustainable development](#), alongside with engineering natural balance expresses improvement of further invention of resources, products as well as processes. Ionic liquids although technically identified as molten salts exist as liquids at relatively low temperatures even at STP usually known as room temperature i.e., 25⁰C. These ionic designer solvents¹⁰⁻¹² have countless attractive properties including melting point, viscometric measurements, and solubilisation of starting materials and other solvents, are determined by substituent on the organic component and by the counter ion both chemically and thermally (i.e., high thermal stability), non flammability and incalculably very low vapor pressure are some other properties like large electrochemical window of the studied promising solvent has been investigated. An overview of the field of ionic liquids was first commenced in 1914 by Walden. The subject focuses on physicochemical research and its development in industrial aspects provides a particular scientific potential within the last few decades. Moreover there arises the possibility of fine-tuning of ionic liquid by various physical, chemical, and biological properties by an appropriate selective combination of cationic and anionic chemical structures for the evolution of an innovative scientific era. An emerging field of IL applications suggests its use and methodologies as to solve critical pharmaceutical problems, in particular, the low solubility and thus bioavailability of pharmaceutical compounds, by the development of strategies to use ILs as carriers of pharmaceutical active ingredient¹³ is an extremely promising and wide avenue. The

physicochemical properties of ILs has been effortlessly be tailored by varying the composition and structure of cation and anion ranging from lipophilic to lipophobic, viscous to nonviscous, polar to nonpolar, and water miscible to immiscible. Industrial development means, as a new paradigm in chemistry, that the solvent can be fine-tuned to optimize the chemistry, in this ternary system being studied. On the other hand, thermodynamic and physical properties of these conventional solvent showing the Lewis acidity along with host molecules predicts various ionic interactions thus reporting various versatile characteristics.

Herein the work is associated to the study of thermodynamic properties, conductometric studies, spectroscopic and surface properties of 1-ethyl-1-methylpyrrolidinium bromide, an ionic liquid with three different compositions of aqueous β -cyclodextrin and 18 C-6 solution at 298.15K (Scheme 1, 2).

2. Result and Discussion

2.1 Densitometry studies

Quantitative analysis depict the volumetric properties such as, Apparent molar volumes, (ϕ_V) and Limiting Apparent molar volumes (ϕ_V^0) are estimated as responsive apparatus designed for the understanding of interactions occurring in solutions (Table 1).

The Apparent molar volume measured as summation of geometric volume of fundamental solute molecule and changes in the solvent volume due to its interface with the solute in the region of the peripheral/co-ordination sphere. For this Apparent volumetric principle, (ϕ_V) has been determined from densitometry of solutions via suitable equation (1). The Apparent molar volumes (ϕ_V) were determined from measured solution densities by means of equation (1) and the solved data's are given in (Table 2, 3).

$$\phi_V = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{c\rho_0}$$

Or

$$\phi_V = \frac{M}{\rho} - \frac{1000(\rho - \rho_0)}{m\rho\rho_0} \quad (1)$$

Where (M) = molar mass of ionic liquid,

(c) = molarity of the solution,

(m)= molality of the solution,

(ρ_0) = density of aq. β -CD and aq. 18 C-6 respectively

(ρ) = density of the (solution of aq. β -CD + IL mixture) and (solution of aq. 18 C-6 + IL mixture).

The extrapolation of apparent molar volume of solution mixture to infinite dilution and expression of concentration dependence of the apparent molar volume has been constructed by a major equation –“Masson equation”, as given in equation (2). Thus Limiting apparent molar volumes (ϕ_V^0) assisted with least-square treatment by plotting of (ϕ_V) versus (\sqrt{m}) using “Masson equation”¹⁶ and shown in (Table 4).

$$\phi_V = \phi_V^0 + S_V^* \sqrt{c}$$

Or

$$\phi_V = \phi_V^0 + S_V^* \sqrt{m} \quad (2)$$

Coverage of (ϕ_V) (Table 3) is found to be maximum and have positive values for all considered systems, therefore suggesting firm and compact solute-solvent interactions. (ϕ_V) data's thus obtained is decreased with the increasing molarity (c) of the studied ionic liquid in 18 C-6 solutions rather than the ionic liquid in β -CD solutions. (ϕ_V), varied linearly with respect to (c) and may possibly be least-squares fitted to Masson equation¹⁴ from where Limiting molar volume (ϕ_V^0) (infinite dilution partial molar volume) have been projected. If the variation of (ϕ_V) with (c) show considerable scatter, (ϕ_V^0) (Figure 1) has been determined either by plotting graphically or has been taken as average of the (ϕ_V) values whilst slope tends to zero, within the range of $R^2=0.9989$ to 0.9999 in linear regression coefficients. The values of (ϕ_V^0) and (S_V^*) are reported in (Table 4).

On account of a quantitative comparison, the magnitude of (ϕ_V^0) are much greater than (S_V^*), in every solutions. This implies that ion-solvent interactions take over over ion-ion interactions in all the solutions studied. The trend in variation of ϕ_V^0 for particular systems is in the order

$$\{\text{IL} + \beta\text{-CD}\} < \{\text{IL} + 18\text{ C-6}\}$$

The increase of (ϕ_v^0) for ionic liquid with rising mass fraction of aqueous 18-C-6 and increasing positive shift volumes suggests that ion-ion and ion-hydrophilic group interactions are stronger and unbending than ion-hydrophobic group interactions (Figure 1).

In the current ternary system (ionic liquid + aqueous. 18-C-6 mixture), interaction is well-built (Scheme 5(a), (b)). It noted that (ϕ_v^0) of IL owing to greater electrostriction. This is because with increasing chain length of IL provides an increasing structure enforcing tendency in 18-C-6 solutions, and as a result, water in the overlapping co spheres is better structured than in the bulk. When water relaxes to the bulk and the studied IL thereby confines the location along with change in volume. In IL, interactions increase with the adding up of long chain, and consequently there is a net raise in volume.

(Table 4), also states that IL is more solvated by 18 C-6 than β -CD. At the initial stage if we consider individual 18-C-6 and β -cyclodextrin in aqueous mixture, we discover that all or maximum of -OH (primary or secondary) groups interact with water molecules present in the solution bulk. After addition of selected IL (independently), the IL trapped that -OH by replacing the water molecules with the proper phase of interaction as a consequence this led to the net increase in solvation. With increasing conc. of 18-C-6, ϕ_v^0 value increases indicating the ion-solvent interaction increases. S_v^* values showed in (Table 4) indicates that ion-ion interaction decreases for IL in β -cyclodextrin and ion-ion interaction increases with increases the conc. of 18 C-6.²⁹

2.2 Viscometric studies

The viscosity data has been analyzed by the Jones-Dole equation ¹²

$$(\eta/\eta_0 - 1)/\sqrt{c} = A + B\sqrt{c} \quad (3)$$

Here η_0 = viscosities of the solvent

η = viscosities of the solution

Values of A-coefficient, B-coefficient are taken from the straight line by plotting $(\eta/\eta_0 - 1)/\sqrt{c}$ versus \sqrt{c} which are described in (Table 4).

The viscosity in aq. 18-C-6 rises with a rise in employed mass fraction $w=0.001, 0.003, 0.005$ (shown in Table 1), endorsed to structure-making influence between 18-C-6 and water by

destroying the hydrogen-bonded structure of water, in its environs. In the case of ternary system (ionic liquid+ aqueous 18-C-6), it is observed that at a given concentration of 18-C-6, viscosity of the studied solution gets increased with increasing molarities of ionic liquids (shown in Table 2). Viscosity *B*-coefficient depends^{13, 14} on dimension and structure of the solute molecules thus signifying ion-solvent interactions.²⁷⁻²⁹ Scope of solute-solvent interaction in the solution systems calculated from viscosity *B*-coefficient data, thus providing valuable information concerning solvation of solvated solutes along with their effects on arrangement of solvent molecules in local vicinity of solute molecules in solutions. As of (Table 4, Figure. 2), it's evident that *B*-coefficient have positive values which are much higher than *A* –coefficient values, this technique therefore suggests that the ion-solvent interactions are prevails over ion-ion interactions. Higher *B*-coefficient values for viscosity are due to the solvated ions and molecule associated by the solvent molecules from all sides, which led to the formation of associated molecule by ion-solvent interaction, would provide greater resistance. With increasing concentration in 18-C-6, viscosity *B*-coefficient value increases indicating the ion-solvent interaction increases and becomes highly solvated. Viscosity *A*-coefficient showed in (Table 4) designates that ion-ion interaction increase with increasing concentration of 18 C-6 in IL³⁰ and decreases for β -CD. These results obtained are in good agreement with those obtained from (ϕ_v^0) values discussed in previous section.

2.3 Refractive index measurements

The refractive index of mixing can be interrelated by the application of a composition-dependent polynomial equation. Molar refraction, R_M in solution thus can be estimated from Lorentz-Lorenz relation¹⁴

$$R_M = \frac{(n_D^2 - 1)}{(n_D^2 + 2)} \left(\frac{M}{\rho} \right) \quad (4)$$

Where R_M = molar refraction

n_D = refractive index

M = molar mass

ρ = density of solution

Optical data of refractive index of a compound provide interesting information allied to molecular interactions, structure of solutions. It describes its capability to refract light as it moves from one medium to another and thus, higher the refractive index of a compound, maximum of the light is refracted.

As investigated by Deetlefs *et al.*¹⁵ refractive index of a matter is high enough, when its molecules are more tightly packed or in general when the compound is denser. Hence a glance of (Table 2, Table 3 and Figure 3) show that refractive indices (n_D) and molar refractions (R_M) of the electrolyte in aq. Host solutions follows:

$$\{18\text{-C-6} + \text{IL}\} > \{\beta\text{-CD} + \text{IL}\}$$

As R_M , is directly proportional to molecular polarizability, it is evident from (Table 2, Table 3 and Figure 3) that the overall polarizability of the electrolyte is highest in case of IL in 18 C-6 in comparison to IL in β -CD.

Thus refractive index (n_D) and molar refraction (R_M) of studied IL is highest in aq. 18-C-6. So, according to the aforesaid statement of Deetlefs *et al.*¹⁵ it can be concluded that the molecules of IL are most tightly packed in aq. 18 C-6 rather than β -CD. The packing is least in case of β -CD.

Refractive index, molar refraction operates as an expensive tool for studying the molecular interaction in solution. More values of refractive index implies that the velocity of light becomes minimum, when it passes through the medium; in other words, more molar refraction (R_M) in addition to limiting molar refraction (R_M^0) point toward the medium being denser or more compact¹⁵. Hence, from (Figure. 3) it is obvious to facilitate greater interaction among IL and 18 C-6 i.e., more closely packed rather than the β -CD system. With increasing the conc. of 18-C-6 molar refraction (R_M) of solution (IL) increases indicating that ion-solvent interaction increases.

2.4 Surface Tension

Commencing the glance of (Table 5), it has been observed surface tension (γ) of IL in aq. β CD and 18-C-6 solutions, the values gradually enhance with increasing concentration of IL and decrease in case of 18-C-6. This is due to ionic interaction between the charged species which accumulates at the surface of the solution. The surface tension values (γ) with subsequent concentration of different mass fraction of aq. β -CD (Figure 4(a)) and 18 C-6 (Figure 4(b))

have been reported for ionic liquid in all cases, trends the curves of surface tensions (γ) against concentration (molarity) to be straight line and decreases with increasing conc. of 18 C-6 and vice versa in case of cyclodextrin. The fact is due to the interaction of these charged species with $-O-$ groups at the surface of 18 C-6 is more than $-OH$ groups at the rims of cyclodextrin molecules, which probably make association by electrostatic forces, this results in the decreases in the electrostatic attraction among the ionic species and the surface tension for the solution decreases. Surface tension of IL in aqueous 18-C-6 solution shows that parachor value is highest and for IL in β -CD lowest. This is due to hydration of these charged species. Charge density is highest for IL in β -CD, and least for the IL in crown ether, this is also the trend of their hydration order. From (Figure.4 (a) and Figure. 4(b)) it is evident that, as the hydration increases, the electrostatic forces between them decreases, as a result the surface tension for the solution decreases. Thus it can be concluded that interaction in case of crown ether shows association phenomenon whereas inclusion in case of cyclodextrin is a bulk phenomenon i.e., incorporation. ^{17, 20-27}

2.5 Conductance studies

The electrolyte was freely soluble in all 18 C-6 and β -CD solutions. Specific conductance (κ , $\mu S\ cm^{-1}$) of solutions under analysis with molar concentration appears within the range of $1.05 \times 10^{-5} - 1.42 \times 10^{-2} M$ in diverse 18-C-6 and β -CD solutions being measured. Molar conductance (Λ_m) for both the studied systems were calculated by using following equation ¹⁶

$$\Lambda_m = 1000 \kappa / c \quad (5)$$

Here c is molar concentration; κ is measured specific conductance of the studied solutions. The molar conductance's (Λ_m) of ionic liquid in different concentration of 18 C-6 and β -CD solutions were calculated at the corresponding molar concentrations (c) with different concentrations of 18 C-6 (Figure 5(b)) and β -CD (Figure 5(a)) solutions given in (Table 6 (a)). From the perusal of (Figure. 5 (a), 5 (b)) it is evident that conductance is higher in case of IL with β -CD than in case of IL with crown.

Since the N^+ ion of IL is highly hydrated with water molecule present in aq. 18 C-6 solutions. The extent of hydration is the order $[IL + \beta\text{-CD}] < [IL + 18\text{ C-6}]$. So, ionic conductance of $[IL + 18$

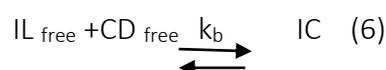
C-6] is lowest and that of [IL + β -CD] is highest. The molar conductance's (Λ_m) of ionic liquid are decreased with increasing the conc. of 18 C-6 and β -CD.

The fact is due to the interaction of these charged species with the –O– groups at the surface of 18 C-6 and –OH groups at the edges of cyclodextrin molecules, which probably construct association by electrostatic forces, this consequences in the shrinks in the electrostatic attraction among the ionic species and the molar conductance's (Λ_m) for the solution decreases^{18,19} shown in (Scheme S5 (a), (b)).

2.6. Binding constants: non-linear isotherms determined by conductivity technique

Binding constants (K_b) for inclusion process have been determined for the [IL–CD] IC with the help of conductivity study. Here, a non-linear programme has been used based upon the modifications in conductivity as a result of incorporation of IL into the apolar cavity of β - CD.^{17, 18}

The following equilibrium is thought to exist linking the host and guest molecule for a [1: 1 IC]:



The binding constant (K_b) for the formation of IC may be expressed as:

$$K_b = [\text{IC}] / [\text{IL}]_{\text{free}} [\text{CD}]_{\text{free}} \quad (7)$$

Here, [IC], [IL]_{free}, [CD]_{free} symbolize equilibrium concentration of IC, free IL molecule and free CD, correspondingly. According to binding isotherm, binding constant (K_b) for the configuration of IC may be articulated as:

$$K_b = [\text{IC}] / [\text{IL}]_{\text{free}} [\text{CD}]_{\text{free}} = (k_{\text{obs}} - k_0) / (k - k_{\text{obs}}) [\text{CD}]_{\text{free}} \quad (8)$$

$$[\text{CD}]_{\text{free}} = [\text{CD}]_{\text{ad}} = [\text{IL}]_{\text{ad}} (k_{\text{obs}} - k_0) / (k - k_0) \quad (9)$$

Here, k_0 , k_{obs} , k are conductivity of IL at preliminary state, during the period of adding CD and final state, respectively. [IL]_{ad}, [CD]_{ad} are concentrations of IL and added CD, correspondingly. As a result, values of K_b for the IC were evaluated from binding isotherm by applying a non-linear programme.^{17, 18}

To investigate the encapsulation of 18 C-6 with [EMPyrr] Br, the molar conductance (Λ_m) is monitored in solution at a definite temperature. The resulting series of molar conductance (Λ_m) -mole ratio in H₂O are presented in (Figure. 5 (b)). It has been noticed that there is a significant change in molar conductance (Λ_m), that is, molar conductance gradually decreases with increase in the fractions of 18 C-6 / [EMPyrr]⁺ mole ratio (Table 6(a)). This suggests that there must be formed cation by ion dipole interactions with crown ether rather than pairing or covalent bond. It results the higher mobility of pyrrolidinium cation in the process than the mobility of [EMPyrr] Br in H₂O in the absence of the selected crown ethers. First, the molar conductance decreases sharply during the addition of crown solution, but after a point minute changes is observed. This point indicates about the stoichiometric behavior of the resulting in encapsulation. As at that point, the mole ratio of 18 C-6 / [EMPyrr]⁺ is close to unity (Table 6 (b)),

It suggests the formation of stable ~ 1:1 complex of 18 C-6: [EMPyrr]⁺ at definite temperature¹⁷⁻²⁷. Consequently, a general reaction can be given by the following equilibrium



The corresponding equilibrium constant (K_b') of the reaction can be represented as,

$$K_b' = \frac{[\text{EMPyrr}]^+\text{Crown}}{[\text{EMPyrr}]^+_{\text{free}} [\text{Crown}]_{\text{free}}} \quad (11)$$

Here, [IC], [IL]_{free} and [Crown]_{free} represent the equilibrium concentration of IC, free IL molecule and free Crown, respectively. Equation 11 is derived on the basis of Debye- Hückel limiting law²⁵. According to binding isotherm, binding constant (K_b') for the development of encapsulation may possibly be expressed as:

$$K_b' = \frac{[\text{EMPyrr}]^+\text{Crown}}{[\text{EMPyrr}]^+_{\text{free}} [\text{Crown}]_{\text{free}}} = \frac{(k_{\text{obs}} - k_0)}{(k - k_{\text{obs}})} [\text{Crown}]_{\text{free}} \quad (12)$$

$$[\text{Crown}]_{\text{free}} = [\text{Crown}]_{\text{ad}} = [\text{EMPyrr}]^+_{\text{ad}} (k_{\text{obs}} - k_0) / (k - k_0) \quad (13)$$

Here, k_0 , k_{obs} , k are conductivity of [EMPyrr] Br at preliminary state, after adding together of Crown ether and concluding state, respectively. $[\text{EMPyrr}]^+_{\text{ad}}$, $[\text{Crown}]_{\text{ad}}$ are concentrations of [EMPyrr]⁺ Br, added Crown respectively. In consequence, values of K_b' for encapsulated complexation were evaluated from the binding isotherm by applying a non-linear programme,²¹⁻²⁵.

Now, using these equation 8, 9 and equation 12, 13 the binding constant (K_b , K_b') and the molar conductance of the two studied systems have been calculated at 298.15K are plotted. So, the aforesaid calculation one can conclude that the host guest binding constant in IC is much more prominent than that of encapsulation of IL into crown ether.

2.7 Explanation for FT-IR

FT-IR spectra also confirm inclusion phenomena in the solid state. The characteristic IR frequencies of [EMPyrr]Br, β -CD, 18 C-6 and [EMPyrr]Br in both β -CD (Figure 6(a)) and 18 C-6 (Figure 6(b)) are listed in (Table 7). The FT-IR spectrum of [EMPyrr] Br is characterized by peaks for C-N and C-H for CH_3 and CH_2 groups.

Broad distinctive peaks of OH at about 3349.23 cm^{-1} is present in the spectra of β -CD. However, quite a lot of peaks of IL are missing which is due to the change in environment after incorporating in cavity of β -CD. The C-H stretching bands for CH_3 and CH_2 of the studied IL are not present in inclusion spectrum.

The O-H stretch of β -CD is shifted to a lower frequency owing to the involvement of O-H groups of host molecules in hydrogen bonding with respect to the guest molecules. Peaks for C-N group of the guest molecule are present in the spectrum of IC, which is an indication of the fact that hydrophobic side chain of IL is incorporated in the hydrophobic cavity of β -CD. In case of interaction of IL with 18-crown-6 one can find from the IR plot that λ value for C-O-C stretching is shifted from 1128.53 to 1109.01 cm^{-1} and the $\nu(\text{C-H})$ stretching frequency for methylene groups of crown is shifted from 2918.23 to 2829.64 cm^{-1} . Those changes in IR frequencies verify the interaction of crown oxygen's with the positive nitrogen of IL. But in this present case the IL retains its C-H frequencies of CH_3 and CH_2 groups (Figure 6 (a), 6 (b)).

23-27

2.8(a) Explanation for (^1H) Nuclear Magnetic Resonance: The creation of IC can be elucidated on the radiance of ^1H NMR spectroscopy study²⁴. So, this technique based on changes of chemical shifts of protons caused by insertion of guest molecule into the β -CD cavity²⁶. In β -CD structure of the H3 (near to wider opening side) and H5 (close to narrow rim side) are positioned in the interior part of β -CD cavity. H6 and H7 of methylene group (bearing primary-OH group) remains on the narrow opening side of β -CD and the rest of the other H-

atoms H1, H2, H4 are positioned on the outer surface of β -CD (Figure 7(a)) as shown in (Scheme 3(b)). $^{18}\text{ }^1\text{H}$ NMR spectrum of β -CD, pure EMPyrr, solid IC of EMPyrr with β -CD (1:1) are given in (Figure. 7(a)). It is noticeably observed from (Table 8) for H3 and H5, a large upfield shift has been viewed. The considerable changes of chemical shifts ($\Delta\delta$) suggested EMPyrr monomer entered into the hydrophobic fissure of β -CD. The upfield shift of H3 ($\Delta\delta = 0.241\text{ppm}$) is to a large extent superior than H5 shifting ($\Delta\delta = 0.101\text{ ppm}$), on the other hand, minor chemical shifts are noted for H1, H2, H4 and H6 that are not part of the interior hydrophobic hole of β -CD molecule. The interacting protons of the considered ILs also show upfield chemical shift. As both ethyl and methyl groups are supposed to enter into the hydrophobic cavity of β -CD, all the protons at 5, 6 and 7 positions, shows significant downfield shifts (Table 8) illustrate the mechanism of insertion as depicted in (Scheme 3(a)).

The shifting of protons of IL (pyrrolidinium cation) and crown ethers is used to analyse the formation of the complex. (Figure 7 (b)) shows ^1H NMR spectra of free 18 C-6 (Figure 7(b)) (Table 9), uncomplexed IL, complexed IL and with 18 C-6 respectively.

In this encapsulated complex, the H1, H4, H5, H6 and H7 protons of pyrrolidinium ion are upfield shifted significantly, whereas the shifting of H2 and H3 protons are marginal. 18 C-6 prefers D_{3d} conformation where all the six oxygen atoms are pointed towards the cavity²⁶ hence, the effectual $\text{N}^+\cdots\text{O}^{\delta-}$ non-covalent electrostatic ion dipole interactions are developed between the pyrrolidinium ion and the oxygen atoms of 18 C-6.²⁷

Comparing with the free component, it is observed that peak of $-\text{OCH}_2$ group protons of 18 C-6 are also upfield shielded in complexed form^{26, 27}. Hence, it is concluded that such chemical shifts must occur due to host guest complex formation of pyrrolidinium cation with 18 C-6 shown in (Scheme 4)

Selected ^1H NMR data

[EMPyrr]Br : ^1H NMR (400 MHz, in D_2O): $\delta=3.30\text{-}3.26$ (2H, m, $J=16\text{ Hz}$), $2.40\text{-}2.30$ (4H, m, $J=40\text{ Hz}$), 2.88 (3H, s), $3.23\text{-}3.21$ (2H, q, $J = 8\text{ Hz}$), $3.23\text{-}3.21$ (2H, t, $J = 8\text{ Hz}$), $1.35\text{-}1.32$ (3H, m, $J=12\text{ Hz}$).

β -CD : ^1H NMR (400 MHz, in D_2O): $\delta=5.00\text{-}4.98$ (6H, *d*, $J=8$ Hz), $4.05\text{-}3.99$ (6H, *t*, $J=24$ Hz), $3.90\text{-}3.85$ (18H, *m*, $J=20$ Hz), $3.82\text{-}3.81$ (6H, *dd*, $J=4$ Hz), $3.68\text{-}3.67$ (6H, *t*, $J=4$ Hz).

18C6: ^1H NMR (400 MHz, in D_2O): $\delta=3.60\text{-}3.51$ (24H, *m*).

β -CD: [EMPyrr]Br : ^1H NMR (400 MHz, in D_2O): $\delta=4.99\text{-}4.98$ (6H, *d*, $J=4$ Hz), $3.91\text{-}3.89$ (6H, *t*, $J=8$ Hz), $3.90\text{-}3.85$ (12H, *m*, $J=20$ Hz), $3.82\text{-}3.81$ (6H, *dd*, $J=4$ Hz), $3.68\text{-}3.67$ (6H, *t*, $J=4$ Hz), $3.63\text{-}3.61$ (6H, *m*, $J=8$ Hz), $3.10\text{-}3.00$ (2H, *m*, $J=40$ Hz), $2.40\text{-}2.30$ (4H, *m*, $J=40$ Hz), 2.76 (3H, *s*), $3.23\text{-}3.21$ (2H, *q*, $J=8$ Hz), $3.23\text{-}3.21$ (2H, *t*, $J=8$ Hz), $1.22\text{-}1.19$ (3H, *m*, $J=12$ Hz).

18C6: [EMPyrr]Br cation (Complex I): ^1H NMR (400 MHz, in D_2O): $\delta=3.21\text{-}3.18$ (2H, *m*, $J=12$ Hz), $2.40\text{-}2.30$ (4H, *m*, $J=40$ Hz), $3.12\text{-}3.11$ (2H, *q*, $J=4$ Hz), 2.76 (3H, *s*), $3.11\text{-}3.09$ (2H, *t*, $J=6$ Hz), $1.29\text{-}1.26$ (3H, *m*, $J=12$ Hz), $3.51\text{-}3.47$ (24H, *m*).

2.8 (b) 2D ROESY NMR elucidates binding mode

2D ROESY NMR provides valuable information about the binding mode of the ionic liquid [EMPyrr] Br with the host β -CD molecule is also helpful to understanding the geometry of the inclusion complex, as any two protons that are closely situated in space within a distance of 0.4 nm can generate a nuclear overhauser effect (NOE) cross correlation in NOE spectroscopy (NOESY) or rotating-frame NOE spectroscopy (ROESY). 2D ROESY NMR has been done using the solid IC of the IL and β -CD system. Part of contour plot of the ROESY spectrum of [EMPyrr] Br + β -CD IC is depicted in (Figure. 7 (c)) whereas the spectra of the IL with β -CD are provided in (Figure. 7 (c)) in the ESI. [†]

As mentioned above, H3, H5 protons of CD are positioned in hydrophobic cavity whereas H1, H2, H4 protons are located outside (Scheme 3(a), 3(b)). In (Figure. 7(c)) and (Figure. 7 (c)), [†] there are appreciable correlations connecting H3 or H5 protons in CD along with methylene and methyl groups of ethyl chains of the IL, therefore confirming that the ethyl chain in the guest IL gets inserted into the hydrophobic cavity of host β -CD molecule. H6 protons of β -CD remains unaltered after the inclusion phenomena which over again supports that the guest IL molecule inserted into the wider rim of the β -CD. Thus, 2D ROESY NMR consequences are in good agreement with the results obtained from 1H NMR chemical shift analysis. ²⁷

2.9 Explanation for HRMS

ESI-mass spectrometric analysis were furthermore used to identify the configuration of IC synthesized by the scheme described above in the solid state of Experimental procedure section and have been shown in (Figure. 8(a), Figure. 8(b)). The observed peaks have been put into, which confirms that in all cases the desired IC and encapsulated complex have been formed in solid state and stoichiometric ratio of the host and guest is 1 : 1.

Positive electrospray ionization mass spectrometry (ESI-MS) is very valuable method that has been used to examine the host guest complexation with crown ethers.²⁵ The mass spectrum of 1:1 stoichiometry of β -CD: [EMPyrr] Br and 18 C-6: [EMPyrr] Br system is analyzed by ESI-MS in (Figure. 8 (a), Figure. 8 (b)).

(Table 10) represents all the preferred mass that one can expect. These experimental facts of the selected IL/ β -CD and IL/crown ether complexes suggested that the [EMPyrr]⁺ cation simultaneously inserted in the cyclodextrin cavity and associated in polyether's cavity with 1:1 stoichiometry.

2.10 Distinctive features of inclusion and interaction in complexation process

Inclusion complexes are energetically favorable, as water molecules from the cavity are displaced by hydrophobic guest moiety to acquire an apolar–apolar interaction and this led to the decrease in cyclodextrin ring strain, thus leading to a more stable lower energy state. Complexation potency depends on factors such as size of guest molecule, Vander waals interactions, release of the water molecules, hydrogen bonding, charge transfer interactions, hydrophobic interactions, release of conformational strain, etc.³⁰ Taking into consideration the above factors, β -CD is proposed in such a way to facilitate the interaction with IL, therefore is considered as the solute–solvent interaction is higher for IL.

Complex formation connecting Crown and chosen pyrrolidinium ion involves different possible modes of interactions.³¹ The most important one is hydrogen bonding interaction among oxygen atom of 18-C-6 (O-Crown) along with acidic N⁺ protons in pyrrolidinium ion [(N⁺) pyrrolidinium] for [(N⁺) pyrrolidinium.O-Crown] interaction.³² Apart from Vander waals-bonding, induced dipole–dipole interaction amid pyrrolidinium ion and O-Crown having δ charge possibly will also contribute to the overall stability of the complex formation.³³ Conversely, this induced dipole–dipole interaction is expected to be weaker as compared with Vander waals bonding interaction as discussed.³¹ The stability constants ($\log K_b'$) in favor

of 1:1 complexation were calculated in aqueous solution by conductivity study and are presented in (Table 6(a)). In these complex Vander waals-bonding to the ether oxygen atoms is obviously responsible for complexation.³¹ This has been shown by the suitable plausible mechanism (Scheme 5(a), (b)).

There may be possibility of ion–dipole interactions between positive N atom of pyrrolidinium cation and ether oxygen atom.³⁴⁻³⁶The stability constant for the complex with 18-C-6 is slightly lower than that of the complex with β -CD (Table 6(b)). The more compact and close geometrical structure of the later seems to increase the strength of H-bonding in the complex explaining the higher stability constant.

3. Novelty of the present work

In recent years, ionic liquids have been used for a wide variety of applications, it may be predictable that, as innovative applications for example those in Chromatographic technique, [Electron microscopic](#) analysis and Bio-chemistry become more widely appreciated; by use of the studied Ionic liquid will become properly recognized. The capacity to control and enhance [proton](#)-catalyzed chemical reactions should be one more feature of studied Protic Ionic liquid chemistry; it is a very effective solvent media for optimum output in several applications with minimum possible environment pollution. Physicochemical investigation of both inclusion and encapsulation complexes for β -CD and 18-C-6 with pyrrolidinium based ionic liquid (1-ethyl-1-methylpyrrolidinium bromide) are overviewed in the present work. In the first case ionic liquid combines with α - and β - CD which has interesting variations in thermo chromic behavior of the dye molecules and would be desirable in the near future. On the other hand 18-C-6 including hydrophobic ionic liquid has a vital role in electrochemistry. Such type of inclusion complexes are used in recycling process. This proposed electrochemical process for remediation of extraction solvent preserves the ionic liquid.³⁷⁻⁴⁰

4. Conclusions

The versatility of β -CD and 18 C-6 structure regarding both inclusion and encapsulation complex capability and functionalization of –OH and –O– groups opens wide, and still not wholly explored, possibilities of creating supramolecular structures. In the present investigation, the measurement of density, viscosity, refractive index and other derived parameters namely limiting apparent molar volume (ϕ_V^0), viscosity *B*-coefficient, limiting

molar refraction (R_M^0) and surface tension (γ) conductance (Λ_m), IR, ^2H NMR have been calculated for IL in aq. β -cyclodextrin and 18 C-6 solutions in various concentrations and it is evident that presence of ion-solvent interactions leads to strong and firm interactions at higher concentrations as well as weak interactions at lower concentration of IL solution. Consequently the above facts promotes the structure breaking characteristics of the aqueous electrolytic solutions. This case shows ion-solvent predominates over ion-ion interaction. In inference, concentration, nature of the solvent, nature of the solute and its interface plays an imperative role in determining the interactions occurring in the solutions. These conclusions have given possibility for further studies on the binding properties for system. Study of literature showed that these techniques confirmed the formation of inclusion and encapsulated complexes in the solid and in the solution state. The structural effect of β -CD and 18 C-6 gives constructive support in the molecular inclusion and interaction. In particular, this study demands a novelty of IL prevailing in the aqueous solutions of β -CD and 18 C-6.

Figures

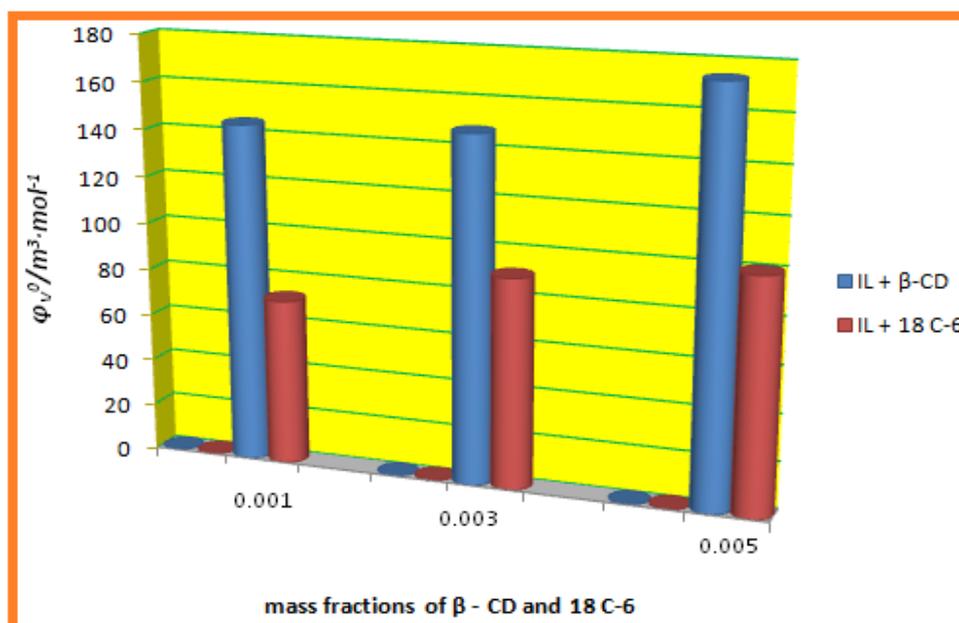


Figure 1

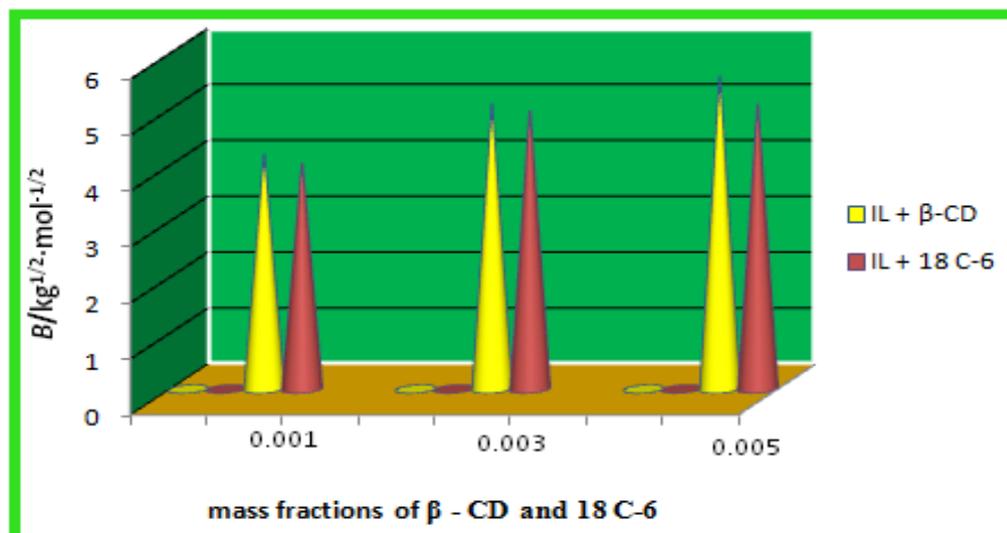


Figure 2

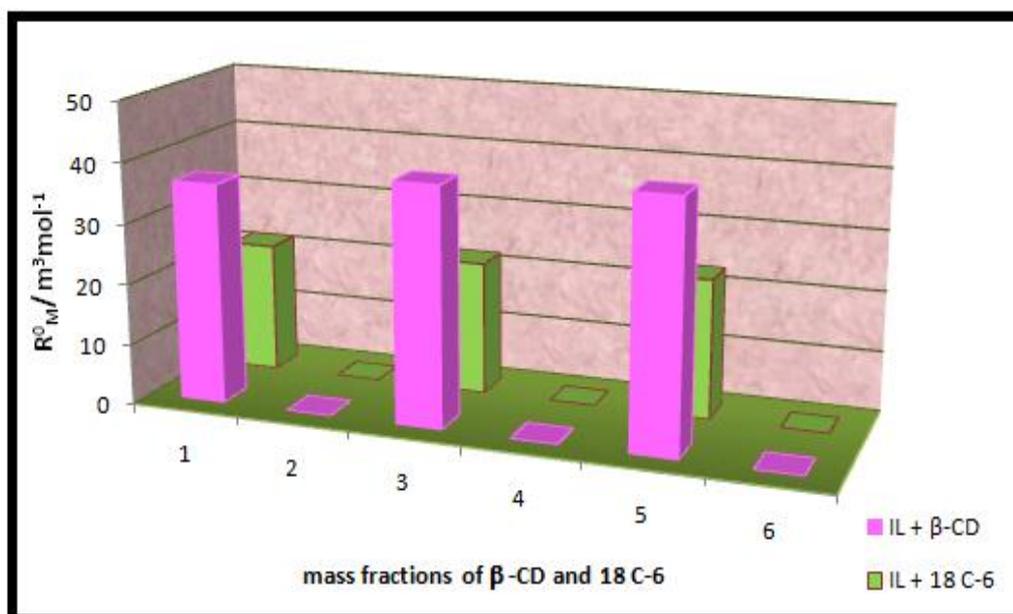


Figure 3.

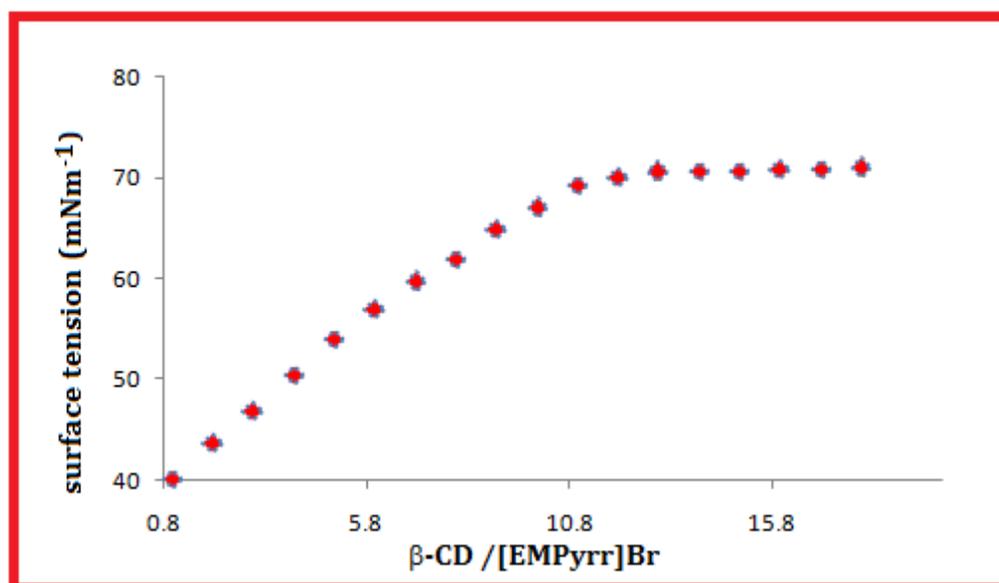


Figure 4(a).

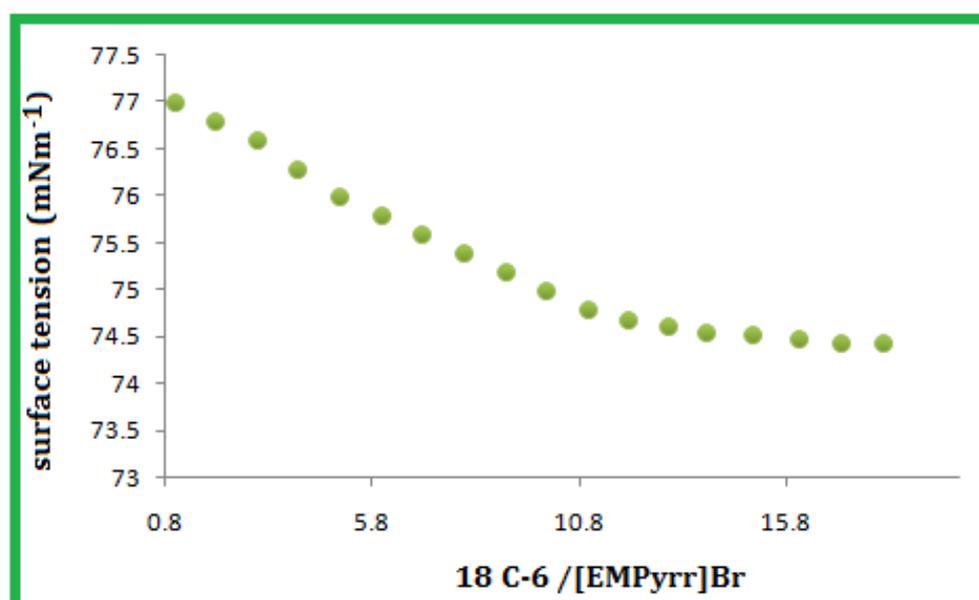


Figure 4(b).

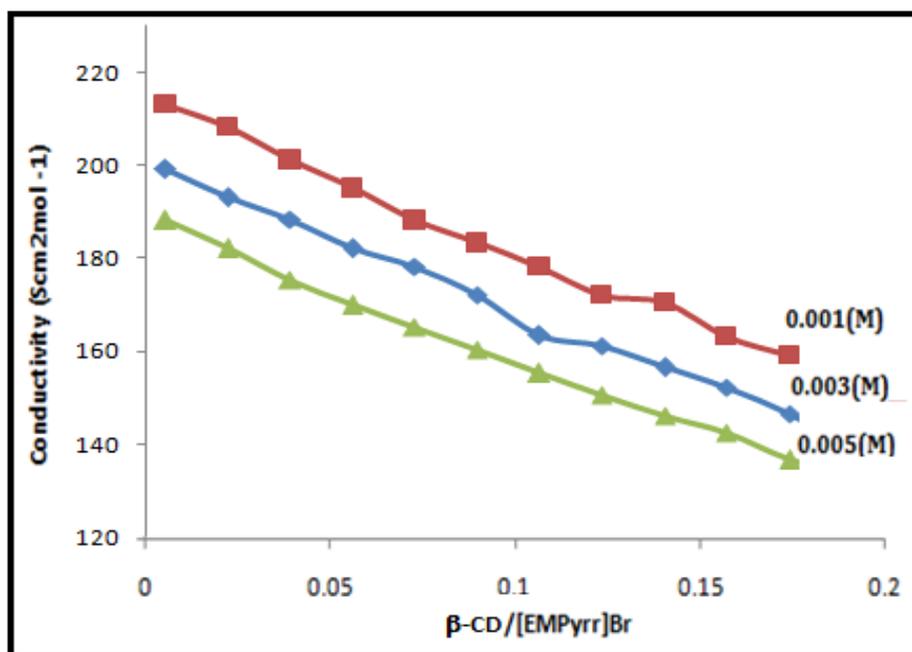


Figure 5 (a).

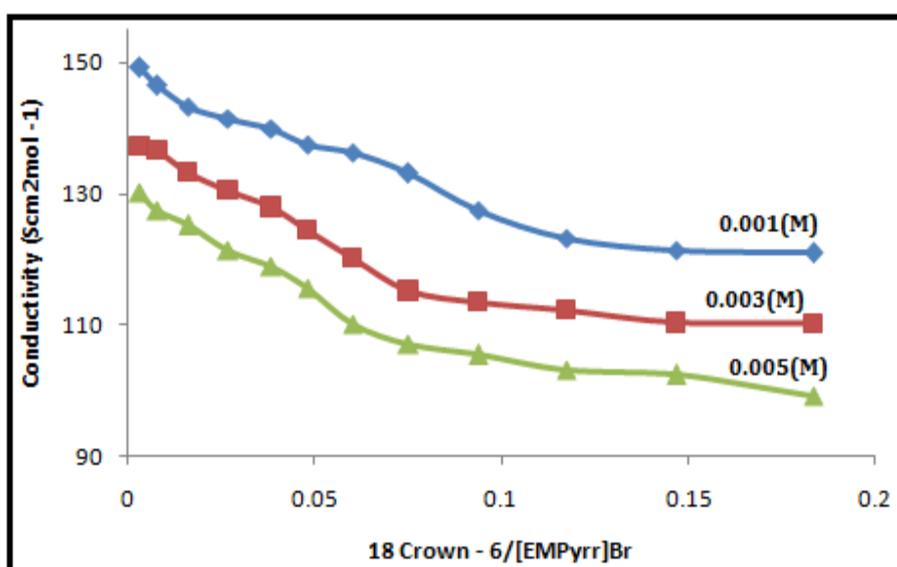


Figure 5 (b).

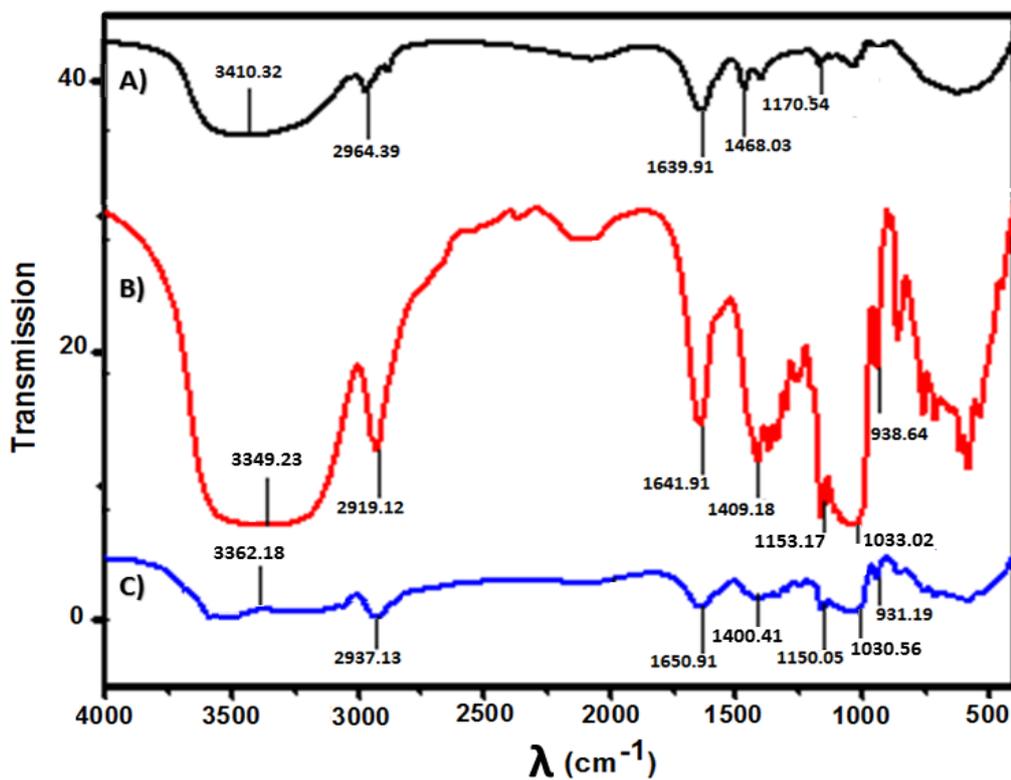


Figure 6(a).

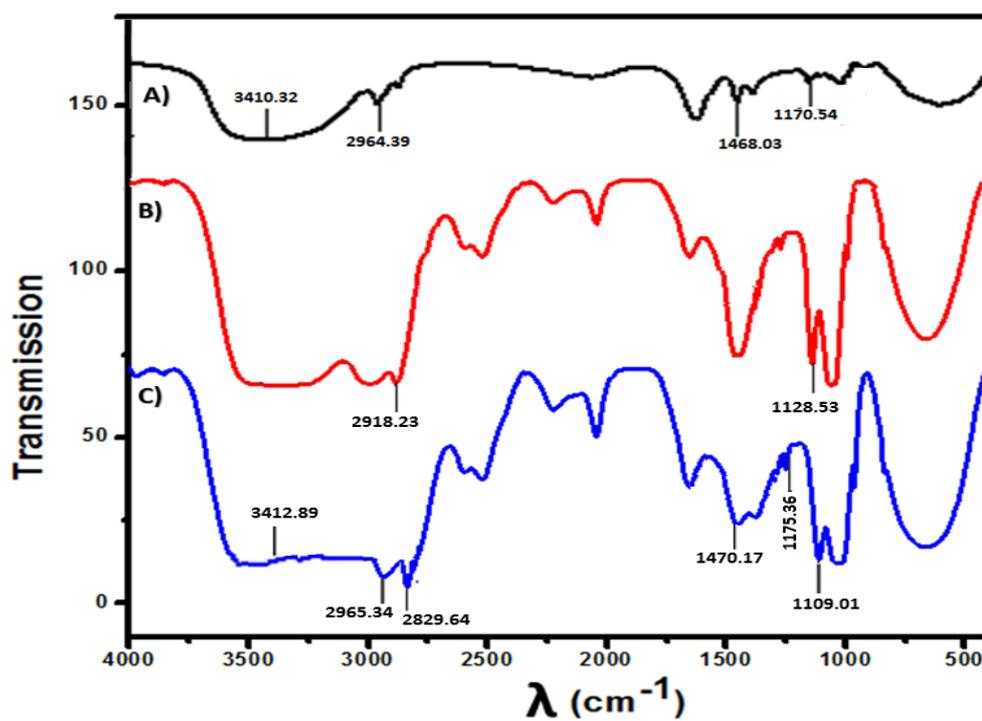


Figure 6(b).

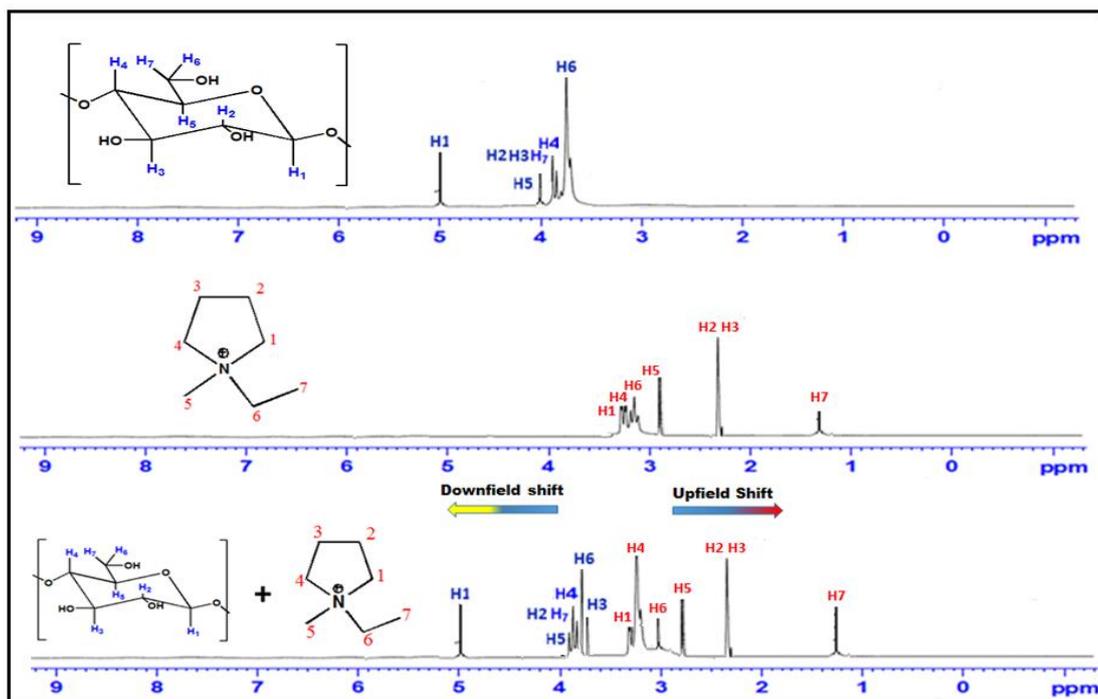


Figure 7(a).

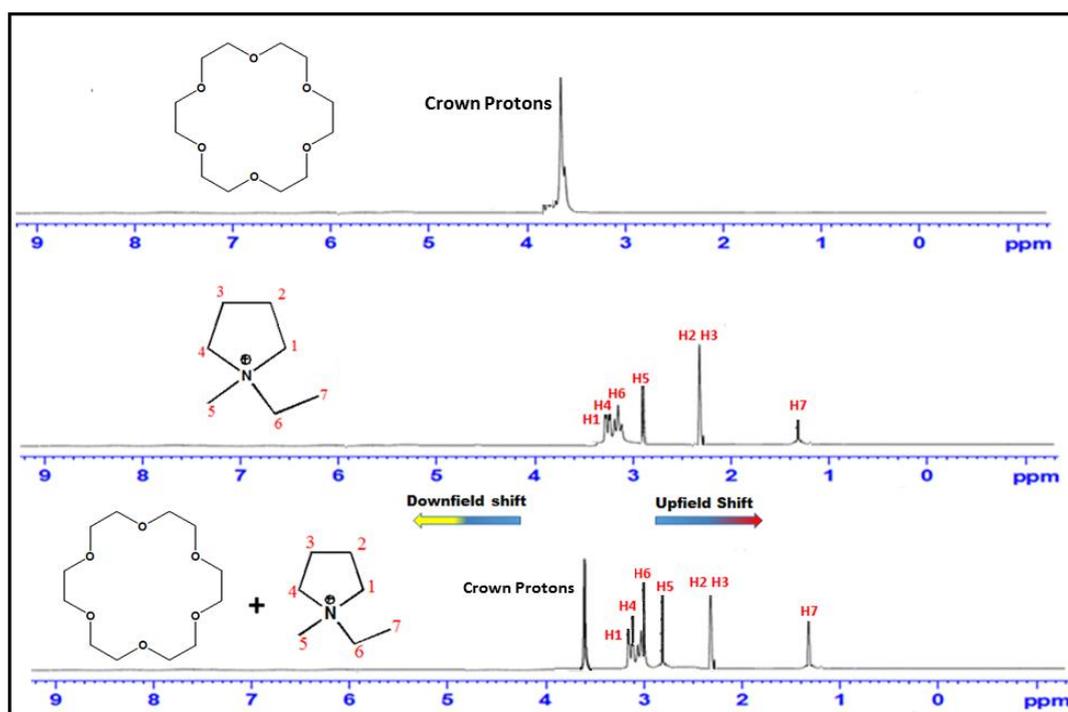


Figure 7(b).

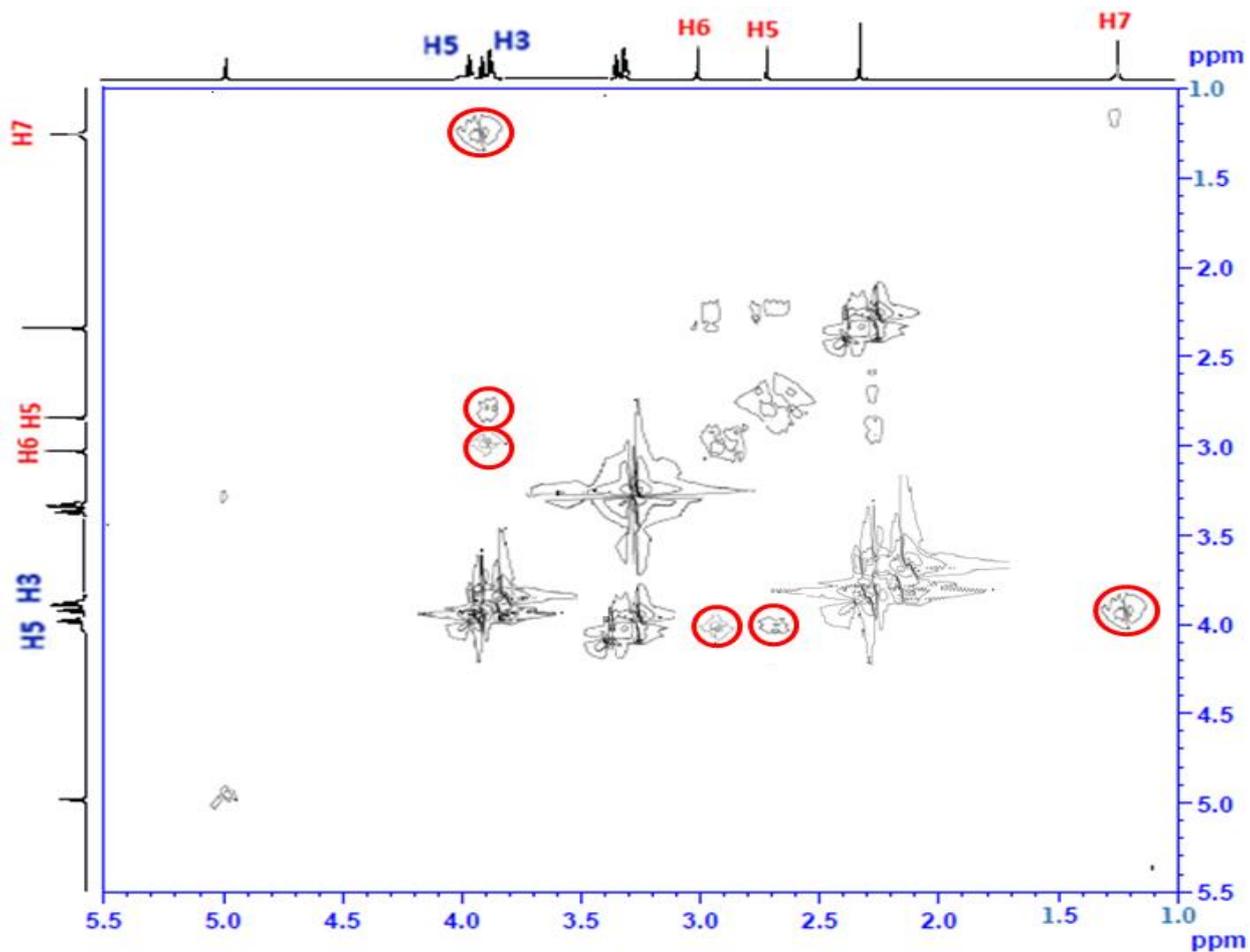


Figure 7(c).

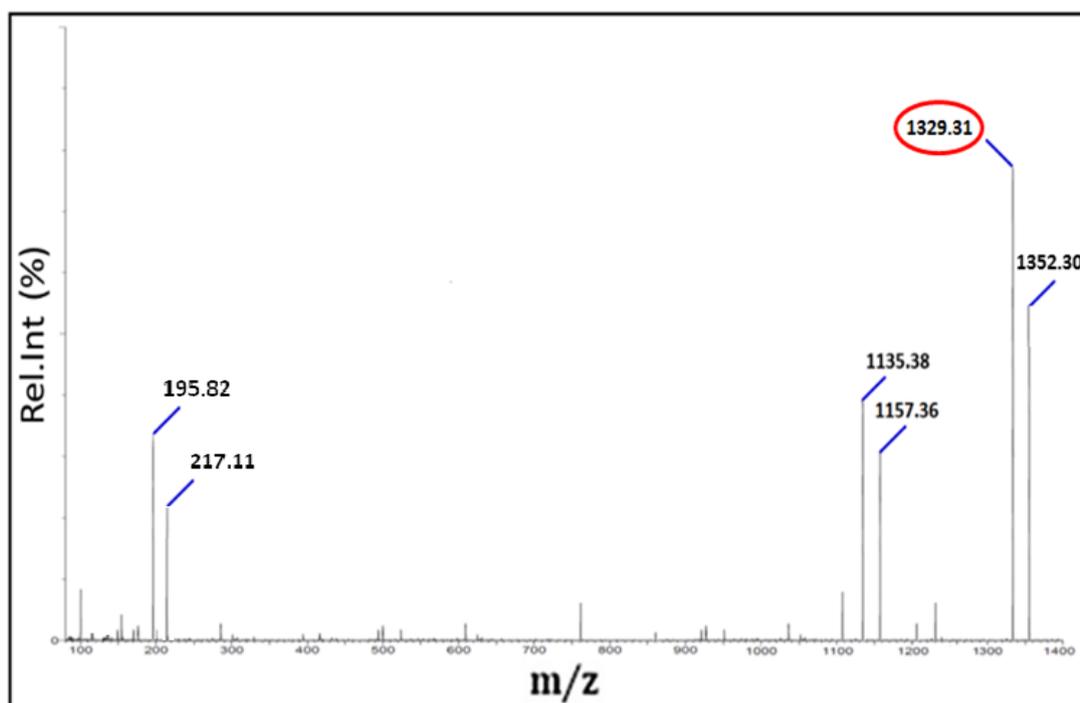


Figure 8(a).

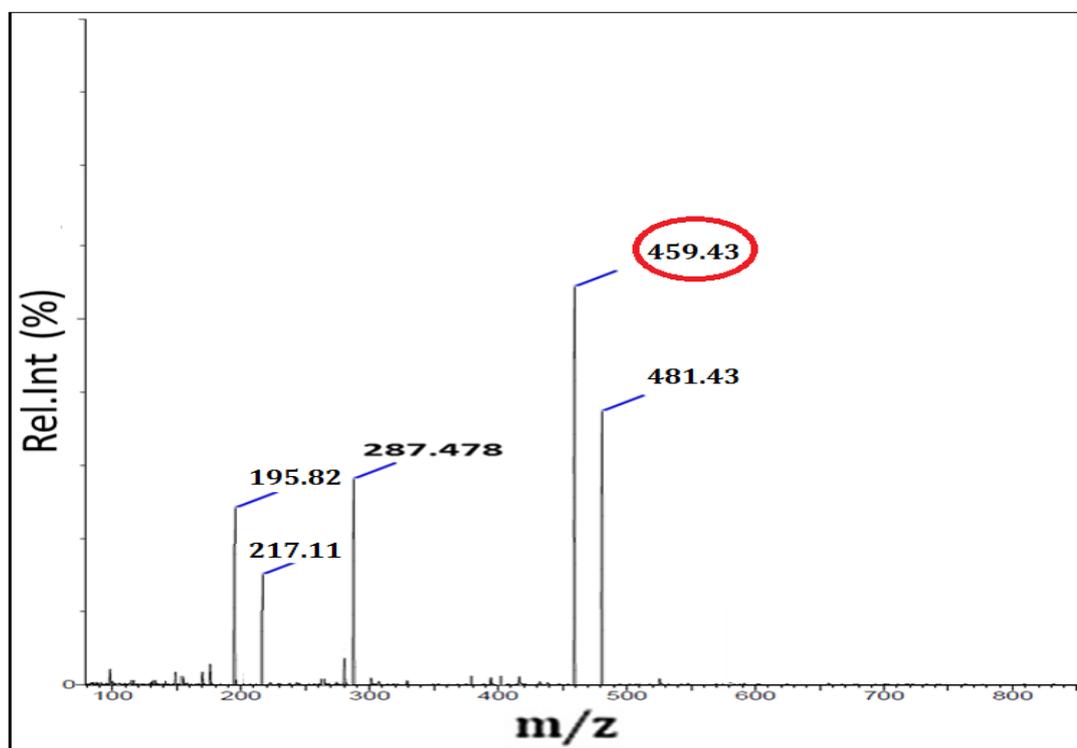


Figure 8(b).

figure Captions

- Figure 1:** Plot of limiting molar volume (ϕ_V^0) vs mass fraction for IL in aq. β -CD (blue), IL in aq. 18 C-6 (brown).
- Figure 2:** Plot of viscosity B -coefficient vs mass fraction for IL in aq. β -CD (yellow), IL in aq. 18 C-6 (brown).
- Figure 3:** Plot of limiting molar refraction (R_M^0) vs mass fraction for IL in aq. β -CD (pink), IL in aq. 18 C-6 (green).
- Figure 4(a):** Plot of surface tension (γ) against concentration for IL in aq. β -CD solutions.
- Figure 4(b):** Plot of surface tension (γ) against concentration for IL in aq. 18 C-6 solutions.
- Figure 5(a):** Plot of Molar conductance (Λ) against concentration aqueous β -cyclodextrin in mass fraction $w_1=0.001$ (M), 0.003 (M) and 0.005 (M) for IL at 298.15K respectively.
- Figure 5(b):** Plot of Molar conductance (Λ) against concentration aqueous 18 crown-6 in mass fraction $w_1=0.001$ (M), 0.003 (M) and 0.005 (M) for IL at 298.15K respectively.

Figure 6(a): FTIR spectra of [EMPyrr] Br (black), β -CD (red) and the [EMPyrr] Br- β -CD inclusion complex (blue).

Figure 6(b): FTIR spectra of [EMPyrr] Br (black), 18 C-6 (red) and the [EMPyrr] Br-18 C-6 encapsulated complex (blue).

Figure 7(a): ^1H NMR spectra of β -CD, [EMPyrr] Br and a 1: 1 molar ratio of β -CD + [EMPyrr] Br in D_2O at 298.15 K.

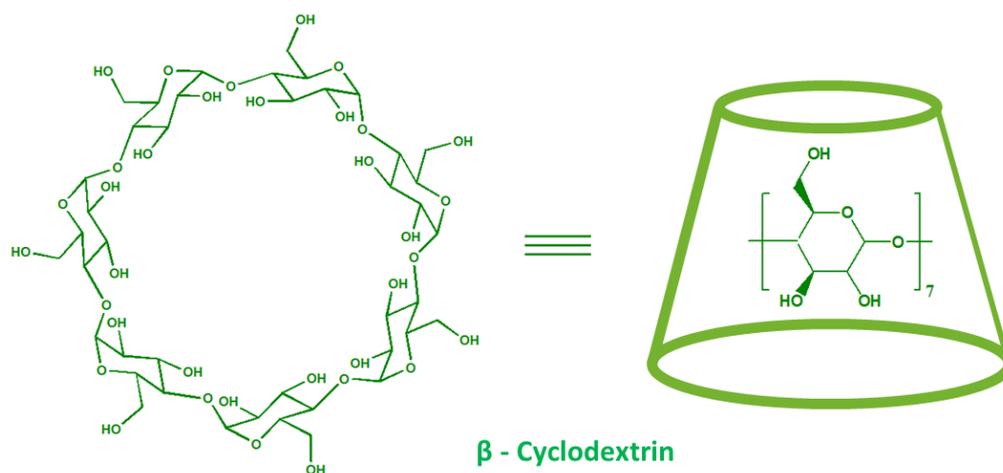
Figure 7(b): ^1H NMR spectra of 18 C-6, [EMPyrr] Br and a 1: 1 molar ratio of 18 C-6 + [EMPyrr] Br in D_2O at 298.15 K.

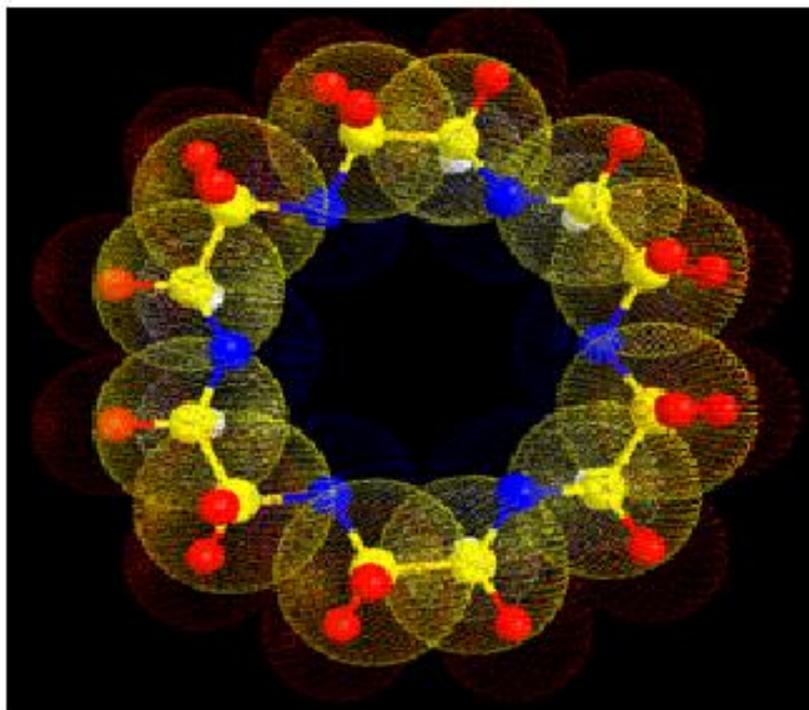
Figure 7(c): 2D ROESY spectra of the solid inclusion complex of [EMPyrr] Br and β -CD in D_2O (correlation signals are marked by red circles).

Figure 8(a): ESI mass spectra of [EMPyrr] Br- β -CD inclusion complex.

Figure 8(b): ESI mass spectra of [EMPyrr] Br-18 C-6 encapsulated complex.

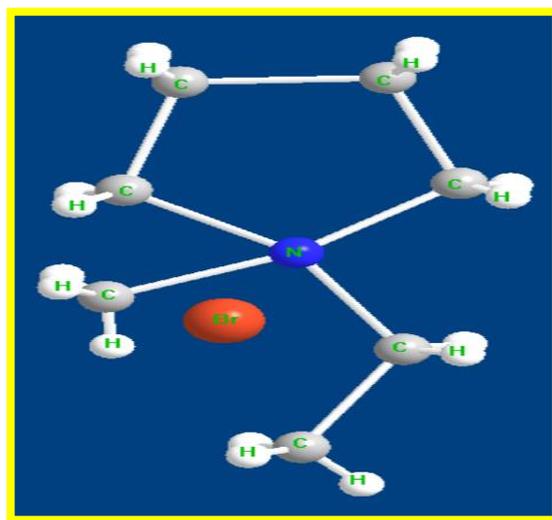
Schemes



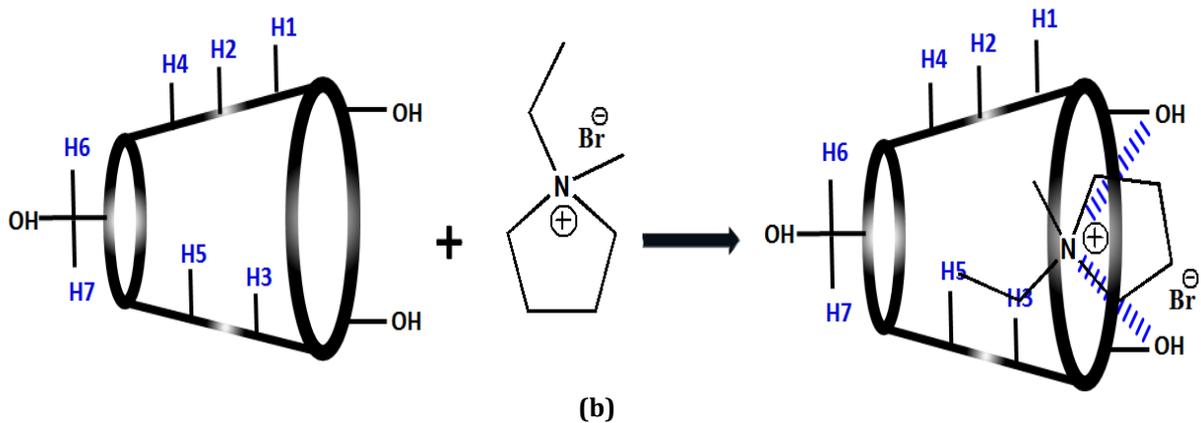
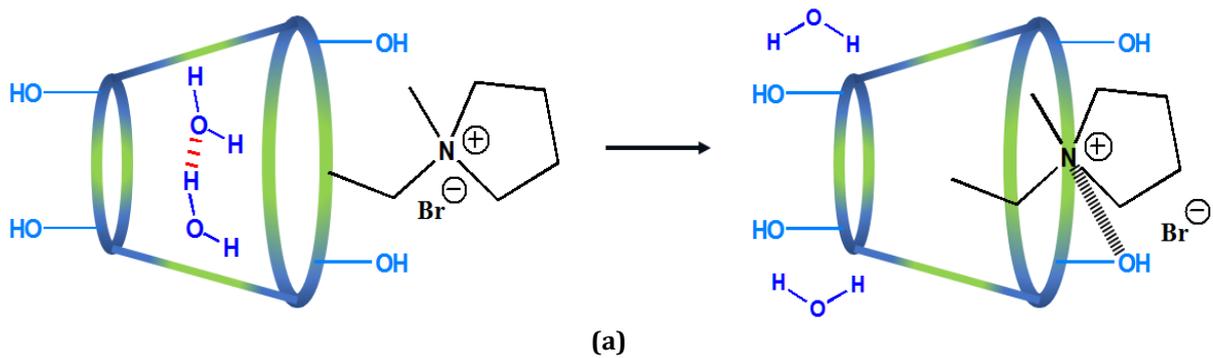


18 Crown - 6

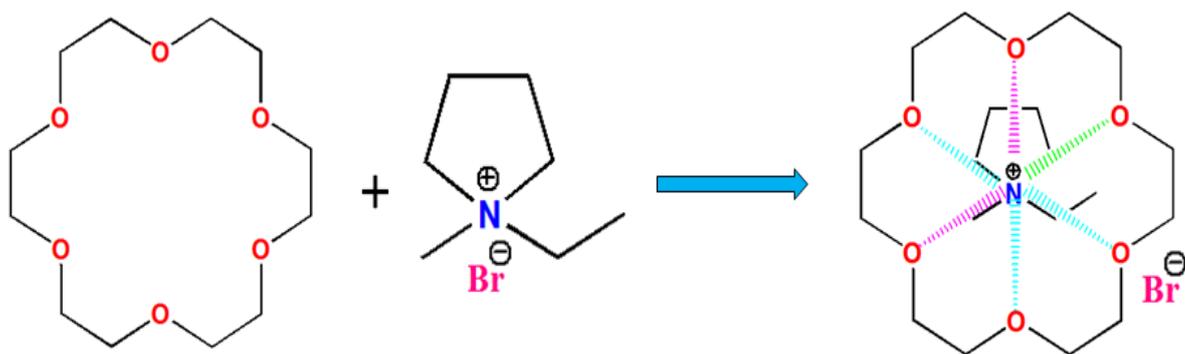
Scheme 1.



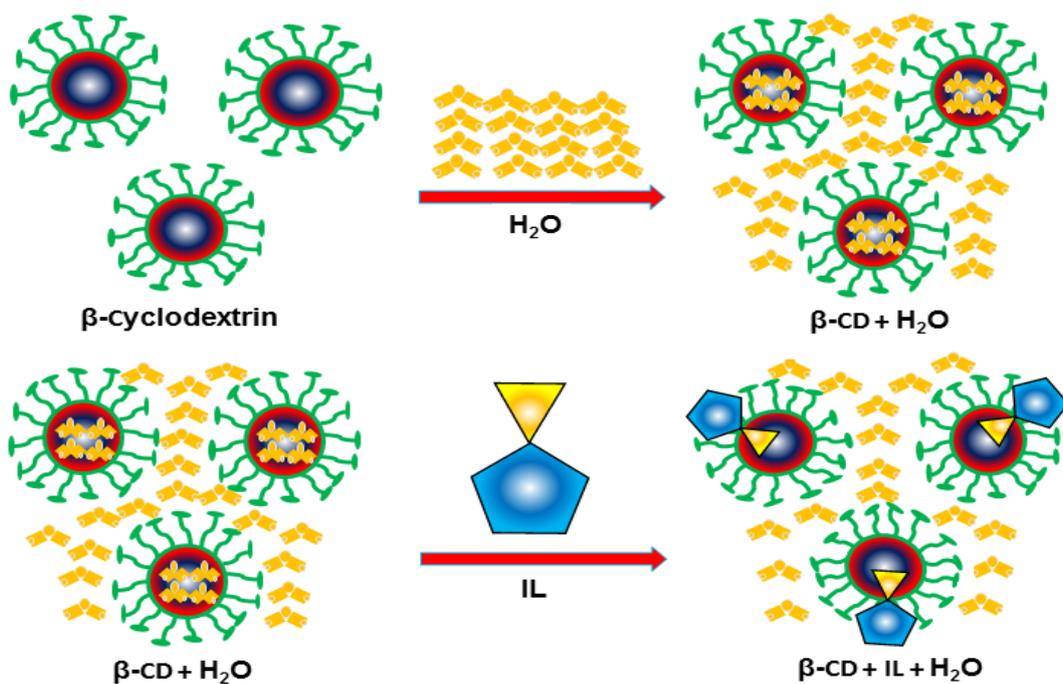
Scheme 2.



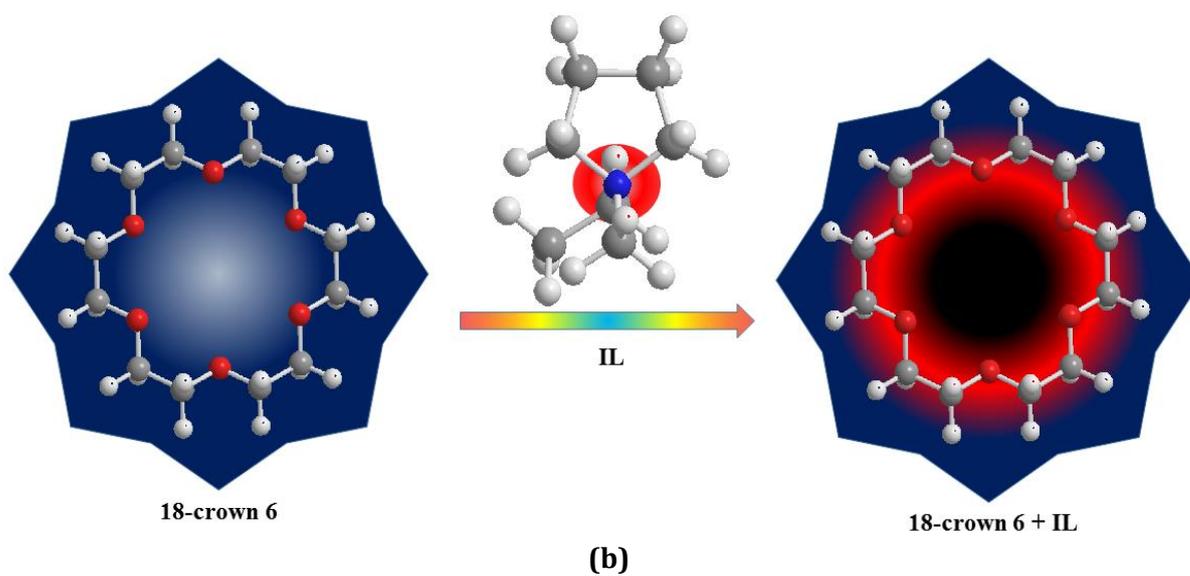
Scheme 3.



Scheme 4.



Scheme 5(a).



Scheme 5(b).

❖ Scheme captions

Scheme 1 Structure: Cyclodextrin and Crown molecules.

Scheme 2 Molecular structure of [EMPyrr] Br.

Scheme 3 (a) Schematic representation of Inclusion complexation of [EMPyrr] Br with β - Cyclodextrin.

(b) Incorporation of [EMPyrr] Br into the cavity of truncated conical structure of β -cyclodextrin showing the stereospecific complexation.

Scheme 4 Schematic representation of encapsulation interaction of [EMPyrr] Br with 18 C-6.

Scheme 5 Schematic representation of solvation of ions screening Solute – Solvent Interactions.

(a) Incorporation of IL into the hollow space of β -CD.

(b) Encapsulation of [EMPyrr] Br with 18 C-6.

+ Tables:

Table 1: Experimental data of density (ρ), viscosity (η), refractive index (n_D), surface tension (γ) in different mass fraction of aqueous 18 C-6 and β -cyclodextrin mixtures at 298.15 K^a

Aqueous. 18-C-6 solvent mixture	$\rho \times 10^{-3}$ /kg·m ⁻³	η /mP·s	n_D	γ /mN·m ⁻¹
w ₂ = 0.001	.94381	1.309	1.3330	71.56
w ₂ = 0.003	.94444	1.507	1.3331	71.42
w ₂ = 0.005	.94403	1.664	1.3333	71.33
Aqueous. β -CD solvent mixture	$\rho \times 10^{-3}$ /kg·m ⁻³	η /mP·s	n_D	γ /mN·m ⁻¹
w ₂ = 0.001	.99747	1.304	1.3329	71.71
w ₂ = 0.003	.99815	1.313	1.3332	71.61
w ₂ = 0.005	.99890	1.323	1.3336	71.57

^a Standard uncertainties u are: $u(\rho) = 2 \times 10^{-6}$ kg·m⁻³, $u(\eta) = 0.003$ mP·s, $u(n_D) = 0.0002$, $u(\gamma) = 0.03$ mN·m⁻¹, and $u(T) = 0.01$ K

Table 2: Experimental values of density (ρ), viscosity (η), refractive index (n_D), of ionic liquid in different mass fraction of aqueous 18 C-6 and β -CD mixtures at 298.15 K^a

molarity /mol·kg ⁻¹	$\rho \times 10^{-3}$ /kg·m ⁻³	η /mP·s	n_D	molarity /mol·kg ⁻¹	$\rho \times 10^{-3}$ /kg·m ⁻³	η /mP·s	n_D
Ionic Liquid + β-CD				Ionic Liquid + 18 C-6			
$w_1 = 0.001^b$				$w_1 = 0.001^b$			
0.010	0.99756	1.32	1.3333	0.010	0.94398	1.32	1.3331
0.025	0.99835	1.33	1.3339	0.025	0.94591	1.34	1.3336
0.040	0.99953	1.35	1.3343	0.040	0.94723	1.36	1.3339
0.055	1.00081	1.37	1.3349	0.055	1.00050	1.38	1.3343
0.070	1.00185	1.38	1.3352	0.070	1.00101	1.39	1.3346
0.085	1.00276	1.40	1.3355	0.085	1.00270	1.42	1.3349
$w_1 = 0.003^b$				$w_1 = 0.003^b$			

0.010	0.99870	1.33	1.3334	0.010	0.94460	1.32	1.3334
0.025	0.99963	1.35	1.3338	0.025	0.94464	1.35	1.3337
0.040	1.00064	1.37	1.3342	0.040	0.94962	1.38	1.3341
0.055	1.00173	1.39	1.3347	0.055	1.00029	1.41	1.3345
0.070	1.00286	1.42	1.3350	0.070	1.00101	1.44	1.3349
0.085	1.00407	1.45	1.3353	0.085	1.00171	1.47	1.3353
$w_1 = 0.005^b$				$w_1 = 0.005^b$			
0.010	0.99918	1.70	1.3332	0.010	0.94559	2.28	1.3326
0.025	0.99969	1.74	1.3336	0.025	0.94681	2.30	1.3330
0.040	1.00028	1.89	1.3339	0.040	1.00020	2.31	1.3333
0.055	1.00093	2.06	1.3343	0.055	1.00083	2.32	1.3335
0.070	1.00163	2.16	1.3347	0.070	1.00149	2.33	1.3338
0.085	1.00238	2.22	1.3356	0.085	1.00222	2.34	1.3341

^a Standard uncertainties u are: $u(\rho) = 2 \times 10^{-6} \text{ kg} \cdot \text{m}^{-3}$, $u(\eta) = 0.003 \text{ mP} \cdot \text{s}$, $u(n_D) = 0.0002$, $u(T) = 0.01 \text{ K}$

^b w_1 is mass fractions of β -CD and 18 C-6 in aqueous mixture

Table 3: Apparent molar volume (ϕ_V), $(\eta_r - 1)/\sqrt{c}$, and molar refraction (R_M) of selected ionic liquid in different mass fraction of aqueous 18 C-6 and β -CD mixtures at 298.15 K^a

Aq. solvent mixture	$\phi_V \times 10^{-6} / \text{m}^3 \text{ mol}^{-1}$	$(\eta_r - 1)/\sqrt{c} / \text{kg}^{1/2} \text{ mol}^{-1/2}$	$R_M / \text{m}^3 \text{ mol}^{-1}$	Aq. solvent mixture	$\phi_V \times 10^{-6} / \text{m}^3 \text{ mol}^{-1}$	$(\eta_r - 1)/\sqrt{c} / \text{kg}^{1/2} \text{ mol}^{-1/2}$	$R_M / \text{m}^3 \text{ mol}^{-1}$
Ionic Liquid + β-CD				Ionic Liquid + 18 C-6			
$w_1 = 0.001^b$				$w_1 = 0.001^b$			
0.010	140.32	2.38	38.4	0.010	67.90	1.60	24.5
0.025	137.73	2.63	40.0	0.025	66.05	1.91	27.3
0.040	135.93	2.82	41.1	0.040	64.72	2.07	28.3
0.055	134.36	2.97	41.9	0.055	63.65	2.20	29.7
0.070	133.12	3.10	42.5	0.070	62.73	2.27	30.6
0.085	132.06	3.18	42.7	0.085	61.89	2.40	31.3
$w_1 = 0.003^b$				$w_1 = 0.003^b$			
0.010	139.37	2.57	41.0	0.010	85.15	1.82	25.3
0.025	135.16	2.88	41.9	0.025	82.35	2.18	28.3
0.040	132.10	3.10	42.4	0.040	80.65	2.40	29.7
0.055	129.26	3.30	42.9	0.055	78.96	2.58	30.9
0.070	127.05	3.40	43.8	0.070	77.57	2.70	32.0
0.085	124.69	3.57	44.6	0.085	76.43	2.84	33.4
$w_1 = 0.005^b$				$w_1 = 0.005^b$			
0.010	166.29	2.76	43.1	0.010	93.10	1.93	26.7
0.025	162.68	3.10	44.5	0.025	89.10	2.30	29.3
0.040	159.78	3.30	45.1	0.040	86.30	2.60	30.7
0.055	157.37	3.54	46.0	0.055	84.00	2.80	31.8
0.070	155.28	3.69	47.0	0.070	82.09	2.94	33.2
0.085	153.33	3.85	47.8	0.085	80.74	3.17	34.3

^a Standard uncertainties u is: $u(T) = 0.01 \text{ K}$

^b w_1 is mass fractions of 18 C-6 and β -CD in aqueous mixture

Table 4: Limiting Apparent molar volume (ϕ_V^0), (S_V^*), Viscosity B - and A - co-efficients and Limiting Molar Refraction (R_M^0) of selected ionic liquid in different mass fractions of aqueous 18 C-6 and β -cyclodextrin mixtures at 298.15 K^a

Conc.	$\phi_V^0 \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	$S_V^* \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-3/2} \cdot \text{dm}^{3/2}$	$B / \text{dm}^3 \cdot \text{mol}^{-1}$	$A / \text{dm}^{3/2} \cdot \text{mol}^{-1/2}$	R_M^0
IL + β-CD					

0.001	144.50	-42.93	4.198	1.197	36.35
0.003	147.10	-40.11	5.098	2.069	39.24
0.005	173.10	-39.01	5.606	2.199	40.60
IL + 18 C-6					
0.001	71.00	-45.12	4.030	1.122	21.55
0.003	89.63	-42.15	4.974	1.139	22.00
0.005	99.43	-40.02	5.089	1.591	22.96

^a Standard uncertainties u is: $u(T) = 0.01\text{K}$

Table 5: Surface tension (γ) and the corresponding concentration (c) of ionic liquid in 0.005(m) mass fraction of aqueous 18 C-6 and β - cyclodextrin mixtures at 298.15 K^a

IL+ β CD		IL+18 C-6	
$c \times 10^4$ (mol dm ⁻³)	γ	$c \times 10^4$ (mol dm ⁻³)	γ
$w_1 = 0.005^b$			
0.010037	40.1	0.010039	77
0.025129	43.7	0.025141	76.8
0.040266	46.9	0.040297	76.6
0.055448	50.4	0.055506	76.3
0.070674	54.0	0.070769	76
0.085945	57.2	0.086087	75.8
0.010031	59.6	0.010033	75.6
0.025119	61.9	0.025131	75.4
0.040254	64.9	0.040283	75.2
0.055433	67.1	0.055484	75
0.070650	69.2	0.070730	74.8
0.085905	70.0	0.086023	74.6
0.010024	70.5	0.010026	74.3
0.025105	70.6	0.025114	74
0.040232	70.8	0.040255	73.8
0.055400	70.9	0.055444	73.6
0.070606	70.9	0.070677	73.4
0.085848	71.0	0.085950	73.2

^a Standard uncertainties u is: $u(T) = 0.01\text{K}$

^b w_1 is mass fractions of 18 C-6 and β -CD in aqueous mixture.

Table 6(a): Molar conductance (Λ_m) and the corresponding concentration (c) of ionic liquid in different mass fractions of aqueous 18 C-6 and β - cyclodextrin mixtures at 298.15 K^a

$c \times 10^4$ (mol dm ⁻³)	$\Lambda_m \times 10^4$ (S m ² mol ⁻¹)	$c \times 10^4$ (mol dm ⁻³)	$\Lambda_m \times 10^4$ (S m ² mol ⁻¹)
0.001 (M)			
IL+β-CD		IL+18 C-6	
0.0323	213.1	0.0032	149.2
0.0492	208.3	0.0080	146.5
0.0665	201.2	0.0161	143.2
0.0832	195.1	0.0269	141.4
0.0995	188.2	0.0384	139.9
0.1147	183.3	0.0480	137.5
0.1340	178.2	0.0600	136.2

0.1445	172.1	0.0751	133.1
0.1624	170.5	0.0938	127.4
0.1764	163.1	0.1173	123.2
0.1958	159.2	0.1466	120.9
0.003 (M)			
IL+β-CD		IL+18 C-6	
0.0324	199.2	0.0032	137.2
0.0492	193.1	0.0080	136.5
0.0595	188.4	0.0161	133.2
0.0840	182.1	0.0269	130.4
0.0995	178.3	0.0384	127.9
0.1147	172.2	0.0480	124.5
0.1341	163.4	0.0600	120.2
0.1445	161.2	0.0751	115.1
0.1619	156.5	0.0938	113.4
0.1764	152.2	0.1173	112.2
0.1958	146.4	0.1466	110.3
0.2084	139.2	0.1833	110.2
0.005 (M)			
IL+ β-CD		IL+18 C-6	
0.0323	188.2	0.0032	130.21
0.0503	182.1	0.0080	127.5
0.0670	175.3	0.0161	125.2
0.0832	169.9	0.0269	121.4
0.0995	165.3	0.0384	118.9
0.1037	160.2	0.0480	115.5
0.1343	155.3	0.0600	110.2
0.1395	150.7	0.0751	107.1
0.1514	146.1	0.0938	105.4
0.1784	142.5	0.1173	103.2
0.1961	136.5	0.1466	102.3
0.2079	133.3	0.1833	99.2

^a Standard uncertainties u is: $u(T) = 0.01\text{K}$

Table 6(b). Binding constants [(K_b) and (K_b')] $\times 10^{-3} \text{ M}^{-1}$ of IL: β -CD and IL: 18 C-6 complexes

Temperature	Complex	Binding constants	R^2
298.15k	IL : β -CD	1.68 (K_b)	0.995
	IL : 18 C-6	0.85 (K_b')	0.858

Std. uncertainties in temperature (T) = $\pm 0.01\text{K}^a$. Mean errors in $K_b = \pm 0.01 \times 10^{-3} \text{ M}^{-1}$

Table 7: Estimated vibrational frequencies for [β - CD : IL] and [18 C-6 : IL] Complex formation

[EMPyrr]Br	
wave number / cm ⁻¹	Group
3410.32	-C-H from ring
2964.39	-C-H from -CH ₃
1468.03	bending of -C-H from -CH ₂
1170.54	-C-N
β-CD	
wave number / cm-1	Group
3349.23	stretch of O-H
2919.12	stretch of -C-H from -CH ₂
1409.18	bend of -C-H from -CH ₂ and bending of O-H
1153.17	bend of C-O-C
1033.02	stretch of C-C-O
938.64	skeletal vibration involving α -1,4linkage
18-Crown 6	
wave number / cm-1	Group
1128.53	Stretchinhg of C-O-C
2918.23	stretching of -C-H from -CH ₂
18-Crown 6 + [EMPyrr]Br	
wave number / cm-1	Group
3412.89	-C-H from ring of [EMPyrr]Br
	-C-H from -CH ₃ of [EMPyrr]Br
2965.34	
2829.64	stretching of -C-H from -CH ₂ in Crown
1470.17	bending of -C-H from -CH ₂ of [EMPyrr]Br
1175.36	-C-N in [EMPyrr]Br
1109.01	Stretching of C-O-C
β-CD +[EMPyrr]Br	
wave number / cm-1	Group
3362.18	Stretch of O-H of β -CD
2937.13	Stretch of -C-H from -CH ₂ Of β -CD
1400.41	Bend of -C-H from -CH ₂ and bending of O-H Of β -CD
1150.05	bend of C-O-C Of β -CD
1030.56	stretch of C-C-O Of β -CD
931.19	Skeletal vibration linking α -1,4linkage of β -CD

Table 8: Analysis of ¹H NMR data of [β -CD + EMPyrr] in D₂O environment

β -CD protons	Free β -CD δ (ppm)	β -CD:EMPyrr δ (ppm)	$\Delta\delta$ (ppm)
H1	4.981	4.978	0.003
H5	4.002	3.901	0.101
H2	3.887	3.887	0.000
H3	3.887	3.646	0.241
H7	3.887	3.887	0.000

H4	3.819	3.816	0.003
H6	3.676	3.673	0.005
EMPyrr Protons	Free EMPyrrδ (ppm)	β-Cyd : EMPyrr δ (ppm)	$\Delta\delta$ (ppm)
H1	3.289	3.284	0.005
H2	2.336	2.336	0.000
H3	2.336	2.336	0.000
H4	3.225	3.220	0.005
H5	2.883	2.762	0.121
H6	3.252	3.089	0.163
H7	1.336	1.216	0.120

Table 9: Analysis of ^1H NMR data of [18 C-6 + EMPyrr] in D_2O environment

Crown protons	Free Crown δ (ppm)	Crown: EMPyrr δ (ppm)	$\Delta\delta$ (ppm)
CH_2	3.552	3.492	0.060
EMPyrr Protons	Free EMPyrr (ppm)	Crown: EMPyrr δ (ppm)	$\Delta\delta$ (ppm)
H1	3.289	3.192	0.097
H2	2.326	2.324	0.002
H3	2.326	2.324	0.002
H4	3.225	3.114	0.111
H5	2.883	2.762	0.121
H6	3.222	3.103	0.129
H7	1.336	1.277	0.059

Table 10: The observed experimental peaks at different m/z with corresponding ions for the solid Inclusion and encapsulated complexes

IL- β -CD inclusion complex		IL-18 C-6 encapsulated complex	
m/z	Ion	m/z	Ion
195.82	$[\text{EMPyrrBr} + \text{H}]^+$	195.82	$[\text{EMPyrrBr} + \text{H}]^+$
217.11	$[\text{EMPyrrBr} + \text{Na}]^+$	217.11	$[\text{EMPyrrBr} + \text{Na}]^+$
1135.38		265.32	$[\text{18 C-6} + \text{H}]^+$
1157.36	$[\beta\text{-CD} + \text{Na}]^+$	287.47	$[\text{18 C-6} + \text{Na}]^+$
1329.31	$[\text{EMPyrrBr} + \beta\text{-CD} + \text{H}]^+$	459.43	$[\text{EMPyrrBr} + \text{18 C-6} + \text{H}]^+$
1352.09	$[\text{EMPyrrBr} + \beta\text{-CD} + \text{Na}]^+$	481.43	$[\text{EMPyrrBr} + \text{18 C-6} + \text{Na}]^+$

Table S1: Experimental values of the density (ρ), viscosity (η), refractive index (n_D), surface tension (γ) in different mass fraction of aqueous 18 C-6 and β -cyclodextrin mixtures at 298.15 K^a

<i>Aq. 18 C-6 solvent mixture</i>	$\rho \times 10^{-3}$ /kg·m ⁻³	<i>H</i> /mP·s	<i>n_D</i>	γ /mN·m ⁻¹
<i>w₂ = 0.001</i>	0.94381	1.309	1.3330	71.56
<i>w₂ = 0.003</i>	0.94444	1.507	1.3331	71.42
<i>w₂ = 0.005</i>	0.94403	1.664	1.3333	71.33
<i>Aq. β-CD solvent mixture</i>	$\rho \times 10^{-3}$ /kg·m ⁻³	<i>H</i> /mP·s	<i>n_D</i>	γ /mN·m ⁻¹
<i>w₂ = 0.001</i>	0.99747	1.304	1.3329	71.71
<i>w₂ = 0.003</i>	0.99815	1.313	1.3332	71.61
<i>w₂ = 0.005</i>	0.99890	1.323	1.3336	71.57

{ ^a Standard uncertainties *u* are $u(\rho) = 2 \times 10^{-6} \text{ kg} \cdot \text{m}^{-3}$, $u(\eta) = 0.003 \text{ mP} \cdot \text{s}$, $u(n_D) = 0.0002$, $u(\gamma) = 0.03 \text{ mN} \cdot \text{m}^{-1}$, and $u(T) = 0.01 \text{ K}$ }

5. Experimental methods

5.1. Materials

The IL 1-ethyl-1-methylpyrrolidinium bromide [EMPyrr] Br of puriss p.a. was procure and used as purchased from Sigma-Aldrich, Germany. The mass fraction purity of the studied IL was $\geq 99\%$. β -cyclodextrin, 18-C-6 of puriss grade was procured from Sigma-Aldrich, Germany. The purities of these compounds were $\geq 99\%$ respectively.

5.2. Apparatus in addition to Procedure

Stock solution for β -cyclodextrin, 18-C-6 were prepared by means of mass measurements (Mettler Toledo AG285 with uncertainty 0.0003 g), and working solutions were obtained by the method of mass dilution at 298.15K. Uncertainty of molarity of different solutions studied was evaluated to $\pm 0.0001 \text{ mol dm}^{-3}$. Thus it was observed that the two solutions viz., [IL+ β CD] and [IL + 18-C-6] were completely miscible in aqueous solutions.

Density was calculated via vibrating-tube Anton Paar density- meter (DMA 4500M) with the precision of $0.00005 \text{ g} \cdot \text{cm}^{-3}$. Densitometer was calibrated by double-distilled water and dry air Table 1.

Viscosity was also measured by using Brookfield DV-III Ultra Programmable Rheometer with spindle size-42 fitted to a Brookfield Digital Bath TC-500.

Refractive index was also measured via Digital Refractometer Mettler Toledo instrument. The light source thus used was LED, ($\lambda = 589.3 \text{ nm}$). Refractometer was calibrated twice by

means of distilled water, and thus the calibration was checked after every few measurements. Uncertainty of refractive index measurement was about ± 0.0002 units.

Surface tension experiments were done by platinum ring detachment method by Tensiometer (K9, KRÚSS; Germany) at studied experimental temperature. The accuracy of measurement was within $\pm 0.1 \text{ mN}\cdot\text{m}^{-1}$. Temperature of the systems has been maintained by circulating auto-thermo stated water through the double-wall glass vessel containing solution.

Conductance measurements were carried via a Systronic-308 conductivity meter (accuracy $\pm 0.01 \%$) using a dip-type immersion conductivity cell, CD-10, with a cell constant of approximately $(0.1 \pm 0.001) \text{ cm}^{-1}$. Measurements were made in water bath maintained within $T = (298.15 \pm 0.01) \text{ K}$ and then the cell were then calibrated. Conductance data were reported at a frequency of 1 kHz, accuracy was maintained at $\pm 0.3\%$.

^1H NMR spectrum were verified in D_2O with Bruker Advance 300 MHz instrument at about 298.15 K. The Signals are therefore given as δ values with ppm by means of residual protonated solvent signals as internal standard (HDO $\delta = 4.79 \text{ ppm}$). Data reported as chemical shift values.

Fourier transform infrared (FT-IR) spectrum was recorded by the use of Perkin Elmer FT-IR spectrometer according to KBr disk technique. Samples were prepared in KBr disks by 1 mg of complex along with 100 mg of KBr. The FTIR measurements were observed in scanning range of $4000\text{--}400 \text{ cm}^{-1}$ at 298.15k.

Each of the two solid inclusion complexes ([EMPyr] Br + 18 C-6, and [EMPyr] Br + β -CD) has been prepared in a 1: 1 molar ratio. In each case 1.0 mmol of cyclodextrin and 18C-6 was dissolved in 20 mL of water and 1.0 m mol of ionic liquid was suspended in 20 mL of H_2O and stirred separately for about 3 hours. Then aqueous solution of the studied ionic liquid was added drop by drop to aqueous CD and 18-C-6 solutions. The mixture was allowed to stir for 48 hours at $50\text{--}55^\circ\text{C}$, then it was filtered at this temperature, further cooled to 5°C and kept for 12 hours. The resulting suspension was slowly filtered and the filtrate appeared as white polycrystalline powder, which was purified and dried in air.

HRMS analyses were performed with a Q-TOF high resolution instrument by positive mode electro-spray ionization by dissolving solid ICs in methanol.

Keywords: 'Ionic liquid', '18-Crown 6', ' β -cyclodextrin', 'encapsulation interaction', 'inclusion complexation'.

Chemical compounds studied in the article: β -cyclodextrin, 18- Crown 6, 1-ethyl-1-methyl pyrrolidinium bromide.

Abbreviation

IC: Inclusion complex

IL : Ionic liquid

β - CD : Beta - Cyclodextrin

18-C-6 : 18 -Crown -6

[EMPyrr] Br: 1-ethyl-1-methylpyrrolidinium bromide

Conflicts of interest

Authors declare that there are no conflicts of interest.

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