



Supramolecular Assembly of Ionic Liquid with Cyclic Polyethers to Form Inclusion Complexes

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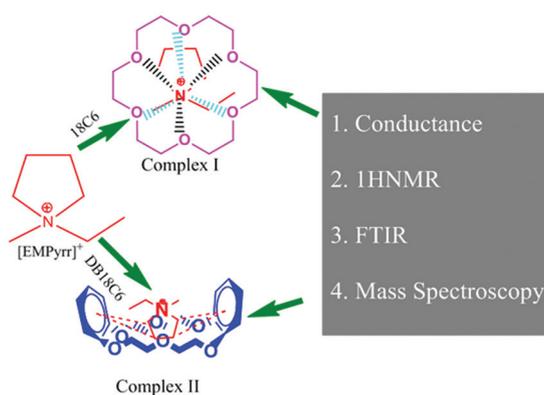
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ABSTRACT

Complexation process of the selected macrocyclic crown compound such as 18-crown-6 (18C6) and dibenzo 18C6 (DB18C6) with 1-ethyl-1-methylpyrrolidinium hexafluorophosphate [EMPyrr]⁺ PF₆⁻ as a guest molecule have been intended in acetonitrile medium at by conductometry (three different temperatures), ¹H nuclear magnetic resonance (NMR) and mass spectra. The formation constants of the complexes are evaluated in solution phase from the molar conductance-mole ratio values. The result shows that the stability of the resulting complexes with the same inward cationic moiety follows in the order 18C6: [EMPyrr]⁺ > DB18C6: [EMPyrr]⁺ and based on the character of the crown ethers. The calculated thermodynamic parameters support this complexation process. The host-guest complexations of the five-membered nitrogen-containing cation with two different macrocyclic polyethers are supported by studying ¹H NMR. The electrospray mass spectrometry has been used to support the complexation process with the proper stoichiometry ratio. The solid complex formation between the selected two crown ethers and the ionic liquid are established by Fourier transform infrared study.

Graphical Abstract



Key words: Formation constant, ¹H nuclear magnetic resonance, Electrospray ionization mass spectrometry, Fourier transform infrared spectroscopy.

1. 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 the various class of guest species, for example, metal ions, amino acids, and ionic liquids (IL) [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 on how well the cation moiety fits into the ring of the polyether; and also influenced by the charge density of the cation, the nature and the number of the heteroatoms

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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, that is, 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. There is a wide range of industrial applications of ILs due to their unique physicochemical character [9-11]. Nowadays, the uses of such ILs increase the interest in the various field to the 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]PF₆) forms complex with 18-crown-6 (18C6) and dibenzo 18C6 (DB18C6) (macrocyclic ligands) (Scheme 1), respectively, reveals a special interest. This work is planned to inspect formation constant using conductance at three different temperatures 20°C, 25°C and 30°C to see the effect of temperature on the complex formation. The ¹H nuclear magnetic resonance (NMR) and electrospray mass spectrometry techniques confirmed the complexation process. The Fourier transform infrared (FTIR) spectral of the solid form of [EMPyrr]PF₆-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.

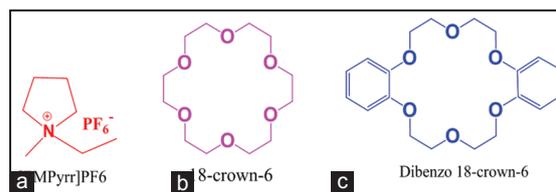
2. EXPERIMENTAL SECTION

2.1. Sources and Purity of Sample

The selected IL [EMPyrr]PF₆ and the crown ethers (viz. 18C6 and DB18C6) were purchased from Sigma-Aldrich, Germany. The mass fraction purity of 18C6, DB18C6 and [EMPyrr]PF₆ 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.

2.2. Instruments and Procedure

Preceding 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



Scheme 1: Structures of selected ionic liquid (a), 18-crown-6 (18C6) (b) and dibenzo 18C6 (DB18C6) (c).

as solvent. All the binary stock solutions of IL were prepared by mass (measured using Mettler Toledo AG-285 with uncertainty 0.0001 g) 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 0.01 M KCl aqueous solution. A thermostated water bath was used to maintain a constant experimental solution temperature (293.15 K, 298.15 K, and 303.15 K) having deviations of ±0.01 K.

The molar conductance (Λ_m) has been calculated using equation 1 at three different temperatures are mentioned in Tables 1 and 2.

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

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 Figures 1 and 2 has been calculated by solving the following two equations of the two lines are listed in Table 3. For instance, in the case of IL+18C6 solution at 298.15 K.

$$y = -19.96x + 140.0,$$

$$y = -3.232x + 125.1.$$

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

IR 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 298.15 K in CD₃CN. Signals are quoted as δ values in ppm using residual protonated solvent signals as internal standard (D₂O: 1.93 δ ppm). Data are reported as chemical shift.

HRMS analyses were studied with quad time of flight high-resolution instrument by positive mode electrospray ionization.

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

Volume of 18C6 added (mL)	Total volume (mL)	Concentration of 18C6[H] (mM)	Concentration of [IL] (mM)	$\frac{[H]}{[EMPyrr]^+}$	Molar conductance S cm ² mol ⁻¹		
					293.15 K	298.15 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

^aStandard uncertainties in temperature (T)=0.01 K. [EMPyrr]=1-ethyl-1-methylpyrrolidinium, 18C6=18-crown-6, IL: Ionic liquid

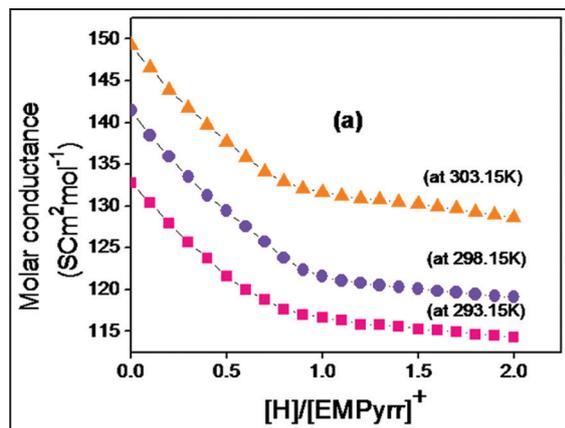


Figure 1: Molar conductance versus mole ratio of [H]/1-ethyl-1 methylpyrrolidinium [EMPyrr]⁺ of 18-crown-6+ionic liquid at 293.15 K (pink), 298.15 K (blue) and 303.15 K (orange).

2.3. Preparation of Solid Complex of Crown Ethers with [EMPyrr]PF₆

A total of 0.2643 g of 18C6 and 0.2592 of [EMPyrr]PF₆ (1:1 ratio) were placed in a 50 ml beaker and 10 ml acetonitrile was added. After that, the mixture was

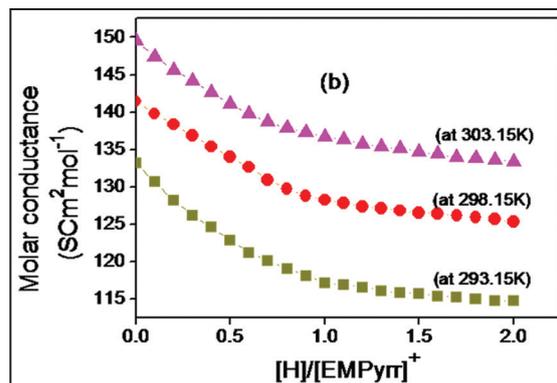


Figure 2: Molar conductance versus mole ratio of [H]/1-ethyl-1 methylpyrrolidinium [EMPyrr]⁺ of dibenzo 18-crown-6 + ionic liquid at 293.15 K (green), 298.15 K (red) and 303.15 K (violet).

set over electromagnetic stirrer in a round bottom flask with a reflux condenser and continuously stirred for 4 h at 75°C with 350 rpm. The resulting solid dried in desiccators over CaC₂ for 5 days (Complex I).

Same procedure was followed in case of DB18C6 and [EMPyrr]PF₆. Here, 0.3604 g of DB18C6 and 0.2592

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

Volume of 18C6 added (mL)	Total volume (mL)	Concentration of DB18C6 [H] (mM)	Concentration 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	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

^aStandard uncertainties in temperature (T)=0.01 K. [EMPyrr]=1-ethyl-1-methylpyrrolidinium, 18C6=18-crown-6, IL: Ionic liquid, DB18C6: Dibenzo 18C6

Table 3: Values of the mole ratio of [H]/[EMPyrr]⁺ for 18C6 and DB18C6 at three different temperatures (K^a).

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

^aStandard uncertainties in temperature (T)=0.01 K. [EMPyrr]=1-ethyl-1-methylpyrrolidinium, 18C6=18-crown-6, IL: Ionic liquid, DB18C6: Dibenzo 18C6

of [EMPyrr]PF₆ (1:1 ratio) has been taken and do the same as mentioned above (Complex II).

3. RESULTS AND DISCUSSION

3.1. Conductivity Study Illustrates Complexation Process with their Stoichiometric Behavior 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]PF₆, 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 IL) in solution at three different temperatures. The resulting series of molar conductance (Λ_m)-mole ratio in acetonitrile are presented in Figures 1 and 2. It has been noticed that there is a significant change in molar conductance (Λ_m), that is, molar conductance gradually decreases with increase in [H]/[EMPyrr]⁺ mole ratio (Tables 1 and 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 complexation process than the mobility of [EMPyrr] PF₆ in acetonitrile in the absence of the selected crown ethers. First, the molar conductance decreases sharply during the addition of crown solution, but after a point slow changes is observed. 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],



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

$$K_f = \frac{[\text{ILH}]f(\text{ILH})}{[\text{IL}][\text{H}]f(\text{IL})f(\text{H})} \quad (3)$$

Where, $[\text{EMPyrr}]^+ \text{crown} = [\text{ILH}]$, $[\text{EMPyrr}]^+ = [\text{IL}]$, $\text{crown} = [\text{H}]$ 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 performed by dilution method, the activity coefficient (f) can be considered as unity. On the basis of Debye-Hückel limiting law the activity coefficient of $f(\text{ILH}) \approx f(\text{IL})$, thus the ratio $f(\text{ILH})/f(\text{IL})$ is also unity. Thus, the equation 3 reduces as [6,13],

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

$$\text{Where, } [\text{H}] = C_c - \frac{C_{\text{IL}}(\Lambda_{\text{IL}} - \Lambda_{\text{obs}})}{(\Lambda_{\text{obs}} - \Lambda_{\text{ILH}})} \quad (5)$$

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 the experiment; C_c the analytical concentration of the crown added and C_{IL} the analytical concentration of the IL.

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.

3.2. Thermodynamics Parameters

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

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

The free energy (ΔG°) values can be calculated using the above thermodynamics parameters and have been listed in Table 5. The negative values of ΔG° suggest that complex formation process proceeds spontaneously, whereas the negative values of ΔH° and positive values of ΔS° specify that the procedure stabilizes the whole system by decreasing energy and entropy-controlled, respectively [6] in case of $18\text{C}6:[\text{EMPyrr}]^+$ complex higher value of $-\Delta G^\circ$ than $\text{DB}18\text{C}6:[\text{EMPyrr}]^+$ implies that for the former the interactions are stronger than the later and more spontaneous.

Table 4: $\log K_f$ values of $18\text{C}6:[\text{EMPyrr}]^+$ and $\text{DB}18\text{C}6:[\text{EMPyrr}]^+$ complexes in acetonitrile medium at different temperatures (K^a).

Complex	$\log K_f$		
	293.15 K	298.15 K	303.15 K
$18\text{C}6:[\text{EMPyrr}]^+$	3.94	3.91	3.89
$\text{DB}18\text{C}6:[\text{EMPyrr}]^+$	3.37	3.34	3.31

^aStandard uncertainties in temperature (T) = 0.01 K.
 $[\text{EMPyrr}] = 1\text{-ethyl-1-methylpyrrolidinium}$,
 $18\text{C}6 = 18\text{-crown-6}$, $\text{DB}18\text{C}6$: Dibenzo 18C6

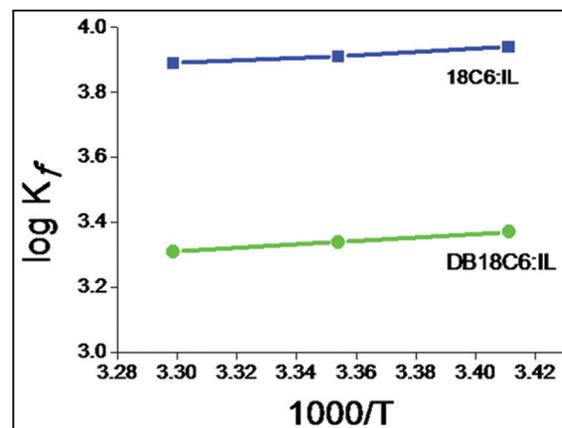


Figure 3: $\log K_f$ versus $1000/T$ for 18-crown-6 (18C6): Ionic liquid (IL) (■) and dibenzo 18C6:IL (●) complexation.

The molar conductance increases, but the formation constant 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 $[\text{EMPyrr}]^+$ ions. This also increases the thermal energy, that is, the process of complex formation is exothermic in nature ($-\Delta H^\circ$). The values of formation constant ($\log K_f$) (Table 4) evidently point out that the $18\text{C}6:[\text{EMPyrr}]^+$ forms more firmly held complex than $\text{DB}18\text{C}6:[\text{EMPyrr}]^+$. Both crown ethers have almost same cavity size 2.6-3.2 Å [17], so such variation must be originated due to the presence of two benzo groups' substitution on 18C6. The electron withdrawing effect of benzo groups reduces the Lewis basic character (electron donor property) of oxygen atoms of DB18C6 toward the incoming guest charged moiety, that is, $[\text{EMPyrr}]^+$ ion that are involved in complexation with the crown ether ring by the hetero (oxygen) atoms. As a result, 18C6 can form $\text{N}^+ \cdots \text{O}^{\delta-}$ non-covalent electrostatic ion-dipole interactions strongly and hence, the interaction in the case of $18\text{C}6:[\text{EMPyrr}]^+$ is predominant over the $\text{DB}18\text{C}6:[\text{EMPyrr}]^+$.

3.3. ¹H NMR Spectra

The ¹H NMR spectra have in addition established the interplay of pyrrolidinium cation $[\text{EMPyrr}]^+$ with the crown ethers in solution phase. The shifting of protons

Table 5: Values of the thermodynamic parameters (ΔH° , ΔS° , ΔG°) are calculated from Van't Hoff equation of the complexes.

Complex	Temperature (K ^a)	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\Delta S^\circ/\text{J mol}^{-1} \text{K}^{-1}$	$\Delta G^\circ (298.15 \text{ K}^a)/\text{kJ mol}^{-1}$
18C6:[EMPyrr] ⁺	293.15	-8.50	46.36	-22.32
	298.15			
	303.15			
DB18C6:[EMPyrr] ⁺	293.15	-10.21	29.70	-19.06
	298.15			
	303.15			

^aStandard uncertainties in temperature (T)=0.01 K. [EMPyrr]=1-ethyl-1-methylpyrrolidinium, 18C6=18-crown-6, DB18C6: Dibenzo 18C6

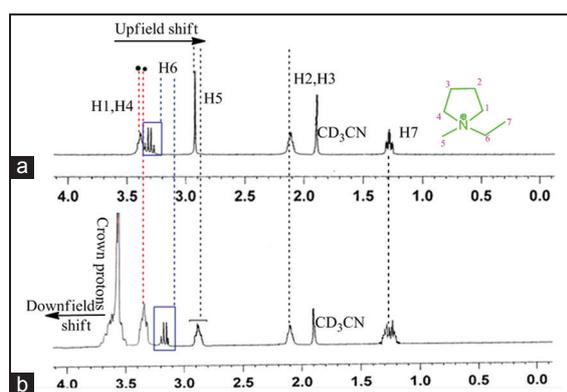
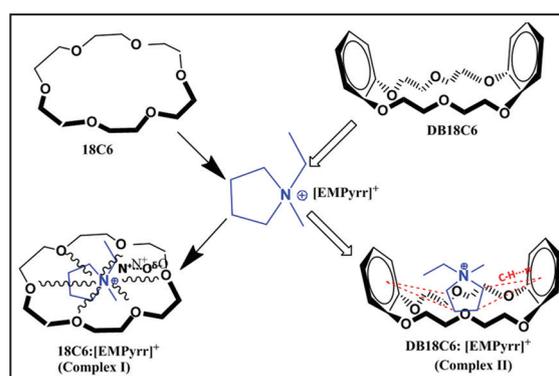


Figure 4: ¹H nuclear magnetic resonance spectra of (a) 1-ethyl-1-methylpyrrolidinium hexafluorophosphate [EMPyrr]PF₆ and (b) 1:1 molar ratio of 18-crown-6:[EMPyrr]⁺ in D₂O at 298.15 K.

of the IL (pyrrolidinium cation) and the crown ethers in Complex I and Complex II are used to analysis for the formation of the complex. Figures 4 and 5 show the ¹H NMR 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, whereas 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 toward the cavity^[2] and hence, the effective N⁺...O^{δ-} 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 -OCH₂ group protons of 18C6 are also upfield shielded in complexed form. Hence, it is concluded that such chemical shifts must occur due to host-guest complex formation of pyrrolidinium cation with 18C6 (Scheme 2).

In case of Complex II (Figure 5) large upfield shift are observed for pyrrolidinium ring protons (H1, H2, H3, and H4), whereas the chemical shifts of alkyl protons



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

(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 the presence of two phenyl substitutions and bowl-like structure of DB18C6, it has two possible arrangements for interactions with incoming guest moiety – (i) -O-CH₂-CH₂-O- chains, the minor site that may possess 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.

3.3.1. ¹H NMR data [EMPyrr]PF₆

¹H NMR (300 MHz, in CD₃CN): 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); 18C6: ¹H NMR (300 MHz, in CD₃CN): δ=3.60-3.51 (24H, m); DB18C6: ¹H NMR (300 MHz, in CD₃CN): δ=6.99-6.87 (8H, m), 4.16-4.10 (8H, m), 3.78-3.67

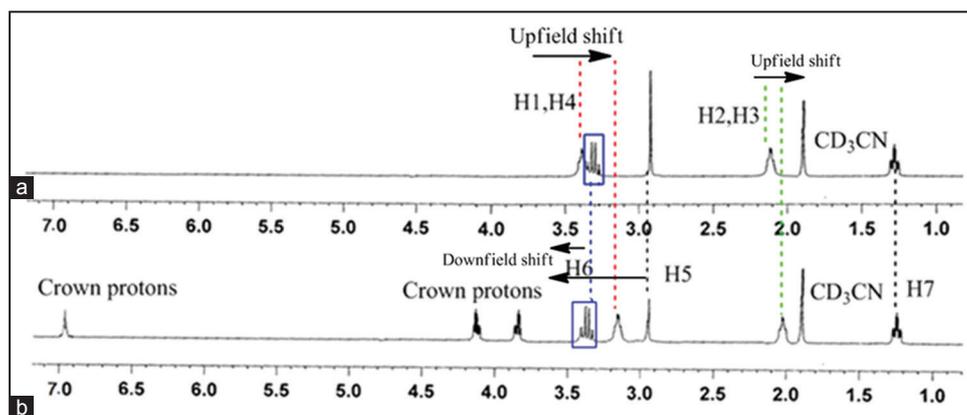


Figure 5: ^1H nuclear magnetic resonance spectra of (a) 1-ethyl-1-methylpyrrolidinium hexafluorophosphate $[\text{EMPyrr}]\text{PF}_6$ and (b) 1:1 molar ratio of dibenzo 18-crown-6: $[\text{EMPyrr}]^+$ in D_2O at 298.15 K.

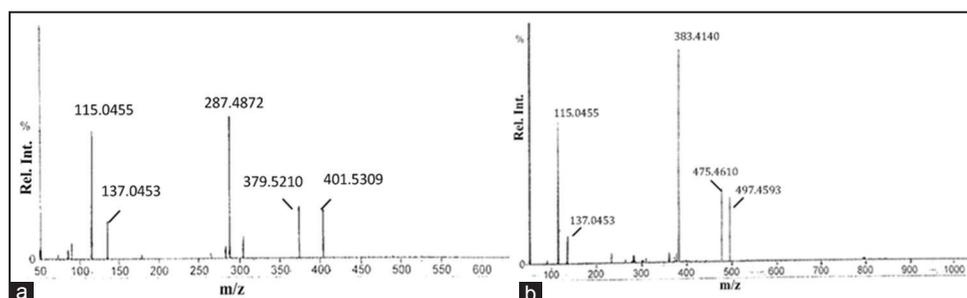


Figure 6: Electrospray mass spectra of equimolar mixture of ionic liquid with (a) 18-crown-6 and (b) dibenzo 18-crown-6.

(8H, m); 18C6+ $[\text{EMPyrr}]$ cation (Complex I): ^1H NMR (300 MHz, in CD_3CN): $\delta=3.45\text{-}3.32$ (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); DB18C6+ $[\text{EMPyrr}]$ (Complex II): ^1H NMR (300 MHz, in CD_3CN): $\delta=3.28\text{-}3.15$ (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).

3.4. Mass Spectra

Positive electrospray ionization 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 stoichiometry of 18C6- $[\text{EMPyrr}]\text{PF}_6$ and DB18C6- $[\text{EMPyrr}]\text{PF}_6$ systems are analyzed by ESI-MS. In Figure 6a, the peaks assigned at m/z 115.0455, 137.0453, 287.4872, 379.5210, 401.5309 indicate the singly charged $[\text{EMPyrr}+\text{H}]^+$, $[\text{EMPyrr}+\text{Na}]^+$, $[\text{18C6}+\text{Na}]^+$, $[\text{EMPyrr}+18\text{C}+\text{H}]^+$, $[\text{EMPyrr}+18\text{C}+\text{Na}]^+$, respectively. The peaks at m/z 383.4140, 475.4610 and 497.4593 correspond to $[\text{DB18C6}+\text{Na}]^+$, $[\text{EMPyrr}+\text{DB18C6}+\text{H}]^+$ and $[\text{EMPyrr}+\text{DB18C6}+\text{Na}]^+$ (Figure 6b). These experimental data of the selected IL/crown ether complexes suggested that the $[\text{EMPyrr}]^+$ cation simultaneously associated in polyethers cavity with 1:1 stoichiometry.

3.5. 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 $[\text{EMPyrr}]\text{PF}_6$ with 18C6 and DB18C6, respectively. The shift in bands in IR spectra in $4000\text{-}500\text{ cm}^{-1}$ region of each crown-ether provides the evidence of complex formation.

In the case of 18C6 the distinctive absorption due to $\nu_{\text{as}}(\text{C-O-C})$ stretching is assigned at 1119 cm^{-1} and shifting of $\nu_{\text{as}}(\text{C-O-C})$ in Complex I from 1129 cm^{-1} to 1111 cm^{-1} is observed (Figure 7). The $\nu_{\text{as}}(\text{C-O-C})$ stretching frequency for DB18C6 is shifted from 1128 cm^{-1} to lower frequency 1116 cm^{-1} when it forms Complex II (Figure 8). These shifting provide the prominent evidence about the interaction of $[\text{EMPyrr}]^+$ with the oxygen atoms of the crown compounds [17,24]. In the case of DB18C6 spectra and in Complex II in the range of $1200\text{-}1302\text{ cm}^{-1}$ two different kinds of assignable strong bands are observed. These indicate to stretching frequencies of anisol $\nu_{\text{s}}(\text{Ph-O-C})$ and $\nu_{\text{as}}(\text{Ph-O-C})$ [17,25]. After complexation, the $\nu_{\text{s}}(\text{Ph-O-C})$ shifts from 1302 cm^{-1} to 1287 cm^{-1} and the $\nu_{\text{as}}(\text{Ph-O-C})$ shifts from 1240 cm^{-1} to 1224 cm^{-1} . The $\nu(\text{C-H})$ stretching frequencies of methylene groups of crown ethers come in the range of $2742\text{-}2938\text{ cm}^{-1}$. It is shifted from 2920 cm^{-1} to

Table 6: Frequencies ($\nu \text{ cm}^{-1}$) of ether linkage in IR spectra of free crown ethers and the complexed crown ethers.

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

[EMPyrr]=1-ethyl-1-methylpyrrolidinium, 18C6=18-crown-6, DB18C6: Dibenzo 18C6, IR=Infrared

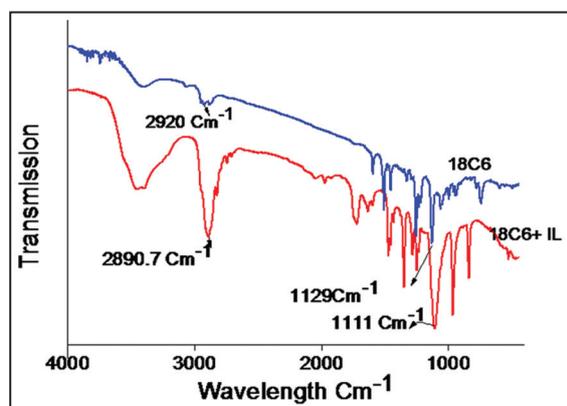


Figure 7: Infrared spectra of 18-crown-6 (18C6) (blue) and the resulting complex I (18C6:1-ethyl-1-methylpyrrolidinium) (red).

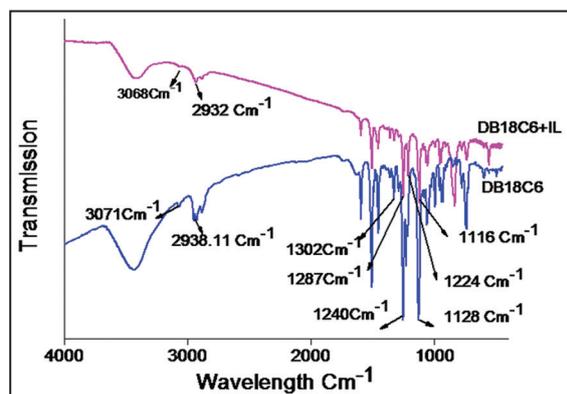


Figure 8: Infrared spectra of dibenzo-18-crown-6 (DB18C6) (blue) and the resulting Complex II (DB18C6:1-ethyl-1-methylpyrrolidinium [EMPyrr]⁺) (violet).

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 $\nu(\text{C-H})$ stretching suggests the effect of complex formations. The comparative study of the IR spectra of 18C6 and DB18C6 reveal the absorption band of substituent; although, it is difficult enough to assign as their distinctive bands may overlap with those ethylene glycol groups. However, the scrutiny on Figure 8 allowed us to identify the absorption of $\nu_{\text{benzene}}(\text{C-H})$ frequency that appears at 3071 cm^{-1} . The aromatic $\nu_{\text{aromatic}}(\text{C-C})$ bonds are at 1586 cm^{-1} , 1511 cm^{-1} , 1480 cm^{-1} [17].

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 are considerable interactions that favor the complexation process and supports the plausible mechanism that is shown in Scheme 2.

4. CONCLUSION

In the present work, the obtained result of conductivity and the association constant (k_f) for the complexation between [EMPyrr]PF₆ 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 $\text{N}^+ \cdots \text{O}^{\delta-}$ non-covalent ion-dipole, H-bonds, and $\text{C-H} \cdots \pi$ interactions (host-guest interactions) has been established by ¹H NMR. 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.

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6. REFERENCES

1. A. F. de Namor, M. C Ritt, (1991) Solution thermodynamics of amino acid-18-crown-6 and amino acid-cryptand complexes in methanol and ethanol, *Journal of the Chemical Society Faraday Transactions*, **87**: 3231-3239.
2. A. Bagaturyents, A. Y. Freidzon, M. V. Alfimov, E. J. Baerends, J. A. K. Howard, L. G. Kuzmina,

- (2002) DFT calculations on the electronic and geometrical structure of 18-crown-6 complexes with Ag^+ , Hg^{2+} , Ag^0 , Hg^2 , Hg^2 , AgNO_3 and HgX_2 ($\text{X}=\text{Cl}$, Br and I), *Journal of Molecular Structure*, **588**: 55-58.
- G. Rounaghi, R. M. Z. Kakhki, (2009) Thermodynamic study of complex formation between dibenzo-18-crown-6 and UO_2^{2+} cation in different non-aqueous binary solutions, *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, **63**: 117-122.
 - M. Fard, G. H. Rounaghi, M. Chamsaz, K. Taheri, (2009) Study of complex formation between 18-crown-6 and diaza-18crown-6 with uranyl cation (UO_2^{2+}) in some binary mixed aqueous and non-aqueous solvents, *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, **64**: 49-56.
 - G. Vendilo, V. I. Chistov, J. M. Dikareva, K. I. Popov, (2015) Crown ethers assisted cesium extraction from aqueous solutions into a hydrophobic room temperature ionic liquid 1-butyl-3-methylimidazolium bis [(trifluoromethyl) sulfonyl] imide, *Macrocyclics*, **8**: 181-184.
 - K. M. Tawarah, F. A. Ababneh, (1997) Conductance study of the binding of K^+ by dibenzo-pyridino-18-crown-6 and 1,10-N, N 0-didecyl-diaza-18-crown-6 in acetonitrile, *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, **29**: 15-22.
 - D. Marji, Z. Taha, (1998) Conductance and thermodynamic study of thallium and silver ion complexes with crown ethers in different binary acetonitrile-water solvent mixtures, *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, **30**: 309-320.
 - K. M. Tawarah, M. A. Khasawneh, S. A. Mizyed, (2005) Conductometric determination of the stability constants of the inclusion complexes of alkali cations with [22-DD] diaza crown ether, [211] and [221] cryptands in acetonitrile, *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, **51**: 143-148.
 - D. Ekka, M. N. Roy, (2012) Conductance, a contrivance to explore ion association and solvation behavior of an ionic liquid (Tetrabutylphosphonium tetrafluoroborate) in acetonitrile, tetrahydrofuran, 1, 3-dioxolane, and their binaries, *The Journal of Physical Chemistry B*, **116**: 11687-11694.
 - M. N. Roy, M. C. Roy, K. Roy, (2015) Investigation of an inclusion complex formed by ionic liquid and β -cyclodextrin through hydrophilic and hydrophobic interactions, *RSC Advances*, **5**: 56717-56723.
 - D. Ekka, M. N. Roy, (2014) Quantitative and qualitative analysis of ionic solvation of individual ions of imidazolium based ionic liquids in significant solution systems by conductance and FT-IR spectroscopy, *RSC Advances*, **4**: 19831-19845.
 - M. Deetlefs, K. Seddon, M. Shara, (2006) Predicting physical properties of ionic liquids, *Physical Chemistry Chemical Physics*, **8**: 642-649.
 - M. S. Kazemi, (2010) Effect of solvent on the stability constant of complex formation and the thermodynamic parameters between dicyclohexyl-18crown-6 with Eu^{3+} , La^{3+} , Er^{3+} and Y^{3+} cations, *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, **68**: 331-338.
 - M. Shamsipur, H. R. Pouredal, (1999) Conductance study of complexation of lead ions by several 18-membered crown ethers in acetonitrile-dimethyl sulfoxide mixtures between 25 and 55°C, *Journal of Solution Chemistry*, **28**: 1187-1205.
 - G. Khayatian, F. S. Karoonian, (2008) Conductance and thermodynamic study of the complexation of ammonium ion with different crown ethers in binary nonaqueous solvents, *Journal of the Chinese Chemical Society*, **55**: 377-384.
 - D. F. Evans, S. L. Wellington, J. A. Nadi, E. R. Cussler, (1972) The conductance of cyclic polyether-cation complexes, *Journal of Solution Chemistry*, **1**: 499-506.
 - E. V. Guseva, T. E. Busygina, L. S. Gracheva, V. K. Polovnyak, R. A. Khasanshin, E. G. Yarkova, R. A. Yusupov, (2001) Complex formation of potassium hexachloroplatinate with 18-crown-6 and dibenzo-18-crown-6 in acetonitrile, *Russian Journal of General Chemistry*, **71**: 217-221.
 - E. V. Guseva, T. E. Busygina, L. S. Gracheva, V. K. Polovnyak, R. A. Khasanshin, E. G. Yarkova, R. A. Yusupov, (2014) Complex formation of potassium hexachloroplatinate with 18-crown-6 and dibenzo-18-crown-6 in acetonitrile, *Russian Journal of General Chemistry*, **84**: 227-234.
 - I. Ling, Y. Alias, A. N. Sobolev, C. L. Raston, (2010) p-sulfonatocalix[4]arene-pyrrolidinium complexation in building multicomponent layered arrays, *Crystal Growth and Design*, **10**: 1312-1318.
 - S. Kiviniemi, M. Nissinen, M. T. J. Jalonen, K. Rissanen, J. Pursiainen, (2000) Complexation of planar, organic, five-membered cations with crown ethers, *New Journal of Chemistry*, **24**: 47-52.
 - C. Zhang, S. Li, J. Zhang, K. Zhu, N. Li, F. Huang, (2007) Benzo-21-crown-7/secondary dialkylammonium salt[2] pseudorotaxane-and [2] rotaxane-type threaded structures, *Organic Letters*, **9**: 5553-5556.
 - Z. Zhou, X. Yan, T. R. Cook, M. L. Saha,

- P. J. Stangm, (2016) Engineering functionalization in a supramolecular polymer: Hierarchical self-organization of triply orthogonal non-covalent interactions on a supramolecular coordination complex platform, *Journal of the American Chemical Society*, **138**: 806-809.
23. W. Z. Shou, R. F. Browner, (1999) Evaluation of crown ether complexation for elemental electrospray mass spectrometry, *Analytical Chemistry*, **71**: 3365-3373.
24. E. S. Stoyanov, A. Christopher, (2004) Unexpected IR characteristics of hydrogen bonds in the 18-crown-6-ether complex of the H_3O^+ hydronium ion. Can the location of the protons be specified? *The Journal of Physical Chemistry A*, **108**: 907-913.
25. Y. Tsivadze, A. Y. Varnek, V. E. Khutorskoi, (1991) *Koordinatsionnye Soedineniya Metallov s Kraunligandami (Coordination Compounds of Metals with Crown Ligands)*, Moscow: Nauka.

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