CHAPTER-IX

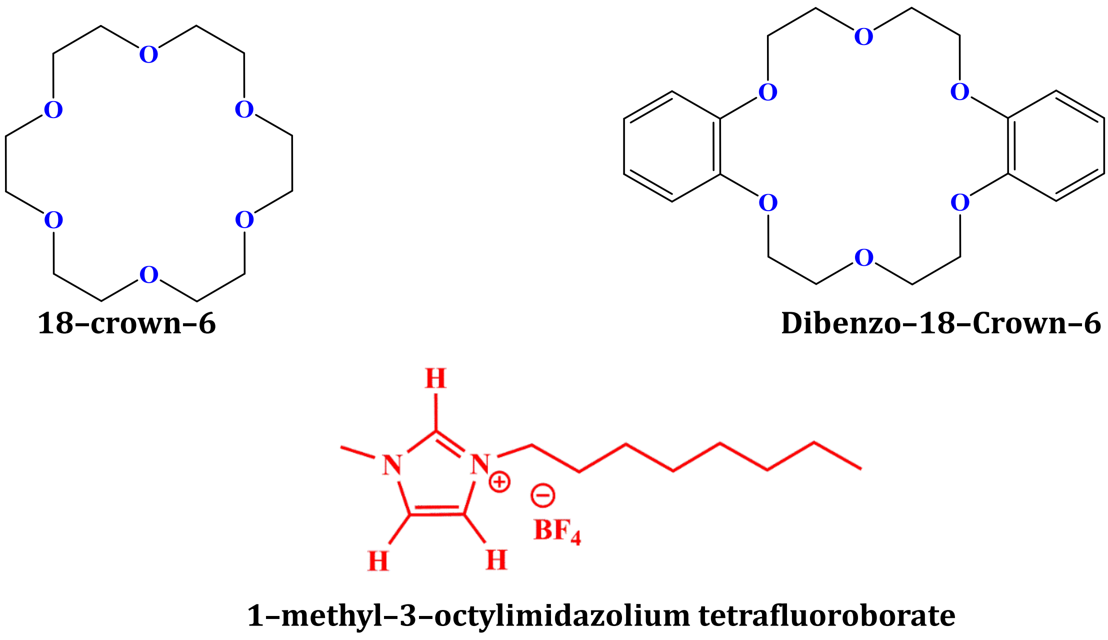
HOLLOW CIRCULAR COMPOUND-BASED INCLUSION COMPLEXES OF AN IONIC LIQUID

IX.1. INTRODUCTION

The crown ether (CE) family of macrocyclic compounds has attracted a huge amount of interest since their discovery in 1967 [1,2], especially in the fields of host–guest and coordination Chemistry. They can form complexes with a variety of guest species, such as metal cations, protonated species and neutral molecules, in their cavity via different types of interactions with multiple oxygen atoms [3,4]. Applications of CEs, such as phase transfer catalyst [5,6], photo-switching devices [7], and drug carriers [8], have been in progress on the basis of the inclusion ability. Crown ethers have proved to be unique cyclic molecules for molecular recognition of suitable substrates by hydrogen bonds, ionic interactions and hydrophobic interactions. The study of interactions involved in complexation of different cations with crown ethers in mixtures of solvents is important for a better understanding of the mechanism of biological transport, molecular recognition, and other analytical applications [9].

It is already known that the imidazolium cation can form inclusion complexes with large crown-ether-type hosts via H-bonding [10]. 1, 3-disubstituted imidazolium salts are known to form an inclusion complex with DB24C8 or its derivatives through intermolecular hydrogen-bond formation as demonstrated by different research groups [11-14]. In 1,3-disubstituted imidazolium salts, all protons on the imidazolium ring are quite acidic, as the positive charge is delocalized over the entire imidazolium ring [15]. The acidic protons are attractive in supramolecular chemistry, since the acidic protons participate in stronger hydrogen-bond formation with the lone pair of electrons of the oxygen this accounts for the stability of the adduct formed. Biologically important heterocyclic bases, like imidazole, form planar cations, act as an effective structural unit at the active sites of various proteins and nucleic acids. However, during enzymatic reactions imidazole can also exist as a protonated cation, and may then interact with the substrate by direct electrostatic or π-π interactions. Imidazolium salts have been and are going to be significant not only in organometallic chemistry as precursors of N-heterocyclic carbenes [16, 17], but also in organic chemistry and material science areas as ionic liquids due to their unique chemical, physical, and electrical properties [18-21].

In this work, we have studied the inclusion complex formation of ionic liquid (IL) 1-methyl-3-octylimidazolium tetrafluoroborate with hollow circular based host 18-crown-6 (18C6) [complex 1] and dibenzo-18-crown-6 (DB18C6) [complex 2] in acetonitrile (ACN). The complexes were characterized by Conductance and IR study. The formation constant and thermodynamic parameters of the above specific interactions in solutions are discussed here. The structure of the IL 1-methyl-3-octylimidazolium tetrafluoroborate and both crown ethers are shown in **Scheme IX.1**.



18–crown–6

Dibenzo–18–Crown–6

1–methyl–3–octylimidazolium tetrafluoroborate

Scheme IX.1: Molecular structure of crown ethers and IL.

IX.2. EXPERIMENTAL SECTION

IX.2.1 Reagents

The ionic liquid (97%) and crown ethers [18C6 (99%), DB18C6 (98%)] were bought from Sigma-Aldrich, Germany and used as purchased.

IX.2.2 Instrumentations

Prior to the start of the experimental work solubility of the chosen CEs and IL in ACN have been precisely checked and it was observed that the selected IL salt freely soluble in all proportion of CEs solution.

The conductance measurements were carried out in a Systronics-308 conductivity bridge of accuracy ±0.01%, using a dip-type immersion conductivity cell, CD-10 having a cell constant of approximately (0.1±0.001) cm^{-1} [22]. The measurements were made in an auto-thermostated water bath maintaining the experimental temperature. The cell was calibrated using a 0.01M aqueous KCl solution. The uncertainty in temperature was 0.01 K.

Infrared spectra were recorded in 8300 FT-IR spectrometer (Shimadzu, Japan). The details of the instrument have formerly been described [23].

^{1}H NMR spectra were recorded in CD_3CN at 300 MHz using Bruker ADVANCE 300 MHz instrument. Signals are quoted as δ values in ppm using residual protonated solvent signals as internal standard (CD_3CN: δ 1.98 ppm). Data are reported as chemical shift.

IX.3. RESULTS AND DISCUSSION

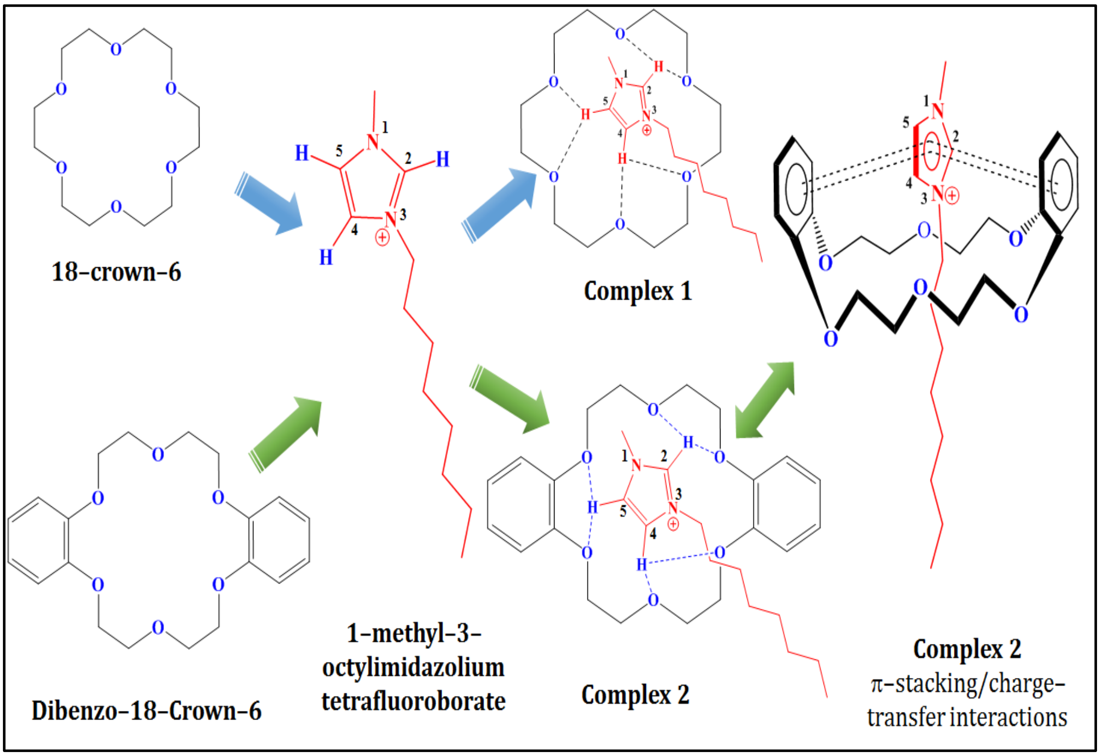
IX.3.1 Conductance

The benefit of the conductometric study is that the measurements can be carried out with high precision at very low concentration in solution systems. Conductance measurements of a solution of IL in presence of a crown ether provide information about the stability and transport phenomena of the cation-crown ether complex in the solution. Also, it is one of the most reliable methods for obtaining the formation constants of cation-macrocyclic complexes (Takeda et al., 1991) [24].

A conductance study of the interaction between imidazolium cation of the IL with 18C6 and DB18C6 in ACN solutions is reported at different temperatures and the values are presented in the **Table IX.1**. The stability of these complexes depends mainly on the strength of the bonds between acidic protons of the imidazolium ring and crown ethers oxygen atoms (**Scheme IX.2**).

Table IX.1: Values of observed molar conductivities, Λ, at various mole ratios for the system IL-18C6 (complex 1) and IL-DB186 (complex 2) at different temperature

Mole Ratio	**Λ (S. cm^2. Mol^{-1})**					
	DB18C6			**18C6**		
	293.15 K	**298.15 K**	**303.15 K**	**293.15 K**	**298.15 K**	**303.15 K**
0	135.80	143.72	152.21	154.00	162.58	168.36
0.099	132.10	138.34	147.60	149.10	156.50	163.84
0.196	128.50	133.80	143.12	144.60	151.68	159.56
0.291	125.07	130.60	139.72	140.76	147.20	154.72
0.385	121.61	127.82	135.80	137.88	143.12	150.50
0.476	117.82	124.92	132.24	134.10	138.34	145.42
0.566	114.24	121.52	128.56	130.18	134.80	141.64
0.654	110.12	117.92	125.14	126.84	130.60	137.68
0.740	107.30	115.60	122.46	123.18	127.82	134.54
0.825	105.20	112.32	119.32	120.24	124.50	131.50
0.909	102.30	109.50	116.22	117.46	121.92	128.96
1.071	100.14	106.44	113.6	113.38	118.06	124.58
1.228	99.06	105.46	111.52	112.14	116.82	121.80
1.379	98.90	104.14	110.72	111.70	116.22	120.62
1.667	98.20	103.56	109.28	111.22	115.54	120.04
1.935	97.70	102.12	108.14	110.82	114.92	119.38
2.187	96.80	101.30	107.58	110.34	114.34	118.92
2.424	95.50	100.28	107.02	109.68	113.62	118.46
2.647	95.00	99.88	106.66	109.06	113.02	117.70
2.857	94.40	99.08	106.16	108.52	112.44	117.32
3.333	94.02	98.52	104.08	108.24	112.06	116.84
3.750	93.36	97.44	103.42	108.58	111.42	115.46



Scheme IX.2: Plausible schematic presentation of complex formation between imidazolium cation and crown ethers.

The molar conductance (Λ) of imidazolium salt (5×10^{-4} M) in ACN solution was monitored as a function of crown ether to imidazolium cation mole ratio at various temperatures. The resulting molar conductance vs. crown/cation mole ratio plots at 298.15, 303.15, and 308.15 K are shown in **Figure IX.1** and **IX.2**. In both case, there is a gradual decrease in the molar conductance with an increase in the crown ether concentration. This behavior indicates that the complexed imidazolium cation is less mobile than the corresponding free imidazolium cation in ACN and since the imidazolium salt is strong electrolyte in acetonitrile the changes are not due to ion pairing, unless the complexation of the cation causes the imidazolium salt to associate. Both **Figure IX.1** and **Figure IX.2** shows that the complexation of imidazolium cation with both crown ethers, addition of the crown solution to the imidazolium salt solution causes a continuous decrease in the molar conductance, which begins to level off at a mole ratio greater than one, indicating the formation of a stable 1:1 complex [25,26]. By comparison of the molar conductance-mole ratio plot for imidazolium cation–crown ether systems obtained at different temperatures (**Figure IX.1** and **Figure IX.2**), it can be observed, that the corresponding molar conductance increased rapidly with temperature, due to the decreased viscosity of the solvent and, consequently, the enhanced mobility of the charged species present.

The stability of these complexes depends mainly on the strength of the bonds between acidic protons of the imidazolium ring and crown ethers oxygen atoms (**Scheme IX.2**). The formation constants determined by the conductivity study and thermodynamic values for the complex formation between crown ethers and imidazolium cation in acetonitrile solution are summarized in **Table IX.2**. The formation constants (log K_f) of the 1:1 complexes at different temperatures varied in the order 18C6 >DB18C6 for the IL. Thus, a decrease in the net charge on oxygen atoms during the introduction of two benzo group into the macrocycle makes the obtained complex less stable.

Table IX.2: Values of formation constant, enthalpy, entropy and free energy change of different crown ethers complexes in ACN solution

Crown	**log K_f (M^{-1})**			**ΔH°** **($kJ\ mol^{-1}$)**	**ΔS°** **($J\ mol^{-1}K^{-1}$)**	**ΔG°** **($kJ\ mol^{-1}$)**
	298.15 K	**303.15 K**	**308.15K**			
18C6	3.35	3.14	2.97	-65.02	-157.67	-18.01
DB18C6	3.05	2.96	2.87	-29.90	-43.57	-16.91

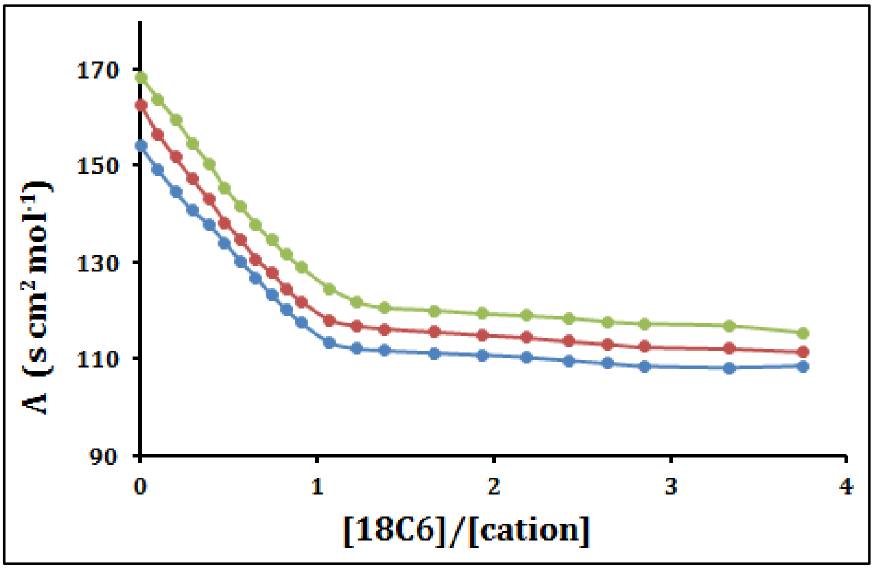


Figure IX.1: Molar conductance vs [18C6]/[cation] at 298.15 K (▲) , 303.15 K (■), 308.15 K (●).

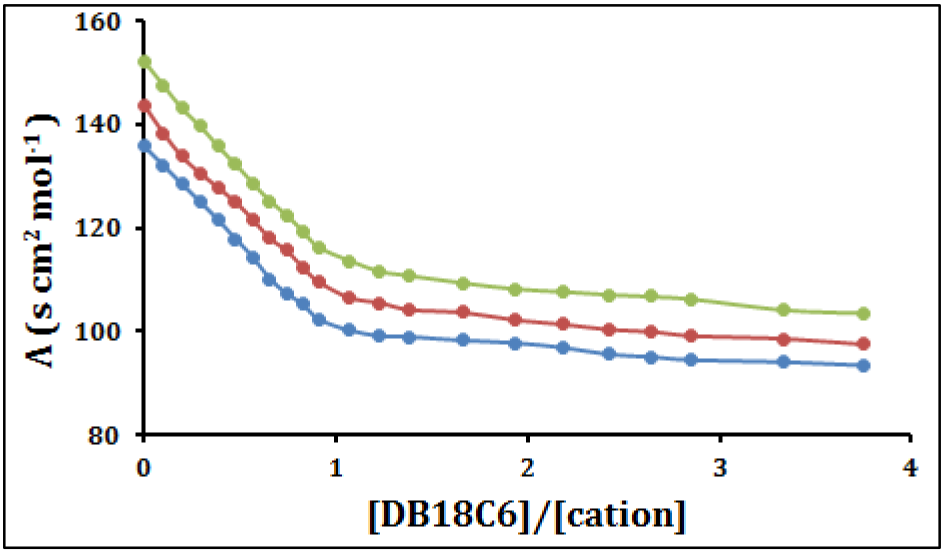


Figure IX.2: Molar conductance vs [DB18C6]/[cation] at 298.15 K (Δ) , 303.15 K (□), 308.15 K (○).

IX.3.2 Association constant and Thermodynamic parameter

The following mathematical treatment to calculate the formation constant is based on Evans et al. (1972) [27]

The 1:1 complexation of IL with 18C6 crown ether can be expressed by the following equilibrium

$$M^{+} + C \xleftrightarrow{K_f} MC^{+} \qquad (1)$$

The corresponding equilibrium constant, K_f is given by

$$K_f = \frac{[MC^{+}]}{[M^{+}][C]} \times \frac{f(MC^{+})}{f(M^{+})f(C)} \qquad (2)$$

where $[MC^{+}]$, $[M^{+}]$, $[C]$ and f symbolize the equilibrium molar concentrations of the complex, free cation, free ligand (crown ethers) and the activity coefficients of the species indicated, respectively. Under the dilute conditions used, the activity coefficient of uncharged macrocycle, $f(C)$, can be reasonably assumed as unity [28]. The use of the Debye-Hückel limiting law [29], leads to the conclusion that $f(M^{+}) \sim f(MC^{+})$, so the activity coefficients in Equation (2) cancel. The complex formation constant in terms of the molar conductances, Λ, can be expressed as [25,28].

$$K_f = \frac{[MC^{+}]}{[M^{+}][C]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{MC})[C]} \qquad (3)$$

$$\text{Where} \qquad [C] = C_C - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{MC})} \qquad (4)$$

Here, Λ_M is the molar conductance of the metal ion before addition of ligand, Λ_{MC} the molar conductance of the complexed ion, Λ_{obs} the molar conductance of the solution during titration, C_C the analytical concentration of the macrocycle added and C_M the analytical concentration of the salt. The complex formation constant, K_f, and the molar conductance of the complex, Λ_{MC}, were evaluated by using Equations (3) and (4).

Complexation enthalpy changes are mainly related to: (i) cation-crown interactions, (ii) solvation energies of the species in solvent systems involved in the complexation reactions (iii) repulsion between neighboring donor atoms, and (iv) steric deformation of the crown (v) number of H-bond present for H-bonding. Entropy changes are linked to: (i) change in the number of particles involved in the complexation process, and (ii) conformational changes of the crown ether accompanying the complexation.

In order to have a better understanding of the thermodynamics of the complexation reactions of imidazolium cation with crown ethers is useful to consider the enthalpic and entropic contributions to these reactions. The ΔH° and ΔS° values for the complexation reactions were evaluated from the corresponding $\log K_f$ and temperature data by applying a linear least-squares analysis according to the equation:

$$2.303 \log K_f = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{5}$$

Plots of $\log K_f$ vs. $\frac{1}{T}$ for both complex (complex 1 and complex 2) is linear (**Figure IX.3**).

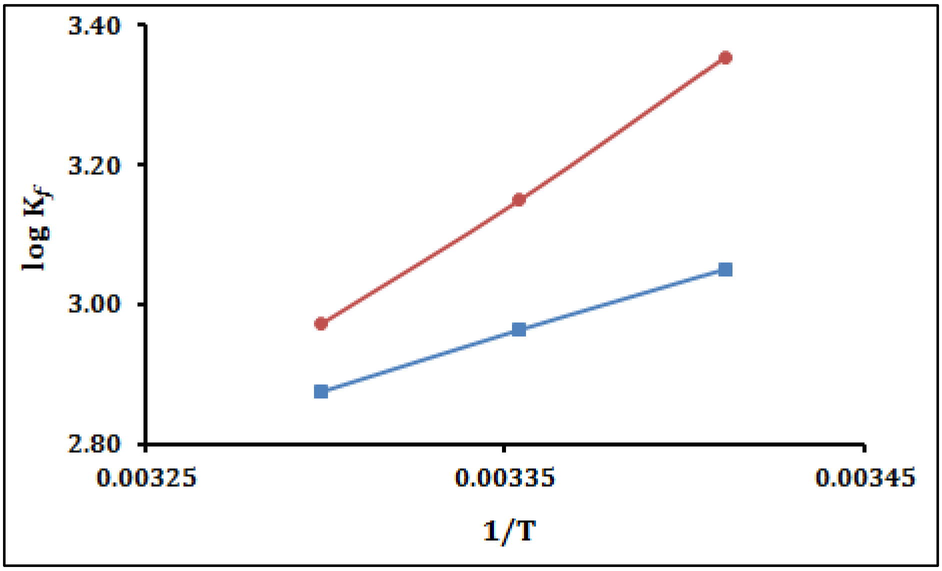


Figure IX.3: The linear relationship of log K_f vs. 1/T for the interaction of IL with 18C6 (●) and DB18C6 (■).

The enthalpy (ΔH^0) and entropy (ΔS^0) of complexation were determined from the slopes and intercepts of the plots and the results are also listed in **Table IX.2**. Both of these two parameters have negative values. True molecular recognition and a physical attraction between host and guest should result in a favorable enthalpy change (ΔH) on complexation. The negative values of enthalpy confirm that when imidazolium cation interact with the crown ether molecules the overall energy of the system is decreased, i.e., there is some stabilization interaction in the system, whereas negative values of entropy factor indicate that there is an ordered arrangement, *i.e.*, complex formation takes place between the imidazolium and the crown molecules. Other investigators [30-32] established that the binding of the free amino acids with 18C6 has negative enthalpy and negative entropy which indicates that the process is driven by a favorable enthalpy change only.

The two fundamental equations $\Delta G = -RT \ln K$ and $\Delta G = \Delta H - T\Delta S$ are useful in comparing the contributions of enthalpy and entropy towards the stability of different complexes. The negative value of entropy is unfavorable for the spontaneity of the complex formation, but this effect is overcome by higher negative value of ΔH^0. The values of ΔG^0 (**Table IX.2**) for the complex formation was found negative suggesting that the complex formation process proceeds spontaneously.

The data shown in **Table IX.2** indicates that formation constant $\log K_f$ for imidazolium cation with both crown is highest at 298.15K and decreases with increase in temperature i.e. imidazolium cation form stable complex with crown at 298.15K.

IX.3.3 IR Study

The IR spectra of 18C6, IL and complex 1 are shown in **Figure IX.4** and the spectra of DB18C6, IL and complex 2 are shown in the **Figure IX.5** in the 4000–500 cm^{-1} region. The shift of IR spectra of crown ethers in ACN solution indicates that the specific interactions observed in the crown ether complexes are in fact typical hydrogen bonds of the imidazolium ring with the donor atoms of the crown ether. Comparing with the spectrum of the free crown ethers, most of these bands are shifted to lower energy presumably due to less restriction on the coupling of some vibrational modes caused by bonding of oxygen atoms of the polyether ring with the C-H protons of the imidazolium ring in both the complexes.

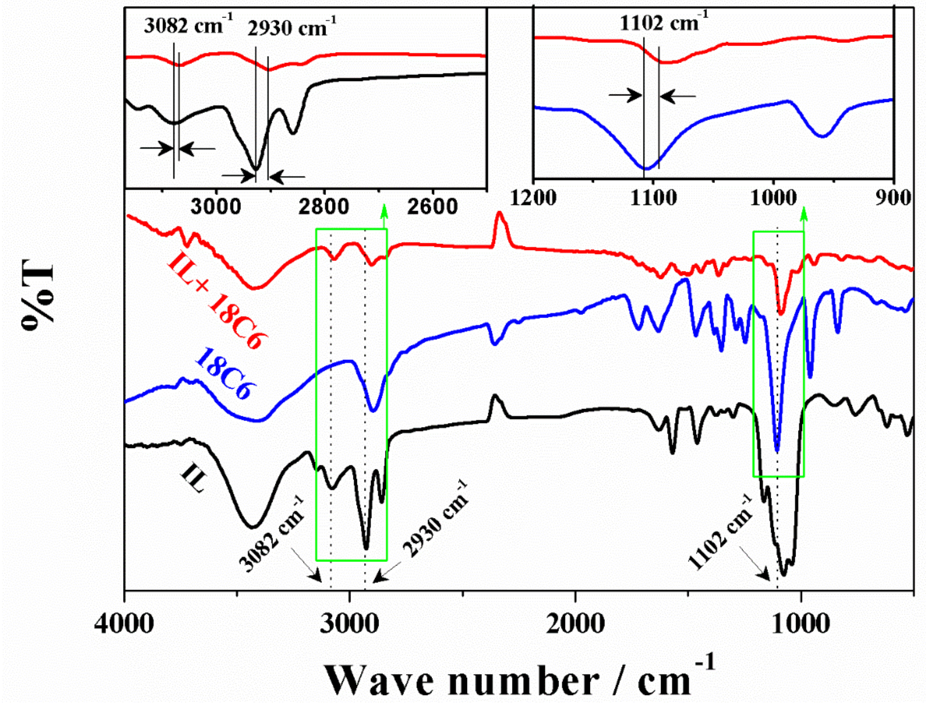


Figure IX.4: FTIR spectra of free IL (Black), 18-crown-6 (Blue) and complex (Red).

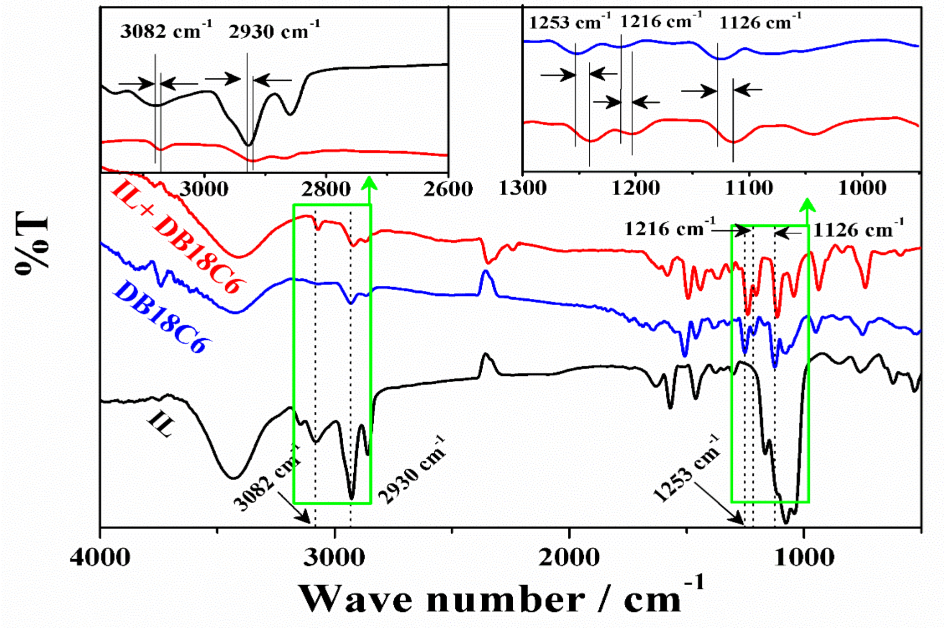


Figure IX.5: FTIR spectra of free IL (Black), Dibenzo-18-crown-6 (Blue) and complex (Red).

In the case of 18C6 a very strong and sharp IR band centered at 1102 cm^{-1} is assigned to the characteristic absorption due to the C-O-C asymmetric stretching vibrational motion [$\nu(C-O-C)_{aliph.}$]. This sharp peak is shifted to lower frequency 1082 cm^{-1} in the complex 1 (**Figure IX.4**).The $\nu(C-O-C)_{arom}$ stretching vibrations of DB18C6 are observed at 1126 cm^{-1} and these peak is also shifted to lower frequency 1108 cm^{-1} in the complex 2 (**Figure IV.5**).The presence of benzene rings in the DB18C6 make the IR spectra more difficult to assign because of their characteristic bands which may overlap with those of ethylene glycol groups. In the IR spectra, the bands in the 2800–3000 cm^{-1} region correspond to the CH stretching vibrations of the methylene groups of crown ethers. The CH stretching frequency of the methylene groups observed at 2895 cm^{-1} in 18C6 is shifted to higher frequency due to the perturbation of the methylene groups. Interaction of the O atoms of the crown with the protons of the imidazolium ring via hydrogen H-bonds are responsible for the perturbation. 1200-1300 cm^{-1} of the IR spectra of DB18C6 and its complex, there are two bands assignable to anisole ν_s(Ph-O-C) and ν_{as}(Ph-O-C) vibrations [33]. These anisole oxygens are involved in H-bond formation in the complex 2, as indicated by the shifts of the ν_{as}(Ph-O-C) and ν_s(Ph-O-C) bands from 1216 and 1253 cm^{-1} to 1198 and 1237 cm^{-1}, respectively. Selected IR data for the free compounds and their complexes and corresponding changes in frequencies are listed in **Table IX.3**.

Table IX.3: Comparison between the Frequencies change (cm^{-1}) of different functional group of free compound and their complexes

Functional Group	**Wavenumber (cm^{-1})**		**Changes (cm^{-1})**
	18C6	**Complex 1**	**Δδ**
$\nu(C-O-C)_{aliph.}$	1102	1082	20
	DB18C6	**Complex 2**	
$\nu(C-O-C)_{arom}$	1126	1108	18
ν_{as}(Ph-O-C)	1216	1198	18
ν_s(Ph-O-C)	1253	1237	16
	IL	**Complex 1**	
$\nu(C-H)$	3082, 2930	3066, 2905	16, 25
	IL	**Complex 2**	
$\nu(C-H)$	3082, 2930	3069, 2921	13, 9

IR spectroscopy has extensively been used to analyze the interaction present in the ILs. The shifts in C-H stretching frequencies in imidazolium-based ILs provide the information about the existence of the H-bonding in the complex. The imidazolium based IL shows the presence of C-H stretching vibrations in the region3000-3100 cm^{-1} which is the characteristic region for the ready identification of C-H stretching vibrations [34,35]. According to Grondin et. al. [36] the IR band at 3160±15 cm^{-1} are assigned to the more or less symmetric and anti-symmetric combination of the C(4)-H and C(5)-H stretching vibration of the imidazolium ring. The feature around 3120±15 cm^{-1} consists of two bands and results from the C(2)-H stretching mode and Fermi resonances of the C-H stretching vibrations with overtones of in-plane ring deformations. In our investigation, the C-H vibrations have been found at 3082 and 2930 cm^{-1} in the FTIR spectrum are shifted to 3066 and 2905 cm^{-1} in complex 1 (**Figure IX.4**) and 3069 and 2921 cm^{-1} in complex 2 (**Figure IX.5**). In the IR spectra the region between 2800 $cm^{-1}$and 3000 cm^{-1} referred to the CH_2 and CH_3 stretching vibrations of the alkyl groups at the nitrogen atoms of the imidazolium ring.

IX.3.4 NMR Study

The complexation of imidazolium salt with crown ethers were investigated by ^1H NMR spectroscopy in CD_3CN at 298.15 K. The ^1H NMR spectra of IL (imidazolium ion) was recorded in absence and the presence of 18C6 (**Figure IX.6**) and DB18C6 (**Figure IX.7**) in CD_3CN.

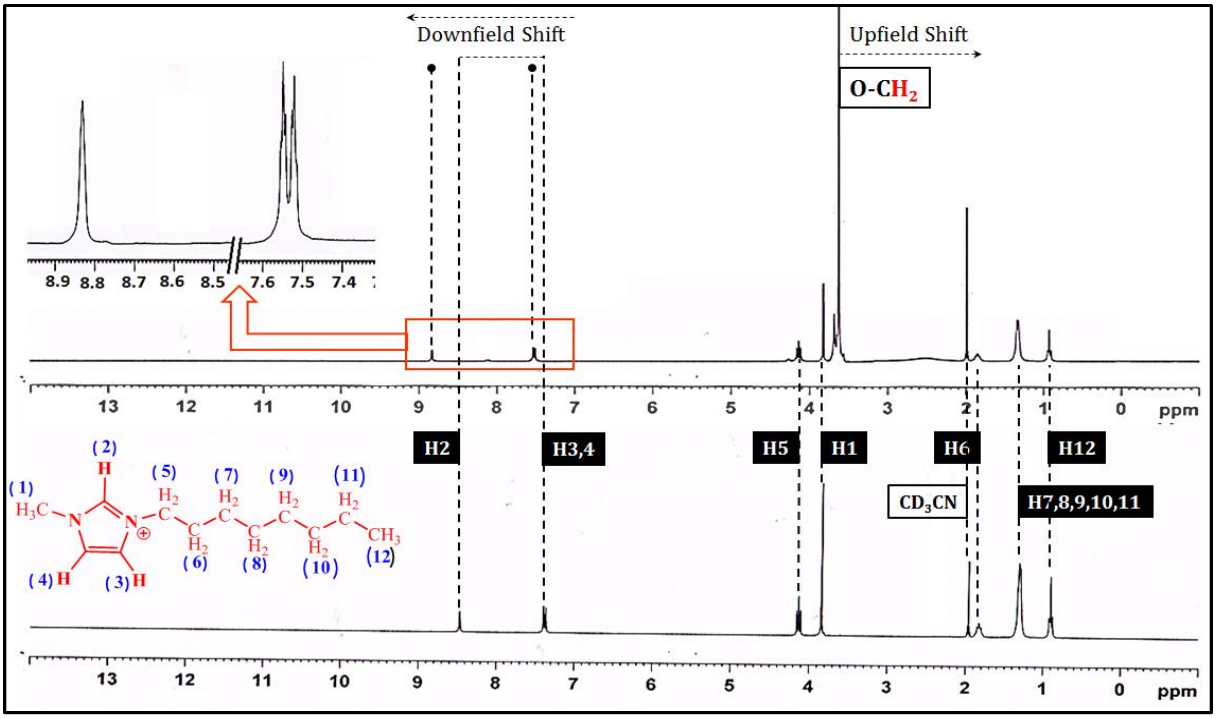


Figure IX.6: The ^{1}H NMR spectra of complex 1 (18C6.IL) (upper) and uncomplexed imidazolium cation (lower) recorded at 300 MHz in CD$_3$CN at 298.15 K.

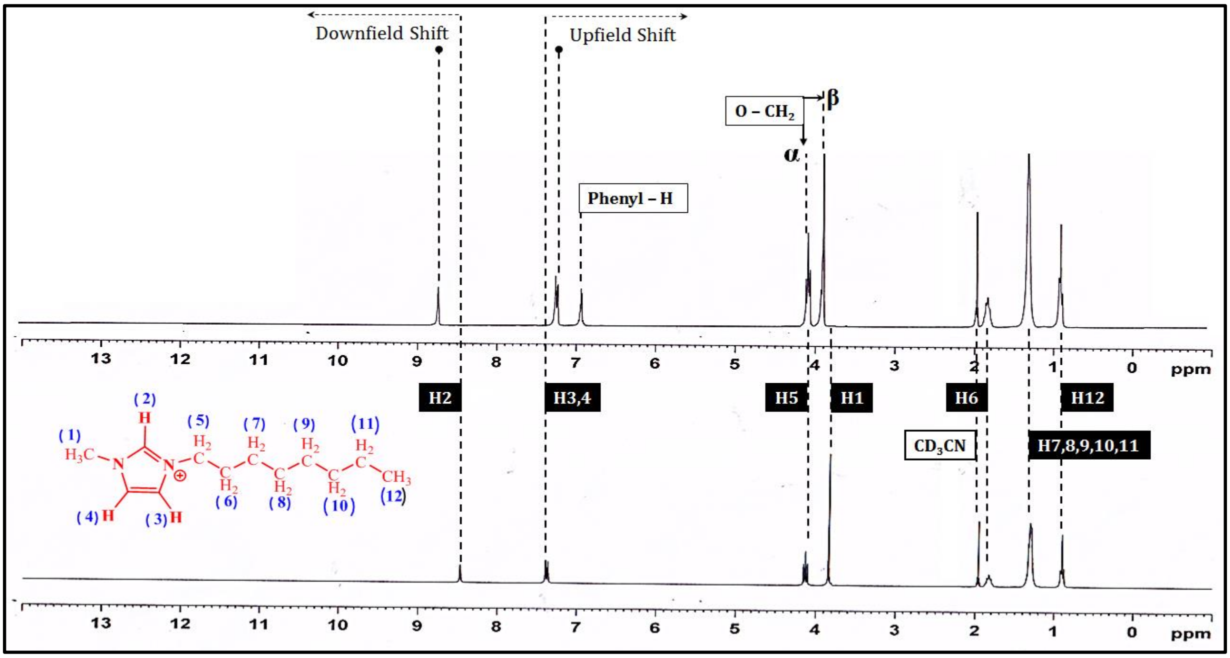


Figure IX.7: The ^{1}H NMR spectra of complex 2 (DB18C6.IL) (upper) and uncomplexed imidazolium cation (lower) recorded at 300 MHz in CD$_3$CN at 298.15 K.

A comparison of the ^{1}H NMR spectra for complex 1(**Figure IX.6**) with free IL revealed that the signals for hydrogen atoms of the imidazolium ion (H2, H3 and H4) were downfield shifted. Downfield shifts of imidazolium protons supports the complex formation through H-bond formation involving for $[(\mathrm{C{-}H})_{\mathrm{Imidazolium}}\ldots\ldots \mathrm{O}_{\mathrm{Crown}}]$– interaction. Signals for the $-OCH_2$ protons of crown ether were found to be little downfield shifted relative to those signals for the free individual component (**Figure IX.6**).

In case of complex 2 (**Figure IX.7**) i.e. complex of DB18C6, downfield shift for the signal of H2 was observed, while small upfield shift for the other two imidazolium protons (H3, H4) was observed [12,37]. This possibly suggest an orientation for the imidazolium ring that allows H-bond formation of H2 and a weak π-π interaction involving H3, H4. Two opposing influences namely H-bonding and π-π interaction were responsible for small upfield shifts for H3 and H4 [37]. The changes in chemical shifts suggest that host-guest complexation between crown ethers and imidazolium salt exists in both the complexes [38,39].

Based on different associated modes of interactions and ^{1}H NMR chemical shifts data for the two complexes, complex 1 and complex 2, a plausible interaction scheme have been proposed and schematic representation of such interaction is shown in **Scheme IX.2**. DB18C6 is a bowl-like host with two possible sites for interactions with the guest : the minor site formed by the $O\text{-}CH_2\text{-}CH_2\text{-}O$ chains and the major site located between the phenyl rings. The minor site may interact with the guest molecules only via hydrogen bonds while the major site can complex both via H-bonding and π-interactions (**Scheme IX.2**). The inclusion of a guest capable of interacting with both sites (imidazolium cation) leads to an interesting structure [11,12].

^{1}H NMR studies revealed apparent perpendicular orientation of the imidazolium moiety of IL in the crown cavity of complex 2; while this seemed to be different for complex 1. The possibility of such an orientation for the imidazolium ion was confirmed by Rissianen and Pursiainen for analogous inclusion complex formation between imidazolium ion and dibenzo-18-crown-6 [11]. The ^{1}H NMR results also suggested that the electron-deficient imidazolium ion may be wrapped by benzene-substituted crown ethers and imidazolium ions are oriented face-to-face, such that the phenyl ring(s) and the substituents in the 1,3 position point away from the cavity of the crown ethers. In 1,3-disubstituted imidazolium salts both 1,3 positions are substituted by alkyl group which are electron donating groups relative to a hydrogen atom. Thus the substituents decrease the positive charge on the imidazolium ring and reduce the π-π stacking between dibenzo crown host and imidazolium guest in complex 2. In the complex 1 imidazolium ring can penetrate into the hollow circular based cavity of the macrocycle 18C6 and form strong H-bonding but the substituents in the 1,3 position point away from the cavity of the crown ethers.

Thus detailed ^{1}H NMR spectral studies indicate that hydrogen bonding interactions [$(C–H)_{\mathrm{Imidazolium}}$……$O_{\mathrm{Crown}}$] apart from the weaker π-π /arene–arene donor–acceptor interactions resulted in moderately strong inclusion complex formation i.e the result of ^{1}H NMR spectral studies support the results obtained from conductivity and IR measurements.

Selected ^{1}H NMR data

1-meyhyl-3-octylimidazolium tetrafluoroborate (IL): ^{1}H NMR (CD_3CN, 298.15 K): δ 8.47 (s, N-CH-N, 2H), 7.40-7.36 (d, N-$(CH)_2$-N, 2H), 3.84-3.81 (s, NCH_3, 3H), 4.15-4.10 (t, CH_2, 2H), 1.31 (m, $C_5H_{10,}$ 10H), 0.92-0.88 (t, oct-CH_3, 3H).

18-crown-6: ^{1}H NMR (CD_3CN, 298.15 K): δ 3.59-3.52 (s, OCH_2, 24H).

Dibenzo 18-crown-6: ^{1}H NMR (CD_3CN, 298.15 K): δ 6.96-6.89 (s, aryl, 8H), 4.13-4.10 (m, $OCH_{2,}$ 8H), 3.88-3.85 (m, $OCH_{2,}$ 8H),

18C6-1-meyhyl-3-octylimidazolium tetrafluoroborate (complex 1): 3.64(m, OCH_2)^{1}H NMR (CD_3CN, 298.15 K): δ 8.83 (s, N-CH-N, 1H), 7.53-7.50 (s, N-$(CH)_2$-N, 2H), 3.64-3.58 (m, OCH_2, 24H).

DB18C6-1-meyhyl-3-octylimidazolium tetrafluoroborate (complex 2): ^{1}H NMR (CD_3CN, 298.15 K): δ 8.75 (s, N-CH-N, 1H), 7.27-7.24 (d, N-$(CH)_2$-N, 2H), 6.95-6.90 (s, aryl, 8H), 4.09-4.05 (m, OCH_2, 8H), 3.89-3.86 (m, OCH_2, 8H).

3.5 Typical Features of Specific Interactions involved in the Complexation

Inclusion complex formation of crown ethers with imidazolium ion involved three possible modes of interaction. The most prominent one is the hydrogen bonding interaction between oxygen atom of crown ethers (O_{Crown}) and acidic C–H protons of imidazolium ion [$(C–H)_{Imidazolium}$] for [$(C–H)_{Imidazolium}$……O_{Crown}]–interaction . π–π stacking interactions between the electron poor imidazolium ring and aryl groups of the crown ether-based host (DB18C6) is the second one which is expected to contribute to the stability of the adduct formation. The possibility of such an interaction for an analogous system was reported earlier [11,14]. Apart from H-bonding and π–π stacking interactions, induced dipole–dipole interaction between imidazolium ion and O_{Crown} having -δcharge could also contribute to the overall stability of the adduct formation; such a proposition was made independently by Schmitzer *et al.* and Pursiainen *et al.* [11-14, 40-42]. However, this induced dipole–dipole interaction is expected to be weaker as compared to two previous modes of interaction discussed.

In the complex 2 (**Scheme IX.2**), hydrogen bonding seems to play a secondary role. Obviously, the π–π interaction is dominant in this complex (**Scheme IX.2**), because the benzene rings of the DB18C6 decrease the negative charge of the oxygen atoms and hence their ability to undergo hydrogen bonding, but under favorable conditions hydrogen bonds can enhance the stability of crown ether complexes. Also the electrostatic interaction between the aromatic ring of the crown and positive charge of the imidazolium ring play an important role to stabilize the complex. The negative charge on the benzene rings of the crown ether skeleton is enhanced by the ether oxygen atoms and this negative face of the aromatic ring interacts with the positive charge of the imidazolium ring. The unsubstituted crown ether imidazolium complex [complex 1] is likely stabilized by hydrogen bonds formed between acidic protons of imidazolium ring and ether oxygen atoms (C-H···O interactions) [43].

The stability constants (log K_f) for 1:1 complexation were measured in ACN solution by conductance study and are presented in **Table IX.2**. In both the complexes [complex 1 and complex 2], H-bonding to the ether oxygen atoms is obviously responsible for complexation. This can be shown by the suitable plausible mechanism

(Scheme 2).Complexation is mainly caused by H-bonding but either π-stacking or charge-transfer interactions (**Scheme IX.2**) also seem to have a minor contribution towards complexation and there may be possibility of ion-dipole interactions between positive N atom of imidazolium cation and ether oxygen atom. The stability constants for complex 2 is slightly lower than the corresponding value of complex 1 (**Table IX.2**). The aromatic rings of the crown ether decrease the electron density of the adjacent oxygen atoms, and this seems to decrease the strength of any H-bonding in complex of complex 2 explaining the lower stability constants. Although complex 2 has the potential for π-stacking or charge transfer interactions which is absent in the complex 1 indicates that H-bonding is dominant here for the complex formation.

IX.4. CONCLUSION

The conductometric titration data support the different types of interactions responsible for complex formation of crown ethers with IL molecule and are consistent with the IR and NMR spectra. The stability of complexes between planar, five-membered imidazolium cations and crown ethers were established by the different types of non-covalent interactions. We have found that the studied complexes are mainly stabilised by hydrogen bonds, and π-stacking or cation–πinteractions play only a secondary role in case of complex 2. Larger formation constant value for complex 1 compared to complex 2 determined by conductivity study indicates that imidazolium cation form stable complex with 18C6 compared to DB18C6 in ACN solution. The 1:1 complexation of the imidazolium based IL by different crown ethers is driven by favourable changes in enthalpy ($\Delta H^0<0$) and proceeds spontaneously ($\Delta G^0<0$).This study also helps to get important information about the other host-guest system with crown ethers.

Here our studies of complexation of imidazolium ion, similar to complexation of pyridinium ions [40], provide further information on the nature of the complexation between positively charged organic guests and macrocyclic polyethers. This study is also significant for the understanding of the vital role of imidazolium cation in the design and construction of supramolecular host-guest materials.