

CHAPTER - VII

STUDY OF COMPLEXATION OF IONIC LIQUID INSIGHT INTO CROWN ETHERS IN AQUEOUS ENVIRONMENTS BY PHYSICOCHEMICAL TECHNIQUES

7.1 Introduction:

Crown ethers (CEs) belong to the family of macrocyclic compounds which draw attention since their discovery in 1967, particularly in the research area of host-guest and coordination chemistry [1,2]. CEs can form complexes with diverse molecules into their cavity through various interactions with multiple oxygen atoms [3]. CEs are useful as phase transfer catalysts, photo-switching devices, drug carriers, etc.[4,5]. These unique cyclic molecules are important for molecular recognition of suitable substrates by hydrogen bonds and ionic interactions [6]. These studies of complexations are noteworthy for a better understanding of the mechanism of biological transfer of molecules [7,8]. It is known that the imidazolium cation can form inclusion complexes with crown-ether-type hosts via H-bonding [8]. 1, 3-disubstituted imidazolium salts are known to form inclusion complex with large CEs through intermolecular hydrogen-bond formation as demonstrated by different researchers [9-11]. In 1,3-disubstituted imidazolium salts, all protons on the imidazolium ring are fairly acidic as the positive charge is delocalized over the entire imidazolium ring [12,13]. The acidic protons are attractive in supramolecular chemistry for the formation of hydrogen-bonds with the electron pair on the oxygen atoms, which is responsible for the stability of the complex formed [14,15]. Imidazolium salts are important not only in organometallic chemistry, but also in organic chemistry and material science as ionic liquids (ILs) due to their exceptional chemical, physical, and electrical properties [16-19].

In the present work we have studied the inclusion complex formation of 1-ethyl-3-methylimidazolium tosylate [EMIm]Ts with 15-crown-5 (15-C-5) and 18-crown-6 (18-C-6) in aqueous medium (scheme 1). The complexations have been explained by ^1H NMR study, the formation constants have been evaluated from conductivity study and the stoichiometries have been derived from surface tension study.

7.2. Experimental Section

7.2. 1. Source and Purity of Samples

15-Crown-5, 18-Crown-6 and 1-ethyl-3-methylimidazolium tosylate were purchased from Sigma-Aldrich, Germany and used as it was. Mass fraction purity of 15-Crown-5, 18-Crown-6 and 1-ethyl-3-methylimidazolium tosylate were 0.98, ≥ 0.99 and ≥ 0.98 respectively.

7.2. 2. Apparatus and procedure

Solubilities of 15-Crown-5, 18-Crown-6 and 1-ethyl-3-methylimidazolium tosylate were precisely checked in triply distilled and degassed water and observed that these were freely soluble in water. All the stock solutions were prepared by mass (weighed by Mettler Toledo AG-285 with uncertainty 0.0003g) at 298.15 K. Sufficient precautions were made to decrease evaporation losses during mixing.

Conductivities of the solutions were studied by Mettler Toledo Seven Multi conductivity meter having uncertainty $1.0 \mu\text{Sm}^{-1}$. The study was carried out by using Omniset thermostat water bath at 298.15 K with uncertainty ± 0.01 K. HPLC grade water was used with specific conductance $6.0 \mu\text{S m}^{-1}$. The conductivity cell was calibrated using 0.01M aqueous KCl solution.

Surface tensions of the solutions were determined by platinum ring detachment technique using a Tensiometer (K9, KRÚSS; Germany) with an accuracy of $\pm 0.1 \text{ mN}\cdot\text{m}^{-1}$. Temperature of the system was maintained by Brookfield TC-550 water bath at 298.15 ± 0.01 K through a double-wall glass vessel holding the solution.

NMR spectra were recorded in D_2O unless otherwise stated. ^1H NMR spectra were recorded at 300 MHz using Bruker Avance 300 MHz instrument. Signals are quoted as δ values in ppm using residual protonated solvent signals as internal standard (D_2O : δ 4.79 ppm). Data are reported as chemical shift.

7.2. 3. ^1H NMR data

15-Crown-5: ^1H NMR (300 MHz, D_2O): $\delta = 3.53$ (20H, s, OCH_2).

18-Crown-6: ^1H NMR (300 MHz, D_2O): $\delta = 3.55$ (24H, s, OCH_2).

[EMIm]Ts: ^1H NMR (300 MHz, D_2O): $\delta = 1.17\text{-}1.32$ (3H, t), 2.20 (3H, s), 3.68 (3H, s), 3.93-4.04 (2H, q), 7.15-7.26 (3H, m), 7.47-7.50 (2H, d), 8.42-8.48 (2H, d).

15-Crown-5 + [EMIm]Ts: ^1H NMR (300 MHz, D_2O): $\delta = 1.14\text{-}1.29$ (3H, t), 2.20 (3H, s), 3.59 (20H, s, OCH_2), 3.60 (3H, s), 3.89-4.00 (2H, q), 7.05-7.15 (3H, m), 7.47-7.50 (2H, d), 8.42-8.48 (2H, d).

18-Crown-6 + [EMIm]Ts: ^1H NMR (300 MHz, D_2O): $\delta = 1.15\text{-}1.30$ (3H, t), 2.20 (3H, s), 3.58 (20H, s, OCH_2), 3.62 (3H, s), 3.90-4.01 (2H, q), 7.07-7.16 (3H, m), 7.47-7.50 (2H, d), 8.42-8.48 (2H, d).

7.3. Result and Discussion

7.3.1. Conductivity study illustrates complexation process and their formation constants

Conductivity studies have been reported to evaluate the interactions between [EMIm]Ts with 15-C-5 and 18-C-6 in aqueous medium at 298.15 K and the values are presented in the table 1. The formation constants ($\log K_f$) of the complexes are found in the order ([EMIm]Ts+15-C-5)>([EMIm]Ts+ 18-C-6) and shown in table 2. The conductivity (κ) of imidazolium salt in aqueous medium was examined as a function of CE/IL mole ratio and the resulting plots at are shown in figure 1 [20,21]. In both cases there are gradual decreases in the conductivity with increase in the CE concentrations. This behaviour indicates that the complexed imidazolium cation is less mobile than the corresponding free imidazolium cation in aqueous solution [22]. In figure 1 addition of the CE solution to the imidazolium salt solution causes a continuous decrease in κ which commence at a mole ratio greater than one, indicating the formation of a stable 1:1 complex [23]. The stability of these complexes depends mainly on the strength of the bonds between acidic protons of the imidazolium ring and oxygen atoms of crown ether (Scheme 2) [24].

The following mathematical treatment was done to calculate the formation constant. The 1:1 complexation of IL with CE can be expressed by the following equilibrium [25]



The corresponding equilibrium constant, K_f is given by

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

where $[MC^+]$, $[M^+]$, $[C]$ and f represent the equilibrium concentrations of the complex, free cation, free ligand and the activity coefficients of the species indicated, respectively. In the dilute conditions the activity coefficient of uncharged macrocycle, $f(C)$, can be reasonably assumed as unity [26]. The use of the Debye-Hückel limiting law, leads to the conclusion that $f(M^+) \sim f(MC^+)$, so the activity coefficients in Equation (2) cancel out [27]. The formation constant in terms of the conductivity (κ), can be expressed as,

$$K_f = \frac{[M^+]}{[M^+][C]} = \frac{(\kappa_M - \kappa_0)}{(\kappa_0 - \kappa_M)[C]} \quad (3)$$

$$\text{where } [C] = C_C - \frac{C_M(\kappa_M - \kappa_0)}{(\kappa_M - \kappa_M)} \quad (4)$$

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

The data shown in table 2 indicates that formation constant $\log K_f$ for imidazolium cation with 15-C-5 is higher than with 18-C-6 at 298.15K might be due to more close and compact structure of the host and the guest in case of former than the later [28].

7.3.2. Surface tension study explains the complexation as well as their stoichiometric ratio

Surface tension (γ) measurement provides significant indication about formation of inclusion complex as well as stoichiometry of the host-guest assembly [29,30]. The values of surface tension at different mole ratio of CE/IL are listed in table 3. In the present work [EMIm]Ts shows surfactant like activity, thus γ of the [EMIm]Ts solution shows decreasing trend with increasing concentration of CEs. In this work as CEs are

added in IL solution the imidazolium group binds to the oxygen atoms of the CE and the formation of inclusion complex takes place [31,32]. As a result charged portion of the IL form complex with CE, the effect of hydrophobic chains increases i.e., surface tension of the solution decreases slowly. At a certain concentration of [EMIm]Ts and CE, a single break was observed in the surface tension curve (figure 2). The single break point in surface tension curve not only indicates the formation of complex between [EMIm]Ts and CE but also about its stoichiometry, i.e., appearance of single break point in the plot indicates 1:1 stoichiometry of the complex [33]. The value of γ at the break point and corresponding concentrations of both CEs and [EMIm]Ts have been listed in table 4, which again shows that the ratio of concentrations of the host and guest at the break point is almost 1:1, indicating the stoichiometries of the complexes as 1:1 [34].

7.3. 3. ¹H NMR study confirms complexation phenomenon

The complexation of imidazolium salt with crown ethers were investigated by ¹H NMR spectroscopy in D₂O at 298.15 K. The ¹H NMR spectra of 15-C-5, [EMIm]Ts and 1:1 molar mixture of the two are shown in figure 3. Comparison of the ¹H NMR spectra in figure 3 reveals that the signals for hydrogen atoms of the imidazolium ion were shifted toward upfield, because of shielding by the electrons from oxygen of CE, which supports the complex formation through H-bond formation involving [(C-H)Imidazolium.....O-Crown] interaction [35]. Signals for the -OCH₂ protons of crown ether were found to be downfield shifted relative to those signals for the free component, because of donation of electrons toward the imidazolium component [29]. In case of complex of 18-C-6 (figure 4), upfield shift for the signals of imidazolium protons and downfield shift of the CE protons were observed. The changes in chemical shifts suggest that host-guest complexation between crown ethers and imidazolium salt exists in both the complexes [36,37]. The blue arrows show the upfield chemical shift of the imidazolium protons, the red arrow show downfield chemical shift of the CE protons and the green arrows show unshifted signals of the tosylate moiety. Based on different interactions and ¹H NMR chemical shifts data for the two complexes, plausible scheme has been proposed and represented in scheme 2. In the complexes the imidazolium ring can penetrate into the hollow circular based cavity of the macrocycle 15-C-5 or 18-C-6 forming strong H-bonding but the substituents in the 1,3 position point away from the cavity of the crown ethers [38]. Thus detailed ¹H

NMR spectral studies indicate that hydrogen bonding interactions [(C-H)Imidazolium.....O-Crown] results in strong inclusion complex formation supporting the data obtained from conductivity and surface tension measurements.

7.3. 4. Typical features of interactions in complexation process

Inclusion complex formation between CEs and imidazolium ion involves different possible modes of interactions [39]. The most important 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 [40]. Apart from H-bonding, induced dipole-dipole interaction between imidazolium ion and O-Crown having δ^- charge could also contribute to the overall stability of the complex formation[41]. However, this induced dipole-dipole interaction is expected to be weaker as compared to hydrogen bonding interaction as discussed [42]. The stability constants ($\log K_f$) for 1:1 complexation were measured in aqueous solution by conductivity study and are presented in table 2. In both the complexes H-bonding to the ether oxygen atoms is obviously responsible for complexation [29]. This has been shown by the suitable plausible mechanism (scheme 2). There may be possibility of ion-dipole interactions between positive N atom of imidazolium cation and ether oxygen atom [42]. The stability constant for the complex with 18-C-6 is slightly lower than that of the complex with 15-C-5 (table 2). The more compact and close structure of the later seems to increase the strength of H-bonding in the complex explaining the higher stability constant.

7.4. Conclusion

The conductivity data communicates the complex formation of crown ethers with IL molecule, which are consistent with the surface tension measurements and ^1H NMR spectra. The studied complexes are mainly stabilised by hydrogen bonds and ion-dipole interactions play only a secondary role. Larger formation constant value for complex with 15-C-5 compared to that with 18-C-8 determined by conductivity study indicates that imidazolium cation form stable complex with 15-C-5 compared to 18-C-8 in aqueous solution. The 1:1 complexation of the imidazolium based IL by different crown ethers is driven by favourable stabilised interactions. This study also helps to get important information about the other host-guest systems having

crown ethers. This complexation study of imidazolium ion 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.

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Tables:

Table 1. Data for the mole ratio against specific conductivity of aqueous 15-crown-5 and 18-crown-6 with 1-ethyl-3-methylimidazolium tosylate at 298.15K^a

Mole Ratio (CE/IL)	κ mS m ⁻¹	
	15-crown-5	18-crown-6
0.00	1.83	1.83
0.10	1.71	1.73
0.20	1.57	1.64
0.30	1.49	1.54
0.40	1.42	1.46
0.50	1.34	1.39
0.60	1.25	1.34
0.70	1.17	1.28
0.80	1.12	1.22
0.90	1.06	1.17
1.00	1.01	1.13
1.10	0.95	1.09
1.20	0.89	1.05
1.30	0.85	1.01
1.40	0.82	0.97
1.50	0.79	0.94
1.60	0.76	0.90
1.70	0.74	0.88
1.80	0.72	0.86
1.90	0.71	0.85
2.00	0.70	0.84

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

Table 2. Values of formation constant of different crown ethers complexes in aqueous solution at 298.15 K^a

CE-IL system	log K _f /M ⁻¹
15-C-5-[EMIm]Ts	2.96
18-C-6-[EMIm]Ts	2.89

^aStandard uncertainties in temperature (T) = 0.01 K.

Table 3. Data for the mole ratio against surface tension of aqueous 15-crown-5 and 18-crown-6 with 1-ethyl-3-methylimidazolium tosylate at 298.15K^a

Mole Ratio (CE/IL)	γ mN m ⁻¹	
	15-crown-5	18-crown-6
0.00	76.8	76.8
0.10	76.4	76.5
0.20	76.1	76.2
0.30	75.7	75.9
0.40	75.4	75.6
0.50	75.0	75.4
0.60	74.7	75.1
0.70	74.3	74.8
0.80	74.0	74.5
0.90	73.8	74.3
1.00	73.6	74.1
1.10	73.5	74.0
1.20	73.4	73.9
1.30	73.3	73.8
1.40	73.2	73.7
1.50	73.1	73.6
1.60	73.0	73.5

1.70	72.9	73.4
1.80	72.8	73.3
1.90	72.7	73.2
2.00	72.6	73.1

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

Table 4. Values of surface tension (γ) at the break point with corresponding to concentrations of IL and crown ethers in aqueous solution at 298.15 K

	Conc of CE	Conc of IL	γ
	/mM	/mM	/mN·m ⁻¹
15-crown-5	5.02	4.98	73.6
18-crown-6	5.05	4.95	74.1

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

Figures:

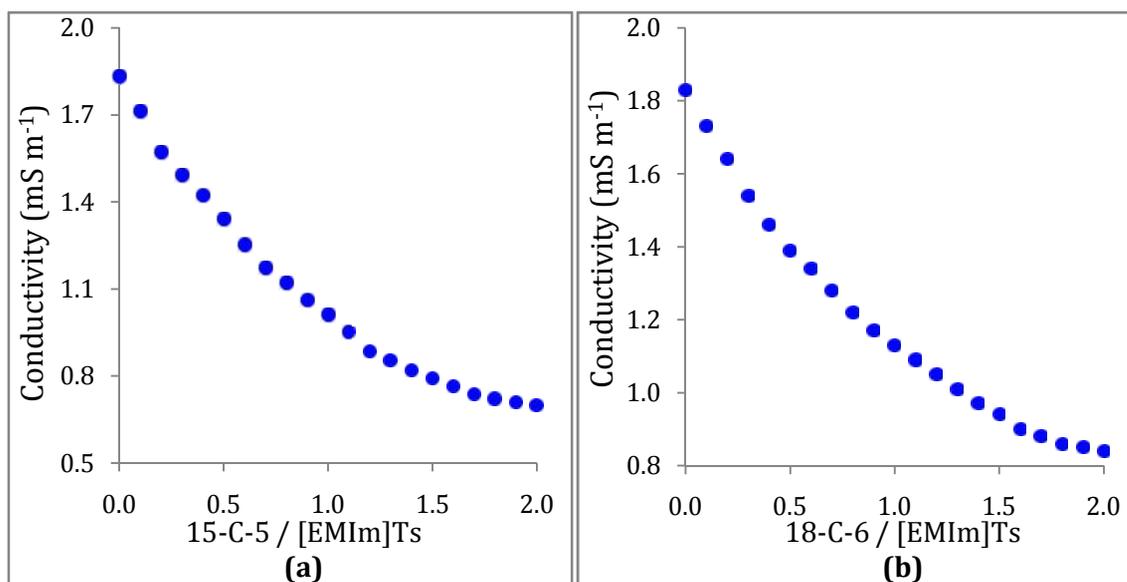


Figure 1. Variation of conductivity of aqueous (a) 15-C-5 and (b) 18-C-6 with mole ratio of CE/IL at 298.15 K.

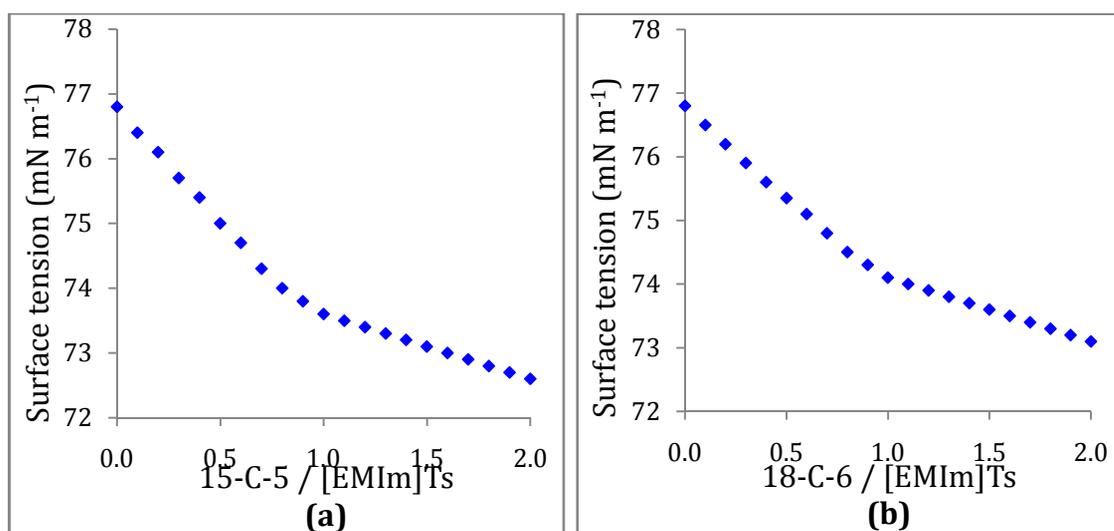


Figure 2. Variation of surface tension of aqueous (a) 15-C-5 and (b) 18-C-6 with mole ratio of CE/IL at 298.15 K.

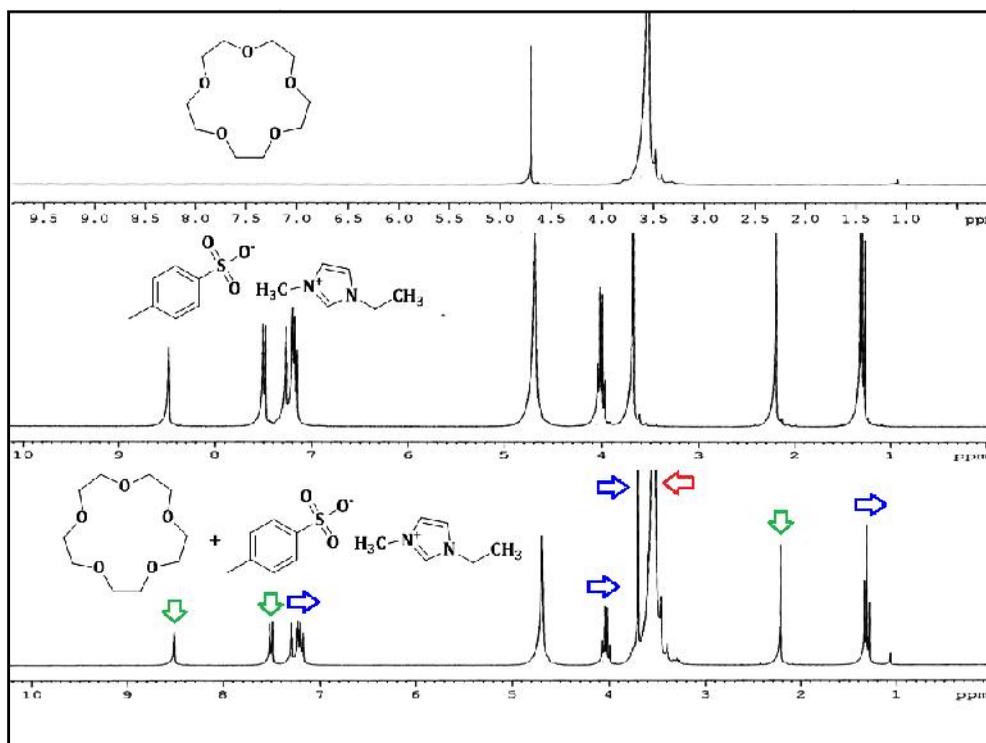


Figure 3. ^1H NMR Spectra of 15-C-5, [EMIm]Ts and 1:1 molar ratio of 15-C-5 + [EMIm]Ts in D_2O in 298.15K.

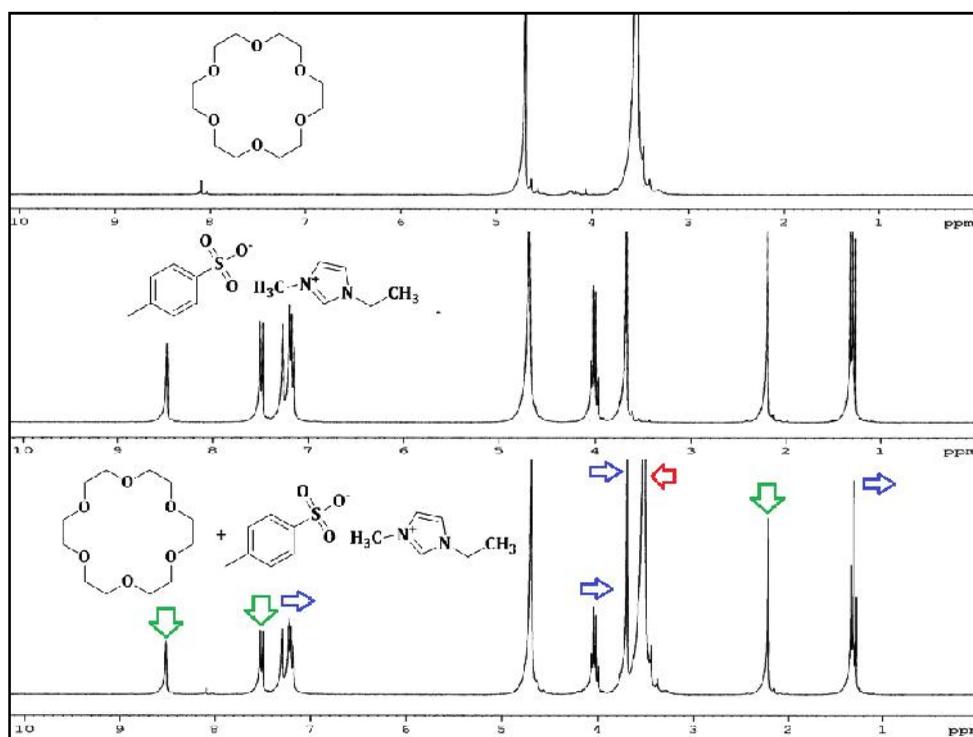
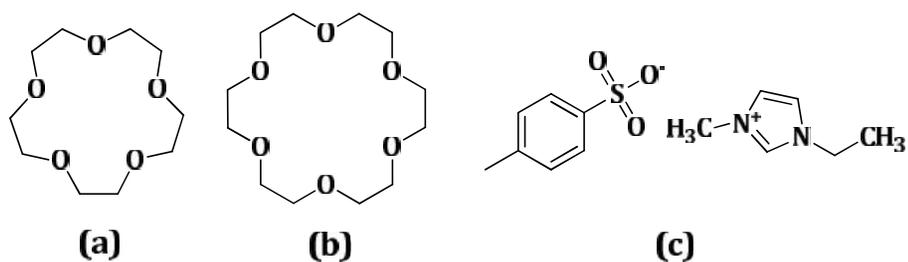
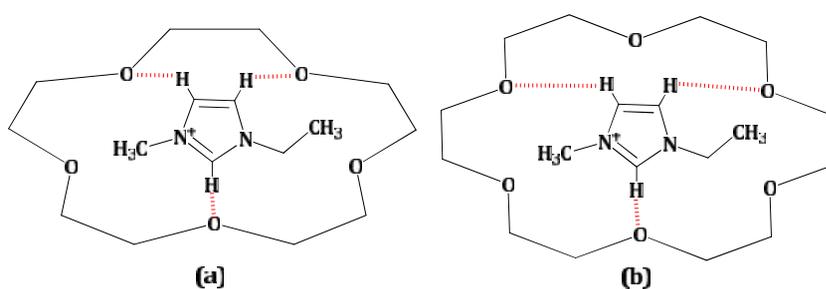


Figure 4. ^1H NMR Spectra of 18-C-6, [EMIm]Ts and 1:1 molar ratio of 18-C-6 + [EMIm]Ts in D_2O in 298.15K.

Schemes:



Scheme 1. Molecular structures of (a) 15-crown-5, (b) 18-crown-6 and (c) 1-ethyl-3-methylimidazolium tosylate.



Scheme 2. Schematic presentation of complex formation between (a) imidazolium cation and 15-crown-5, (b) imidazolium cation and 18-crown-6.