CHAPTER V

Supramolecular assembly of ionic liquid with cyclic polyethers to form Inclusion Complexes

V.1. HIGHLIGHTS

- 18-Crown-6 and dibenzo 18-crown-6 forms host-guest inclusion complex succesfully with ionic liquids with 1:1 stoichiometry.
- Association constant measuemented by conductrometric method.
- ^{1}H NMR provides confirm evidence about inclusion phenomenon (ICs).
- Solid complex formation between crown ether and ionic liquids is established by FTIR spectroscopy.
- Direct evidence of formation of solid 1:1 ICs has been provided from mass analysis.

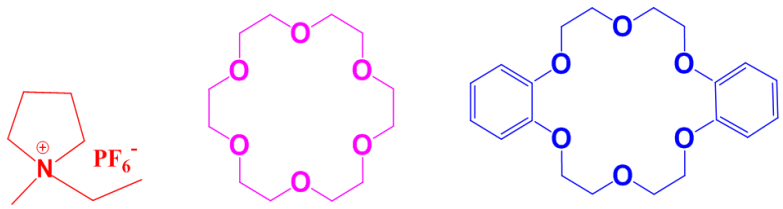
V.2. INTRODUCTION

Crown ethers are the macrocyclic polyether. The most significant and exceptional property of the macrocyclic "crown compounds" (used as host, also known as ligand) is their affinity to form complexes with various class of guest species e.g. metal ions ,amino acids, ionic liquids [1-5]. Over the past years they have engrossed broad attention due to their unique capacity to form complex with cations [2,4] Such complexes are held together in unique structural relationships by electrostatic attraction between the cation and the negative end of the C-O dipoles other than those of full covalent bond. The firmness of such crown ether-guest complexes strongly depends upon how well the cation moity fits into the ring of the polyether; and also influenced by the charge density of the cation, the nature and the number of the hetaro atoms in the ring and the variety of the substituent on the ligand. The nature of solvent also plays an important role on the stability and selectivity of the complex formation [6-8].

Among various guest molecules the IL has been chosen because of having a vast area of interest for vital reasons associated with their negligible vapor pressure

i.e they do not evaporate to the environment and their potential as "designer solvents" and "green" replacement for toxic volatile organic solvent, good ionic mobility, excellent thermal and chemical stabilities etc. There is a wide range of industrial applications of ILS due to their unique physicochemical character (9-11). Now a day the uses of such ILs increase the interest in various fields to develop of some new ideas and methods.

IL-crown ether has versatile and remarkable self-assembly ability and can form various novel nanostructures with fine sizes. In the present work the information about the 1-ethyl-1-methyl pyrrolidinium hexafluorophosphate ([EMPyrr]PF_6) forms complex with 18-Crown-6 (18C6) and dibenzo 18-crown-6 (DB18C6) (macrocyclic ligands) (**Scheme 1**) respectively reveals a special interest. This work is planned in order to inspect formation constant by using conductance at three different temperatures 20°C, 25°C and 30°C to see the effect of temperature on the complex formation. The 1HNMR and electrospray mass spectrometry techniques confirmed the complexation process. The FTIR spectral of the solid form of [EMPyrr]PF_6-crown compounds are also scrutinized and try to shed some light on the host-guest interaction. As both the selected compounds having huge applications in different fields of science, so, the resulting complexes would be definitely very useful and valuable in the field of science.



Scheme 1. structures of selected ionic liquid (a), 18-Crown-6 (b) and dibenzo 18-Crown-6 (c).

V.3. EXPERIMENTAL SECTION

V.3.1. Sources and Purity of sample

The selected ionic liquid 1-ethyl-1methyl pyrrolidinium hexafluorophosphate [EMPyrr]PF_6 and the crown ethers (viz. 18-crown-6 and dibenzo-18-crown-6) were purchased from Sigma-Aldrich, Germany. The mass fraction purity of 18C6, DB18C6 and [EMPyrr]PF_6 were ≥ 0.98, 0.98 and 0.99 respectively. The acetonitrile purchased from Sigma-Aldrich, Germany. The mass fraction of purity of acetonitrile was ≃ 0.998.

V.3.2. Instruments and procedure

Foregoing to the start of the experimental work the solubility of two selected crown ethers and the chosen IL in acetonitrile has been checked separately and it is seen that they were properly soluble. Here the binary acetonitrile solution of crown ether was used as solvent. All the binary stock solutions of IL were prepared by mass (measured using Mettler Toledo AG-285 with uncertainty 0.0001g) and the working solutions were obtained by mass dilution.

Specific conductance values of experimental solution were measured by systronics-308 conductivity Bridge of accuracy ±0.01%, using a dip-type immersion conductivity cell CD-10. The cell was calibrated using a 0.01M KCl aqueous solution. A thermostated water bath was used to maintain a constant experimental solution temperature (293.15K, 298.15K and 303.15K) having a deviations of ±0.01K.

The molar conductance (Λ_m) has been calculated by using equation 1 at three different temperatures and mentioned in **Table 1** and **Table 2**

$$\Lambda_m = 1000\kappa/c \qquad (1)$$

Where c= molar concentration of the studied solution.

Now, the mole ratio of [H]/ $[EMPyrr]^+$ at the point from where the Λ_m starts to change not **Figure 1** and **Figure 2** has been calculated by solving the followoing two equations of the two lines and listed in **Table 3**. For instance, in case of IL+18-Crown-6 solution at 298.15 K.

$$y = -19.96x + 140.0$$

$$y = -3.232x + 125.1$$

Where, $y = ([H]/ [EMPyrr]^+) = 0.89$.

Infrared spectra were measured in 8300 FTIR spectrometer (Shimadzu, Japan). The details of the instrument have already been described (12) KBr pellet is used for solid samples.

NMR spectra were recorded at 300 MHz Bruker ADVANCE at 298.15K in CD_3CN. Signals are quoted as δ values in ppm using residual protonated solvent signals as internal standered (D_2O: 1.93 δ ppm). Data are reported as chemical shift.

HRMS analyses were studied with Q-TOF high resolution instrument by positive mode electro-spray ionization.

V.3.3. Preparation of solid complex of crown ethers with [EMPyrr]PF_6

0.2643 gm of 18C6 and 0.2592 of [EMPyrr]PF_6 (1:1 ratio) were placed in a 50 ml beaker and 10 ml acetonitrile was added. After that the mixture was set over electromagnetic stirrer in a round bottom flask with a reflux condenser and continuously stirred for 4 hours at 75°Cwith 350rpm. The resulting solid dried in a desiccators over CaC_2 for 5 days (complex I).

Same procedure was followed in case of DB18C6 and [EMPyrr]PF_6. Here 0.3604 gm of DB18C6 and 0.2592 of [EMPyrr]PF_6 (1:1 ratio) has been taken and do the same as mentioned above (complex II).

V.4. RESULT AND DISCUSSION

V.4.1. Conductivity study illustrates complexation process with their stoichiometric behaviour and formation constant

The study of molar conductance of 18C6:[EMPyrr]$^+$and DB18C6:[EMPyrr]$^+$ systems give a vital clue about the intermolecular complex formations between the IL and macrocyclic ligand. To investigate the complexation of 18C6 and DB18C6 with [EMPyrr]PF_6, the molar conductance (Λ_m) is monitored as a function of mole ratio of [H]/[EMPyrr]$^+$ (where, [H]= mole concentration of 18C6, DB18C6 and [EMPyrr]$^+$= molar concentration of selected ionic liquid) in solution at three different temperatures. The resulting series of molar conductance (Λ_m)-mole ratio in acetonitrile are presented in **Figure 1** and **Figure 2**. It have been noticed that there is significant change in molar conductance (Λ_m) i.e. molar conductance gradually decreases with increase in [H]/ [EMPyrr]$^+$ mole ratio (**Table 1** and **Table 2**). This suggests that there must be formed complexation of cation by ion-dipole interactions with crown ether rather than pairing or covalent bond. It results the higher mobility of pyrrolidinium cation in the complextation process than the mobility of [EMPyrr]PF_6 in acetonitrile in absence of the selected crown ethers. First the molar conductance decreases sharply during addition of crown solution but after a point slow changes is ovserved. This point indicates about the stoichiometric behavior of the resulting complex formation. As at that point the mole ratio of [H]/ [EMPyrr]$^+$ is close to unity (**Table 3**), it suggests the formation of stable ~1:1

complex of 18C6:[EMPyrr]$^+$ and DB18C6:[EMPyrr]$^+$ at different temperatures [13-15]. Consequently the general reaction can be given by the following equilibrium [16]

$$[\mathrm{EMPyrr}]^+ + \mathrm{Crown} \rightleftarrows [\mathrm{EMPyrr}]^+\mathrm{Crown} \qquad (2)$$

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

$$K_f = \frac{[\mathrm{ILH}]\, f(\mathrm{ILH})}{[\mathrm{IL}][\mathrm{H}]\, f(\mathrm{IL})\, f(\mathrm{H})} \qquad (3)$$

Where, [EMPyrr]$^+$crown=[ILH], [EMPyrr]$^+$=[IL], crown=[H] and *f* are the molar concentration of the complex, uncomplexed IL, uncomplexed macrocyclic crown compound and the activity coefficient of the indicated species respectively. Since the experiment has been done by dilution method, the activity coefficient (*f*) can be considered as unity. On the basis of Debye- Hückel limiting law the activity coefficient of *f*(ILH) ≃ *f*(IL), thus the ratio *f*(ILH)/ *f*(IL) is also unity. Thus the equation 3 reduces as (6,13)

$$K_f = \frac{[\mathrm{ILH}]}{[\mathrm{IL}][\mathrm{H}]} = \frac{(\Lambda_{\mathrm{IL}} - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{\mathrm{ILH}})[\mathrm{H}]} \qquad (4)$$

$$[\mathrm{H}] = \mathrm{C_C} - \frac{\mathrm{C_{IL}}(\Lambda_{\mathrm{IL}} - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{\mathrm{ILH}})} \qquad (5)$$

Here, Λ_{IL}= molar conductivity of the IL before addition of ligand; Λ_{ILH}= molar conductivity of complexed ion; Λ_{obs}= molar conductivity of the experimental solution during experiment; C_c the analytical concentration of the crown added and C_{IL} the analytical concentration of the IL.

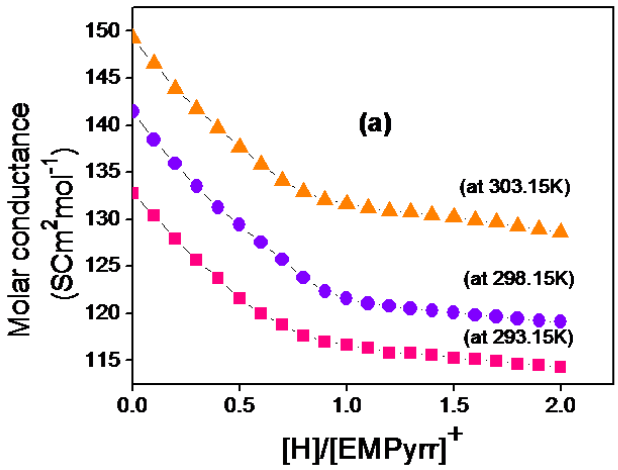


Figure 1. Molar conductance vs mole ratio of [H]/[EMPyrr]$^+$ of 18C6+IL at 293.15K (pink), 298.15K (blue) and 303.15K (orange).

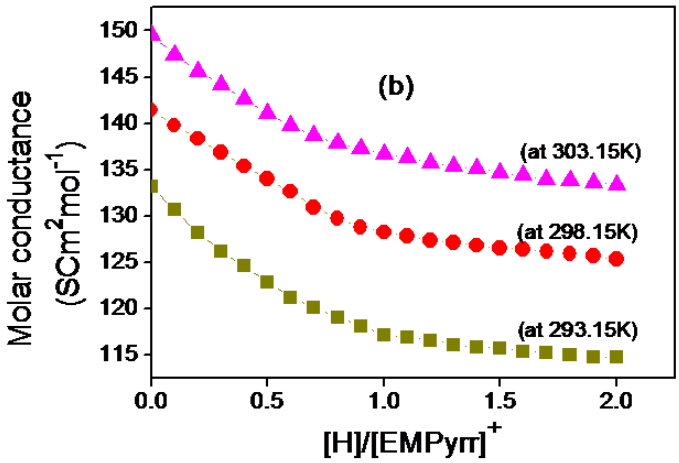


Figure 2. Molar conductance Vs mole ratio of [H]/[EMPyrr]$^+$ of DB18C6+IL at 293.15K (green), 298.15K (red) and 303.15K (violet).

Table 1: Conductivity values for the [EMPyrr]$^+$+18C6 system at three different temperatures(K^a)

Vol. of 18C6 added (mL)	Total vol. (mL)	Conc. of 18C6[H] (mM)	Conc. of [IL](mM)	$\frac{[H]}{[EMPyrr}$	Molar conductance S cm^2 mol^{-1}		
					293.15 K	293.15 K	303.15 K
0	10	0.000	10.000	0.0	132.791	141.439	149.241
1	11	0.909	9.091	0.1	130.389	138.458	146.558
2	12	1.667	8.334	0.2	127.968	135.914	143.914

3	13	2.308	7.692	0.3	125.657	133.519	141.719
4	14	2.857	7.143	0.4	123.778	131.251	139.751
5	15	3.333	6.667	0.5	121.534	129.399	137.699
6	16	3.750	6.250	0.6	119.979	127.535	135.868
7	17	4.118	5.882	0.7	118.752	125.695	134.095
8	18	4.445	5.556	0.8	117.659	123.779	132.879
9	19	4.737	5.263	0.9	116.971	122.319	132.119
10	20	5.000	5.000	1.0	116.645	121.589	131.619
11	21	5.238	4.762	1.1	116.289	121.048	131.248
12	22	5.455	4.545	1.2	115.839	120.775	130.935
13	23	5.652	4.348	1.3	115.769	120.489	130.789
14	24	5.833	4.167	1.4	115.589	120.265	130.411
15	25	6.000	4.000	1.5	115.269	120.072	130.189
16	26	6.154	3.846	1.6	115.098	119.812	129.899
17	27	6.296	3.704	1.7	114.934	119.611	129.683
18	28	6.429	3.571	1.8	114.651	119.452	128.252
19	29	6.552	3.448	1.9	114.547	119.221	128.946
20	30	6.667	3.333	2.0	114.242	119.089	128.589

[a] Standard uncertainties in temperature (T) = 0.01 K.

Table 2: Conductivity values for the $[EMPyrr]^+$+DB18C6 system at three different temperatures(K[a])

Vol. of 18C6 added (mL)	Total vol. (mL)	Conc. of DB18C6[H] (mM)	Conc. of IL (mM)	$\frac{[H]}{[EMPyrr}$	Molar conductance S cm^2 mol^{-1}		
					293.15 K	293.15 K	303.15 K
0	10	0.000	10.00	0.0	133.191	141.439	149.541
1	11	0.909	9.091	0.1	130.634	139.759	147.436
2	12	1.667	8.334	0.2	128.214	138.356	145.673
3	13	2.308	7.692	0.3	126.156	136.837	144.171
4	14	2.857	7.143	0.4	124.565	135.382	142.675
5	15	3.333	6.667	0.5	122.785	134.023	141.126

6	16	3.750	6.250	0.6	121.135	132.654	139.762
7	17	4.118	5.882	0.7	120.073	130.935	138.671
8	18	4.445	5.556	0.8	119.021	129.743	137.823
9	19	4.737	5.263	0.9	118.063	128.743	137.292
10	20	5.000	5.000	1.0	117.164	128.245	136.723
11	21	5.238	4.762	1.1	116.852	127.823	136.286
12	22	5.455	4.545	1.2	116.583	127.353	135.783
13	23	5.652	4.348	1.3	116.092	127.072	135.338
14	24	5.833	4.167	1.4	115.838	126.782	135.135
15	25	6.000	4.000	1.5	115.662	126.521	135.684
16	26	6.154	3.846	1.6	115.364	126.383	134.385
17	27	6.296	3.704	1.7	115.273	126.156	133.973
18	28	6.429	3.571	1.8	114.937	125.878	133.832
19	29	6.552	3.448	1.9	114.774	125.647	133.642
20	30	6.667	3.333	2.0	114.693	125.339	133.367

[a] Standard uncertainties in temperature (T) = 0.01 K.

Table3. Values of the mole ratio of [H]/ [EMPyrr]$^+$ for 18C6 and DB18C6 at three different temperatures (K[a]).

	293.15K	298.15 K	303.15K
18C6/[EMPyrr]$^+$	0.95	0.89	0.85
18C6/[EMPyrr]$^+$	0.93	0.86	0.84

[a] Standard uncertainties in temperature (T) = 0.01 K.

Now, using these equation 4 and equation 5 the formation constant (K_f) and the molar conductance of the complex have been calculated at different temperatures and the corresponding values of log K_f have been listed in **Table 4** and are plotted in **Figure 3**.

Table4: log K_f values of 18C6:[EMPyrr]$^+$and DB18C6:[EMPyrr]$^+$ complexes in acetonitrile medium at different temperatures (K[a]).

Complex	log K_f		
	293.15 K	298.15 K	303.15 K
18C6:[EMPyrr]$^+$	3.94	3.91	3.89
DB18C6:[EMPyrr]$^+$	3.37	3.34	3.31

[a] Standard uncertainties in temperature (T) = 0.01 K.

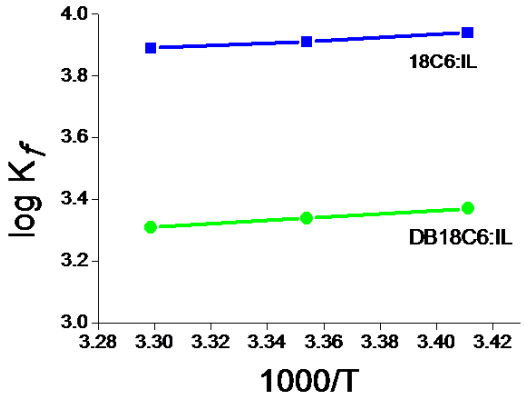


Figure 3. logK_f Vs 1000/T for 18C6:IL (■) and DB18C6:IL (●) complexation.

V.4.2. Thermodynamics parameters:

According to van't Hoff equation (equation 6) various values of thermodynamics parameters (ΔH^0, ΔS^0) are derived (**Table 5**) from the slope and intercept of the plot of **Figure 3**.

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

The free energy (ΔG^0) values can be calculated by using the above thermodynamics parameters and have been listed in **Table 5**. The negative values of ΔG^0 suggest that complex formation process proceeds spontaneously, where as the negative values of ΔH^0 and positive values of ΔS^0 specify that the procedure

stabilizes the whole system by decreasing energy and entropy controlled respectively [6]. In case of 18C6:[EMPyrr]$^+$ complex higher value of $-\Delta G^0$ than DB18C6:[EMPyrr]$^+$ implies that for the former the interactions are stronger than the later and more spontaneous.

Table5: Values of the thermodynamic parameters (ΔH°, ΔS°, ΔG°) are calculated from Van't Hoff equation of the complexes.

	Temp.(K[a])	ΔH^o /kJ mol^{-1}	ΔS^o /J mol^{-1}K^{-1}	ΔG^o(298.15K[a]) /kJ mol^{-1}
18C6:[EMPyrr]$^+$	293.15 298.15 303.15	-8.50	46.36	-22.32
DB18C6:[EMPyrr]$^+$	293.15 298.15 303.15	-10.21	29.70	-19.06

[a] Standard uncertainties in temperature (T) = 0.01 K.

The molar conductance increases but the formation constant are decreases with the increase in temperature ($K_f^{293.15} > K_f^{298.15} > K_f^{303.15}$), this is due to the high mobility of the 1-ethyl-1-methyl pyrrolidinium [EMPyrr]$^+$ ions. This also increases the thermal energy i.e. the process of complex formation is exothermic in nature ($-\Delta H^0$). The values of formation constant (log K_f) (**Table 4**) evidently point out that the 18C6: [EMPyrr]$^+$ forms more firmly held complex than DB18C6:[EMPyrr]$^+$. Both crown ethers have almost same cavity size 2.6-3.2Å [17], so such variation must be originated due to presence of two benzo groups' substitution on 18-crown-6. The electron withdrawing effect of benzo groups reduces the Lewis basic character (electron donor property) of oxygen atoms of DB18C6 towards the incoming guest charged moiety i.e. [EMPyrr]$^+$ ion that are involved in complexation with the crown

ether ring by the hetaro (oxygen) atoms. As a result 18C6 can form $N^{+}\cdots O^{\delta-}$ non-covalent electrostatic ion-dipole interactions strongly and hence, the interaction in case of 18C6:$[EMPyrr]^{+}$is predominant over the DB18C6:$[EMPyrr]^{+}$.

V.4.3. 1HNMR spectra:

The ^{1}HNMR spectra has additionally established the interplay of pyrrolidinium cation $[EMPyrr]^{+}$ with the crown ethers in solution phase. The shifting of protons of the IL (pyrrolidinium cation) and the crown ethers in complex I and complex II are used to analysis for the formation of complex. **Figure 4** and **Figure 5** show the 1HNMR spectra of uncomplexed IL, complexed IL and free 18C6 and DB18C6 respectively. In complex I the H1, H4, H5 and H6 protons of pyrrolidinium ion are upfield shifted significantly where as the shifting of H2, H3 and H7 protons are marginal. In acetonitrile (polar solvent) 18C6 prefers D_{3d} conformation where all the six oxygen atoms pointed towards the cavity [2] and hence the effective $N^{+}\cdots O^{\delta-}$ non-covalent electrostatic ion-dipole interactions are developed between the pyrrolidinium ion and the oxygen atoms of 18C6 [1,18]. Comparing with the free component, it is seen that peak of -OCH_2 group protons of 18C6 are also upfielded shielded in complexed form. So, it is concluded that such chemical shifts must occur due to host- guest complex formation of pyrrolidinium cation with 18C6 (**Scheme 2**).

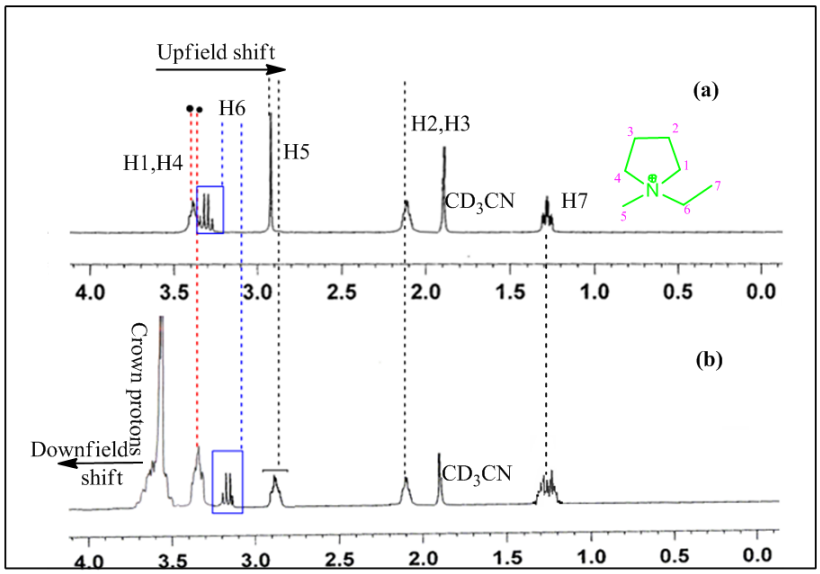


Figure 4. ^{1}H NMR spectra of (a) 1-ethyl-1 methylpyrrolidinium hexafluorophosphate and (b) 1:1 molar ratio of 18C6:$[EMPyrr]^{+}$ in D_2O at 298.15K.

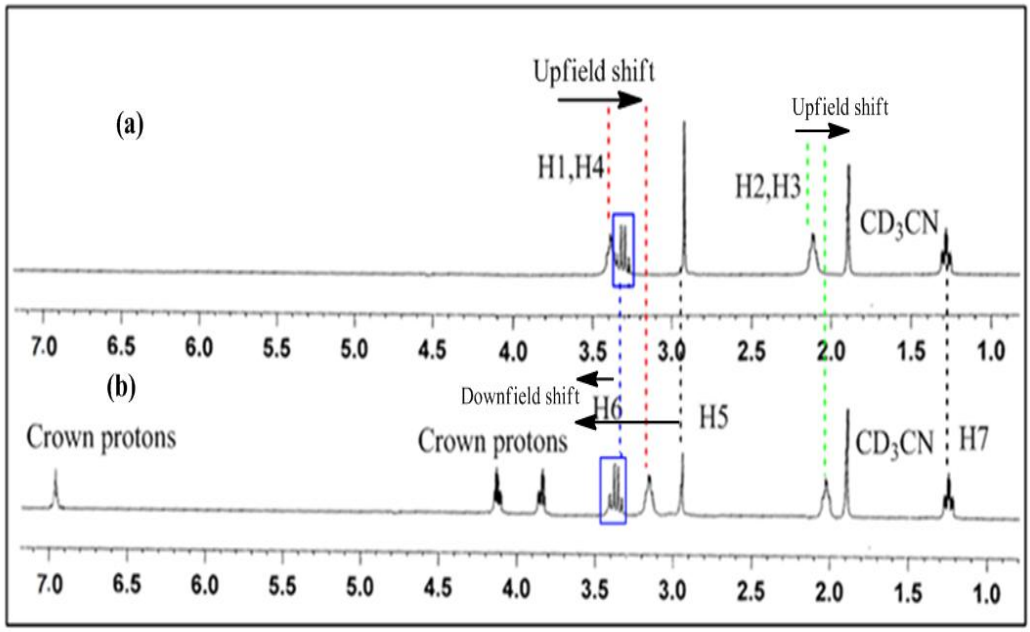
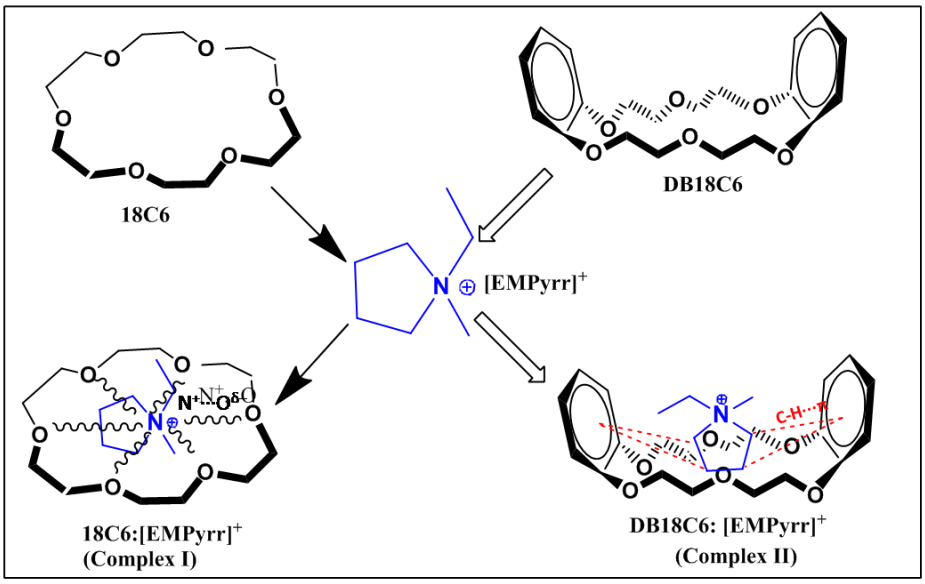


Figure 5. ^{1}H NMR spectra of (a) 1-ethyl-1 methylpyrrolidinium hexafluorophosphate and (b) 1:1 molar ratio of DB18C6:$[EMPyrr]^{+}$ in D_2O at 298.15K.

In case of complex II (**Figure 5**) large upfield shift are observed for pyrrolidinium ring protons (H1, H2, H3 and H4) while the chemical shifts of alkyl protons (H5 and H6) displayed small downfield changes. This suggests that

pyrrolidinium ion $[EMPyrr]^+$ resides in the DB18C6 network with the alkyl groups directed away from the cavity to form host-guest complex [19] Due to presence of two phenyl substitutions and bowl-like structure of DB18C6, it has two possible arrangements for interactions with incoming guest moiety– (i) -O-CH_2-CH_2-O- chains, the minor site that may possesses very weak H- bonds with the H5 and H6 protons and (ii) the major site, the two phenyl rings [20-22]. The H-atoms of five membered pyrrolidinium ring are involved strongly in C–H···π interactions with the phenyl π ring systems (**Scheme 2**) [19]. This leads to formation of successful 1:1 host-guest complexation between of $[EMPyrr]^+$ with DB18C6(**Scheme 2**) and also supported the results that we have got from conductance method.



Scheme 2. Schematic representation of complexation of 1-ethyl-1-methylpyrrolidinium hexafluorophosphate with 18-Crown-6 (18C6) and dibezo-18-crown-6 (DB18C6).

^{1}HNMR data: 1-ethyl-1-methyl pyrrolidinium hexaflurophosphate: ^{1}HNMR (300 MHz, in CD_3CN): δ= 3.49-3.37 (2H, m), 2.14-2.08 (2H, m), 2.92 (3H, s), 3.35-3.27 (2H, q, *J*= 7.32 Hz), 1.31-1.25 (3H, m);***18-Crown-6:*** ^{1}HNMR (300 MHz, in CD_3CN): δ= 3.60-3.51 (24H, m); ***Dibenzo-18-crown-6:*** ^{1}HNMR (300 MHz, in CD_3CN): δ= 6.99-6.87 (8H, m), 4.16-4.10 (8H, m), 3.78-3.67 (8H, m); ***18-Crown-6 + 1-ethyl-1-methyl pyrrolidinium cation (Complex I):*** ^{1}HNMR (300 MHz, in CD_3CN): δ= 3.45-3.32 (2H,m), 2.11-2.07 (2H, m), 2.94-2.86 (3H,m), 3.24-2.14 (2H, q, *J*= 7.32 Hz), 1.32-1.25 (3H, m), 3.67-3.55 (24H, m); ***Dibenzo-18-crown-6+1-ethyl-1-methyl pyrrolidinium (Complex II):*** ^{1}HNMR (300 MHz, in CD_3CN): δ= 3.28-3.15 (2H, m), 2.09-1.97 (2H, m), 2.94(3H, s), 3.37-3.30 (2H, q, *J*= 7.32 Hz), 1.30-1.25 (3H, m), 6.98-6.89 (8H, m), 4.15-4.09 (8H, m), 3.77-3.68 (8H,m).

V.4.4. Mass spectra:

Positive electrospray mass spectrometry (ESI-MS) is very useful method that has been used to examine the host-guest complexation with crown ethers (20-23) The mass spectrum of 1:1 stiochiometry of 18C6-[EMPyrr]PF_6 and DB18C6-[EMPyrr]PF_6 systems are analyzed by ESI-MS. In fig. 6a the peaks assigned at m/z 115.0455, 137.0453, 287.4872, 379.5210, 401.5309 indicate the singly charged $[EMPyrr + H]^+$, $[EMPyrr + Na]^+$, $[18C6+ Na]^+$, $[EMPyrr +18C+ H]^+$, $[EMPyrr+18C +Na]^+$ respectively. The peaks at m/z 383.4140, 475.4610 and 497.4593 correspond to $[DB18C6+ Na]^+$, $[EMPyrr+DB18C6+ H]^+$ and $[EMPyrr+ DB18C +Na]^+$ (**Figure 6b**). These experimental data of the selected IL/crown ether complexes suggested that the $[EMPyrr]^+$ cation simultaneously associated in polyethers cavity with 1:1 stiochiometry.

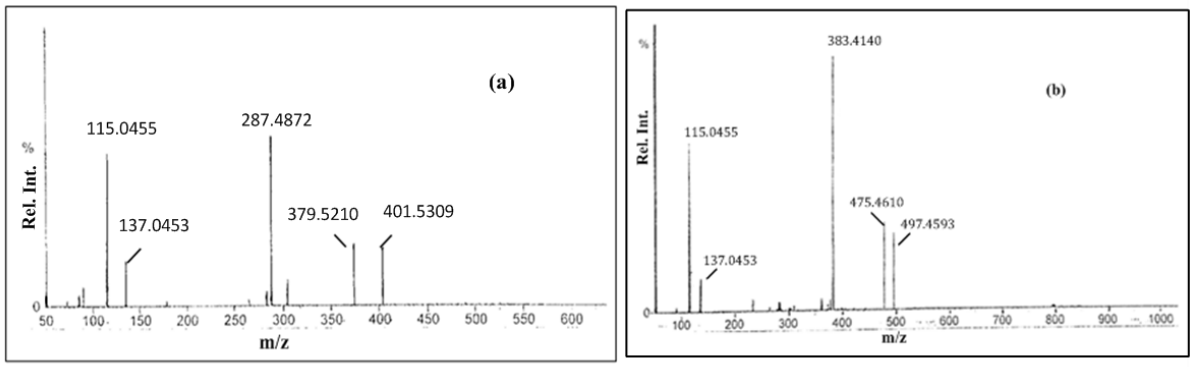


Figure 6. Electrospray mass spectra of equimolecular mixture of IL with (a) 18-crown-6 and (b) dibenzo 18-crown-6.

V.4.5. FTIR Spectroscopy study: effect of complex formation on the IR spectra

The interactions have been investigated also by comparing the FTIR spectroscopy of the solid 18C6 and DB18C6 with the solid form of complexes of 1-ethyl-1-methylpyrrolidinium hexafluorophosphate with 18C6 and DB18C6 respectively. The shift in bands in IR spectra in 4000-500 cm^{-1} region of each crown-ether provides the evidence of complex formation.

In case of 18C6 the distinctive absorption due to ν_{as}(C-O-C) stretching is assigned at 1119 cm^{-1} and shifting of ν_{as}(C-O-C) in complex I from 1129cm^{-1} to 1111 cm^{-1} is observed (**Figure 7**). The ν_{as}(C-O-C) stretching frequency for DB18C6 is shifted from 1128Cm^{-1} to lower frequency 1116 Cm^{-1} when it forms complex II (**Figure 8**). These shifting provide the prominent evidence about the interaction of $[EMPyrr]^+$ with the oxygen atoms of the crown compounds [17,24]. In case of DB18C6 spectra and in complex II in the range of 1200-1302 cm^{-1} two different kinds of assignable strong bands are observed. These indicate to stretching frequencies of anisol ν_s(Ph-O-C) and ν_{as}(Ph-O-C) [17,25] After complexation the ν_s(Ph-O-C) shifts from 1302 Cm^{-1} to 1287 Cm^{-1} and the ν_{as}(Ph-O-C) shifts from 1240 cm^{-1} to 1224 cm^{-1}. The ν(C-H) stretching frequencies of methylene groups of crown

ethers come in the range of 2742 cm^{-1} - 2938 cm^{-1}. It is shifted from 2920 cm^{-1} to lower frequency 2890.7 cm^{-1} in complex I and from 2938 cm^{-1} to 2932 cm^{-1} in complex II. The remarkable shifts in ν(C-H) stretching suggest the effect of complex formations. The comparative study of the IR spectra of 18C6 and DB18C6 reveal the absorption band of substituent though it is difficult enough to assign as their distinctive bands may overlap with those ethylene glycol groups. But the scrutiny on **Figure 8** allowed us to identify the absorption of $\nu_{benzene}$(C-H) frequncy that appears at 3071 cm^{-1}. The aromatic $\nu_{aromatic}(C\text{-}C)_{br}$ bonds are at 1586 cm^{-1}, 1511 cm^{-1},1480 cm^{-1} (17).

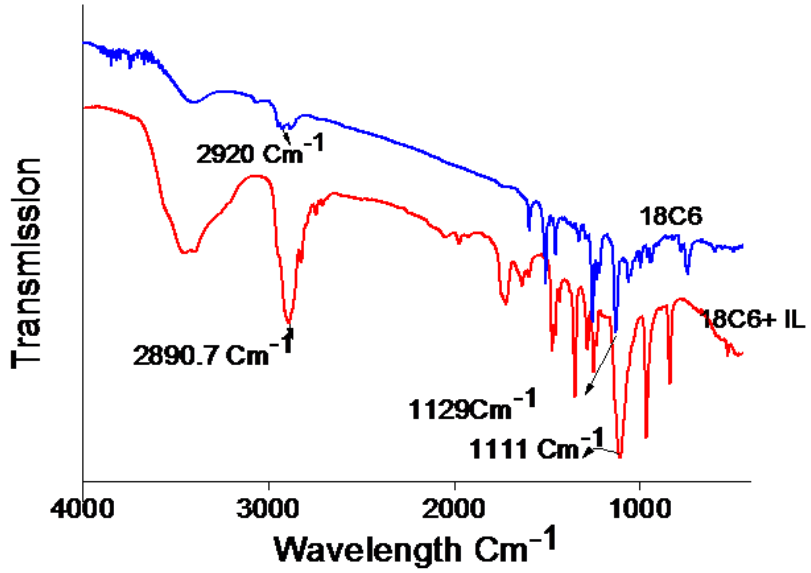


Figure 7. IR spectra of 18-crown-6 (blue) and the resulting complex I (18C6:$[EMPyrr]^+$) (red).

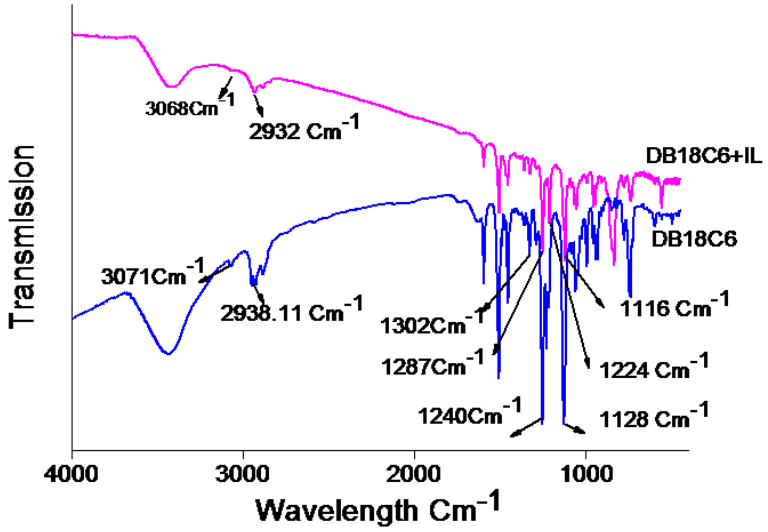


Figure 8. IR spectra of Dibenzo-18-crown-6 (blue) and the resulting complex II (DB18C6:[EMPyrr]$^+$) (violet).

As the interactions involved mainly on the electron donor ability of oxygen atoms of the crown compounds so it is seen that there are significant shifts for all ether linkage (**Table 6**). On the basis of these observations, it is suggested that there is considerable interactions that favors the complextation process and supports the plausible mechanism that is shown in **scheme 2**.

Table6. Frequencies (ν Cm^{-1}) of ether linkage in IR spectra of free crown ethers and the complexed crown ethers.

	ν Cm^{-1} (Free)	ν Cm^{-1} (Complexed)	$\Delta\nu$ Cm^{-1}
18C6:[EMPyrr]$^+$	1129 ν_{as}(COC)	1111 ν_{as}(COC)	18
DB18C6:[EMPyrr]$^+$	1128 ν_{as}(COC) 1240 ν_{as}(Ph-OC) 1302 ν_s(Ph-OC)	1116 ν_{as}(COC) 1224 ν_{as}(Ph-OC) 1287 ν_s(Ph-OC)	12 16 15

V.5. CONCLUSION

In this present work, the obtained result of conductivity and the association constant (k_f) for the complexation between 1-ethyl-1 methylpyrrolidinium hexafluorophosphate and 18C6 and DB18C6 can be explained in terms of the electrons donor ability of oxygen atoms to substrate. The thermodynamics parameters for this complexation process articulate that the overall complex formation path thermodynamically favorable. The five membered pyrrolidinium cationic head group is integrated into the macrocyclic polyether network via $N^{+}\cdots O^{\delta-}$ non-covalent ion-dipole, H-bonds and C–H···π interactions (host-guest interactions) has been established by 1HNMR. ESI-MS study confirmed the host-guest complexation process with 1:1 ratio. The FTIR spectroscopy study of the resulting solids between crown ethers and IL also gives distinct evidence about this host-guest complexation process.

V.6. REFERENCES

References of CHAPTER V are given in BIBLIOGAPHY (Page: 231-232).