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SUPRAMOLECULAR ASSEMBLY OF IONIC LIQUID WITH CYCLIC OLIGOSACCHARIDE IN AQUEOUS ENVIRONMENTS

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ABSTRACT

A suitable host-guest inclusion complex has beenmade with a guest molecule, 1-methyl-3-octylimidazolium chloride ([MOIm]Cl) and a host molecule, *α*-cyclodextrin in aqueous medium. Formation of the host-guest inclusion complex has been established by Surface tension and conductivity readings while ^{1}H NMR and ultraviolet spectroscopy readingconfirms1:1 host-guest stoichiometry. These results have implications for the formation of host-guest inclusion complex of studied ionic liquid as guest in aqueous α–cyclodextrin media.

INTRODUCTION

Alpha Cyclodextrin(*α*-CD) is a cyclic oligosaccharide having six glucopyranose units bounded by (Zain *et al*., 2006; Bender *et al*., 1978; Gao, 2006 and Szejtli *et al*., 1998), connections establishingaabbreviated narrowed structure, which has hydrophobic interior and hydrophilic frames (Zain, *et al*., 2016). The molecular structures of the studied cyclodextrinis represented in Scheme 1.Their whole molecular shape is that of a truncated cone, with a hydrophobic hollow and a polar interface, categorized by hydroxylated, hydrophilic frames (a narrower, primary border and a wider, secondary border). This geometry gives CD a highly adaptable ability to form inclusion (Bender, 1978), complex with different kinds of organic solutes that makes them suitable in food industry, as drug carriers, and as adsorbents for parting techniques, to cite a few relatedapplications (Gao *et al*., 2006; Szejtli, 1998 and Saenger, 1980). The studied surface active ionic liquid (IL),1-methyl-3-octylimidazolium chloride as a part of green solvents at room temperature, is attractive because of their exceptional properties, such as non-volatile nature, huge liquid range, capability of dissolving a diversity of chemicals, extraordinary thermal stability and their potential as "designer solvents" and "green" replacements (Ekka *et al*., 2012; Welton, 1999 and Earle, 2000) and as well as bio-catalysts. Additionally, they have many other appropriate properties, such as easy recyclability, a wide electrochemical potential window etc., creating them essential as unique solvents in organic synthesis, chemical separations and so on (Dupont *et al*., 2002; Plechkova, 2008; Endres *et al*., 2006; Singh *et al*., 2016 and Freire, 2015). The molecular structure of the studied ionic liquid is denoted in Scheme 2. In sight of the above and in extension of our earlier study (Roy *et al*., 2014; Roy *et al*., 2014; Bhattacharjee, 2010 and Roy *et al*., 2015), we have tried to determine the nature of formation of inclusion complex(IC) of IL inside into the α-cyclodextrin in w_1=0.001, 0.003, 0.005 mass fraction of aq. α-cyclodextrinenvironments a literature survey exposes that no work has been carried out in the present systems.

Experimental Section

Materials

The investigated IL and α-cyclodextrinwere procured and purchased from Sigma-Aldrich, Germany. The mass fraction

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purity of IL and α-cyclodextrinwere ≥ 0.97 and ≥0.96 respectively.

Apparatus and procedure

The solubility of the chosen cyclodextrinand ionic liquid in aqueous cyclodextrin has been checked and confirmed that the studiedcompounds are freely soluble in aqueous medium. Aqueous binary solution of IL was prepared by mass dilution at 298.15 K (Roy *et al.*, 2015). The surface tension experiments were finished by platinum ring detachment method by a Tensiometer (K9, KRŰSS; Germany) at the studied temperature (Roy, 2014). UV-visible spectra were noted by JASCO V-530 UV/VIS Spectrophotometer, with an uncertainty of wavelength resolution of ±2 nm. The measuring temperature was held constant by a thermostated. Specific conductance values of the investigational solutions were taken by Mettler Toledo Seven Multi conductivity meter (Roy *et al.*, 2015). NMR spectra were informed as chemical shift^{1}H NMR spectra,noted at 300 MHz using Bruker ADVANCE 300 MHz and instrument at 298.15K.

RESULTS AND DISCUSSIONS

Surface tension

Surface tension (γ) measurement provides significant clue about formation of IC as well as stoichiometry of the host-guest assembly (Pineiro *et al.*, 2007). Surface tension of the aqueous solution of IL showsextraordinary change with growing concentration of α-CD (Fig 1). Surface tension value increases with increasing concentration due to the presence of side chain hydrophobic group with the cyclodextrin. Surface tensionswith corresponding concentration of IL in different mass fraction of aq. α-CD have been reported for studied IL.

The surface tension curve against concentration (molality) apparently shows a break point in surface tension at a certain concentration, that is, the γ values increases with corresponding concentration, reach a definite point (break point), and then become approximately balanced, which obviously indicates the formation of inclusion complex. The values of surface tension at the break point are represented in Table 1.The probability of formation of inclusion complex can be predicted from surface tension study, where the formation of inclusion complex has been bearing out from the break point in the curve of surface tension vs concentration. The single, double, etc. break in the surface tension curve indicates1:1, 2:1 and so on stoichiometry (Scheme 3) of host-guestin the γ vs. conc. curve. The above mention IL, hence, form soluble 1:1 complex with the cyclodextrinin which the hydrophobic long chain of IL included in the hydrophobic cavity of cyclodextrin (Scheme 4). The geometrically allowed suitable hydrophobic cavity of α-CD from the wider rim can easily encounter suitable guest molecule. The hydrophilic part of the IL remains outside and can make H-bonds with the hydrophilic rim of cyclodextrin and also surrounded by water molecules. This is also in connection with the data from conductance measurement, discussing underway, definitely establish that α-CD has the appropriate structure for the formation of inclusion complex with the studied IL.

Ultraviolet spectroscopy: Job plot

UV-visible study confirms the formation of inclusion complex in aqueous media. Job's method of continuous variation was applied to recognize the stoichiometry of the host-guest assembly by using UV-visible spectroscopy (Job, 1928). Here the solution of IL and cyclodextrin were mixed at various concentration ratios R = [IL]/([IL] + [CD]) taking the total concentration [IL] + [CD] constant and the mole fraction of the IL varies in the range 0–1 (Table 2). The stoichiometry for each complex was determined by plotting $\Delta A \times R$vs$R$ (where ΔA is the absorbance change of the IL without and with cyclodextrin), (Renny, 2013), (Fig 2).

Table 1. Values of surface tension at the break point (γ) with corresponding concentration of IL in different mass fraction ofaqueousα-cyclodextrin at 298.15K^a

mass fraction (w)	conc (m)x10^4	γ /mNm^{-1}
	IL	
w_1=0.001	4.7	58.59
w_1=0.003	4.0	58.72
w_1=0.005	3.3	59.05

^{a} Standard uncertainties u are: $u(T)$ =0.01K

^{b}w_1 is the mass fractions of α-cyclodextrin in aqueous mixture.

Table 2. Data for the Job plot performed by UV-Vis spectroscopy for aqueous- α-CD system

IL (mL)	α-CD (mL)	IL (μM)	α-CD (μM)	[IL]/([IL]+[α-CD])	Absorbance (A)	ΔA	ΔA×[IL]/([IL]+[α-CD])
0.0	3.0	0	300	0.0	0.00	0.45	0.000
0.3	2.7	30	270	0.1	0.04	0.40	0.040
0.6	2.4	60	240	0.2	0.07	0.37	0.075
0.9	2.1	90	210	0.3	0.12	0.32	0.098
1.2	1.8	120	180	0.4	0.17	0.28	0.112
1.5	1.5	150	150	0.5	0.23	0.22	0.110
1.8	1.2	180	120	0.6	0.27	0.18	0.108
2.1	0.9	210	90	0.7	0.31	0.13	0.096
2.4	0.6	240	60	0.8	0.35	0.09	0.075
2.7	0.3	270	30	0.9	0.37	0.08	0.072
3.0	0.0	300	0	1.0	0.45	0.00	0.000

Absorbance values were measured at 210 nm for IL at 298.15 K forthe solutions. The Rvalues in which the plot represents the maximum deviation provides the stoichiometry of the inclusion complex (R = 0.5 for 1:1 complexes; R = 0.33 for 1:2 complexes; R = 0.66 for 2:1 complexes). In ourstudy, the plots of IL+α-CD, at R = 0.46 suggesting inclusion complex having molar ratio 1:1.

inside into the cavity of α-CD. After a certain concentration of α-CD a break was found in each of the conductivity curves (Fig 4), indicating the formation of IC.

Table 3. Data for the Benesi-Hildebrand double reciprocal plot performed by UV-Vis spectroscopy for aqueous IL -*α*-CD system

Temp /K^a	[U] /μm	[α-CD] /μm	A$_o$	A	ΔA	1/[α-CD] /m^{-1}	1/ΔA	Intercept	Slope	Ka /m^{-1}
298.15	50	30	0.046	0.1641	0.1178	0.0333	8.5	1.0682	229.12	4662.18
	50	40		0.1885	0.1422	0.0250	7.0			
	50	50		0.2136	0.1673	0.0200	6.0			
	50	60		0.2554	0.2091	0.0167	4.8			
	50	70		0.2903	0.2440	0.0143	4.1			

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

Table 4. Values of Specific conductance at the break point (κ) with corresponding concentration of IL in different mass fraction ofaqueous α-cyclodextrin at 298.15K^a

mass fraction (w)	conc (m) x10^4	κ /S.m^{-1}
	IL	
w_1=0.001	4.8	1.43
w_1=0.003	4.3	1.50
w_1=0.005	3.7	1.56

^{a} Standard uncertainties u are: $u(T)$ =0.01K

Table 5. Change in chemical shifts (ppm) of the H3 and H5 protons of the cyclodextrin host molecule when complexed with ionic liquid guest molecule in D$_2$O at 298.15 K

Change in chemical shift		
Ionic Liquid		
	H3	H5
α-cyclodextrin	0.237	0.062

^{a}Standard uncertainties in temperature u are: u(T) = 0.01 K.

Ultraviolet spectroscopy: association constant

The association constants K_a for different IL-cyclodextrin systems have been estimated by spectroscopic methods on the basis of changes of molar absorptivity of the IL when complexed into the cyclodextrin molecules. The reason is the changes in the polarity of the atmosphere of the IL when it drives from the polar aqueous environment to the apolar cavity of cyclodextrin. Changes in absorption intensity of IL (210 nm), was studied as a function of concentration of cyclodextrin to define the value of K_a (Table 3). Using the reliable Benesi–Hildebrand method for 1:1 host-guest complex the double reciprocal plot has been drawn (Fig 3), (Cramer *et al.*, 1967 and Yan-AnGao, 2005).

$$\frac{1}{A} = \frac{1}{\varepsilon[Guest]K_a}\ \frac{1}{[Host]} + \frac{1}{\varepsilon[Guest]}$$

Conductivity study

Conductivity measurement (Yan-AnGao, 2005), method used to elucidate not only whether inclusion can occur but also the stoichiometry of the inclusion complex (IC) formed (Palepu, 1989). The conductivity of different α-CD concentrations in aqueous IL were dignified at 25^{0}C, and the need of the conductivity on α-CD concentration is shown in Fig 4.The studied IL shows considerable κvalues because of having their charged structures. As α-CD was added to the aqueous solution ofIL, the κvalues was observed to show decreasing trend probably because of encapsulation of the IL molecules

The values of κ and corresponding concentrations of α-CD at each break have been shown in Table 4, which reveal that the ratio of the concentrations of aIL and α-CD at the break point was found to be approximately 1:1, suggesting the host-guest ratio to be equimolar (Topchieva, 2004). This finding is supported by the surface tension curves above.

NMR study

In the NMR spectra we have found the chemical shift of the guest and α-CD molecule due to the interaction of the α-CD with the guest molecule (Caso, 2015). In aromatic compounds the spectral variations that can be observed upon inclusion is the diamagnetic shielding of the aromatic guest with the interacting atoms of the host molecule (Wang *et al.*, 2014). In the structure of cyclodextrin the H^3 and H^{5}hydrogens are situated inside the conical cavity, particularly, the H^3 are placed near the wider rim whereas H^5 are placed near the narrower rim of cyclodextrin molecule. The other H^1, H^2 and H^{4}hydrogens are located at the exterior part of thecyclodextrinmolecule (Sambasevam, ?), (Scheme 5). During inclusion the signals of H3 and H5 of cyclodextrin show considerable upfield shift (Δδ) (Fig5). Therefore when a guest molecule arrives into the hollow of cyclodextrin it relates with the H^3 and H^5 protons, ensuing in the upfield chemical shift of these protons (Roy, 2014). In our recent work the molecular interfaces of IL with cyclodextrin have been studied by 1H NMR spectra by taking 1:1 molar ratio of the IL and cyclodextrin in D$_2$O at 298.15 K.After inclusion the upfieldchange of chemical shift values of the H3 and H5 protons of cyclodextrin have been listed in Table 5. As found from the chemical shifts, interaction of the H^3 with the aromatic guest was much higher than that of the H^5, proving the guest entered through the wider rim of α-CD (Scheme 6).

Structural influence of Cyclodextrin

The most notable feature of cyclodextrin molecule (cavity diameter of α-CD is 4.7-5.3Å) provides a micro environment into which appropriately sized non-polar moiety enters and form strong inclusion complex (Roy, 2014) (Scheme 1).

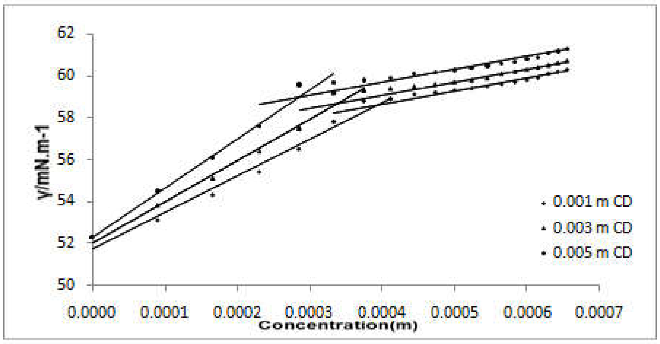


Fig 1. Plot of surface tension of ionic liquid corresponding to the added conc. of aq. α-cyclodextrin

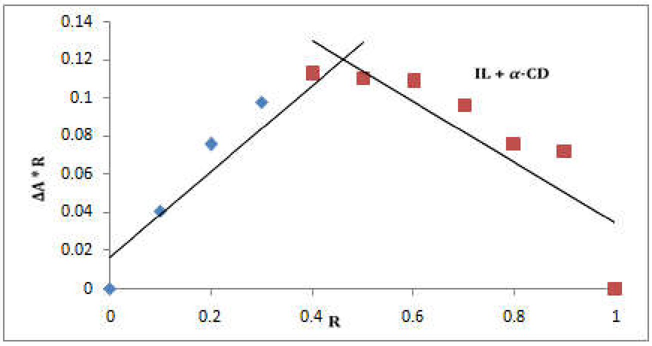


Fig 2. Job plot of IL-cyclodextrin systems at λ_{max} (nm) = 210 and at 298.15 K

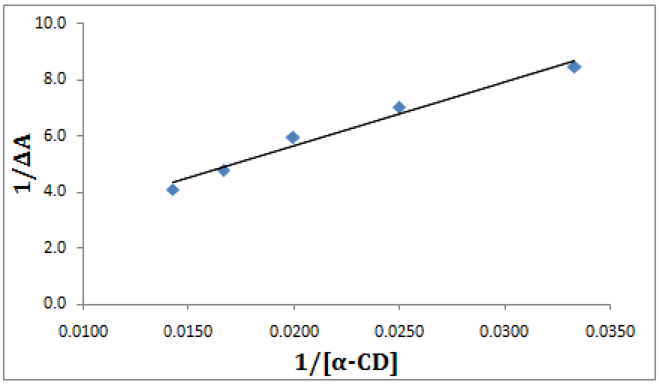


Fig. 3. Benesi-Hildebrand double reciprocal plot for the effect of α-CD on the absorbance of IL at 210 nm at 298.15 K

But, no covalent bonds are broken or formed throughout formation of the inclusion complex (Schneiderman *et al.*, 2000). The main dynamic force in aqueous solution is that the marginallyapolarcyclodextrin cavity is employed by water molecules (Pineiro *et al.*, 2007), which are dynamicallyunfavoured, thus can be readily replaced by more hydrophobic side chain group of IL which is less polar than water, to achieve an apolar–apolar association and decrease of cyclodextrin ring strain resulting in a more stable lower energy state (Szejtli, 1998).

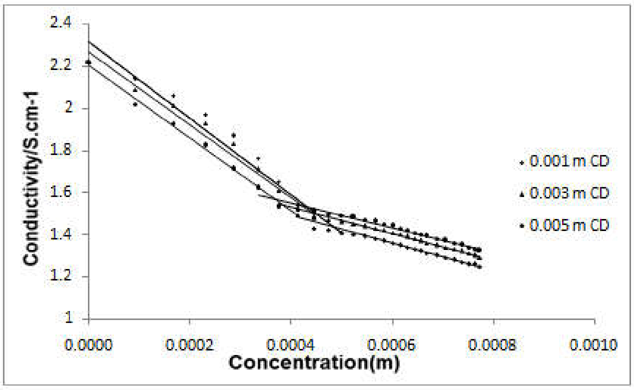


Fig. 4. Plot of conductance of ionic liquid corresponding to the added conc. of aq. α-cyclodextrin

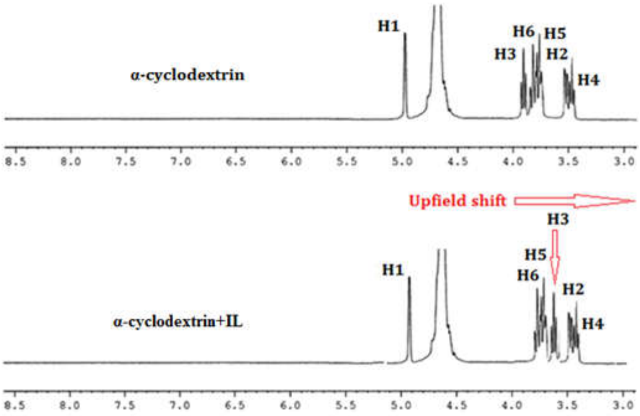
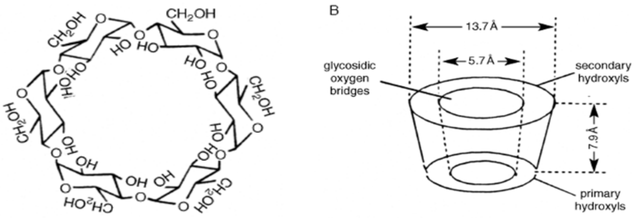
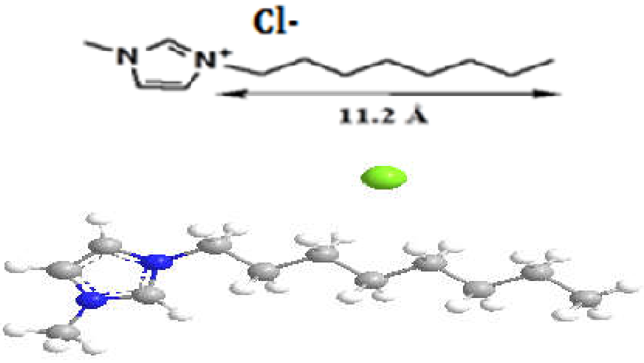


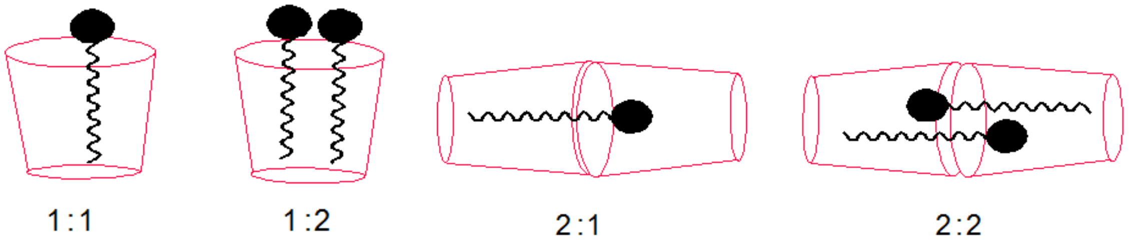
Fig. 5. ^{1}H NMR spectra of α-CD and 1:1 molar ratio of α-CD & IL in D_2O at 298.15K



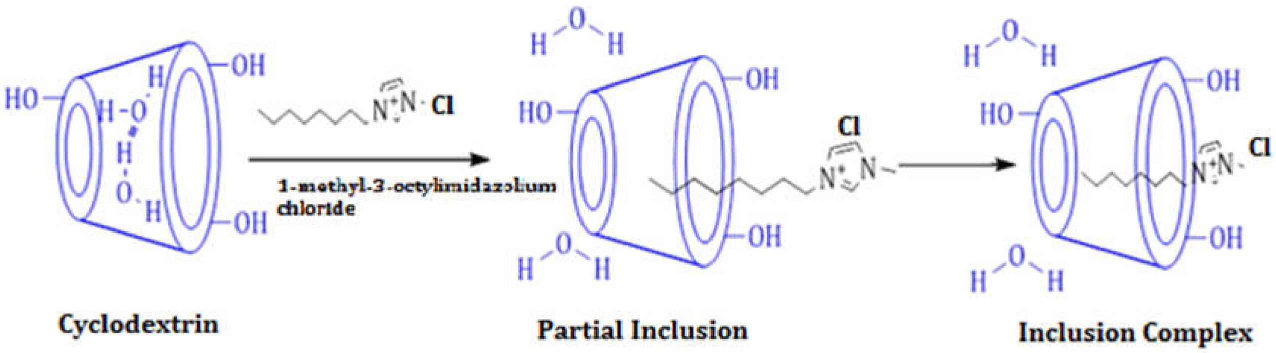
Scheme 1. The molecular structure of α-CD



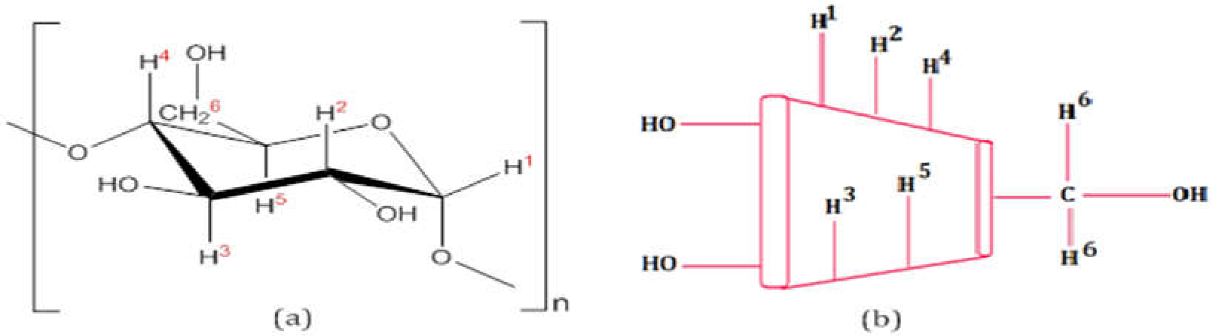
Scheme 2. The molecular structure of IL



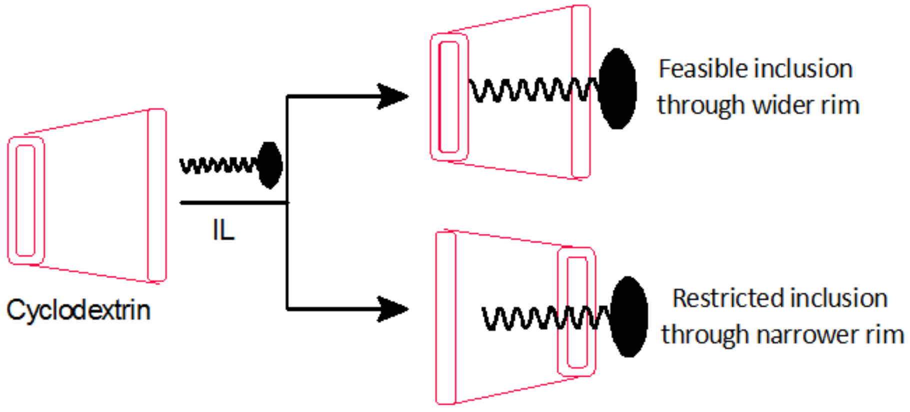
Scheme 3. Different possibilities of Host-guest ratio for inclusion complex



Scheme 4. Schematic of the convincing mechanism for 1 : 1 inclusion complexes' with insight into α-cyclodextrin with the titled ionic liquid

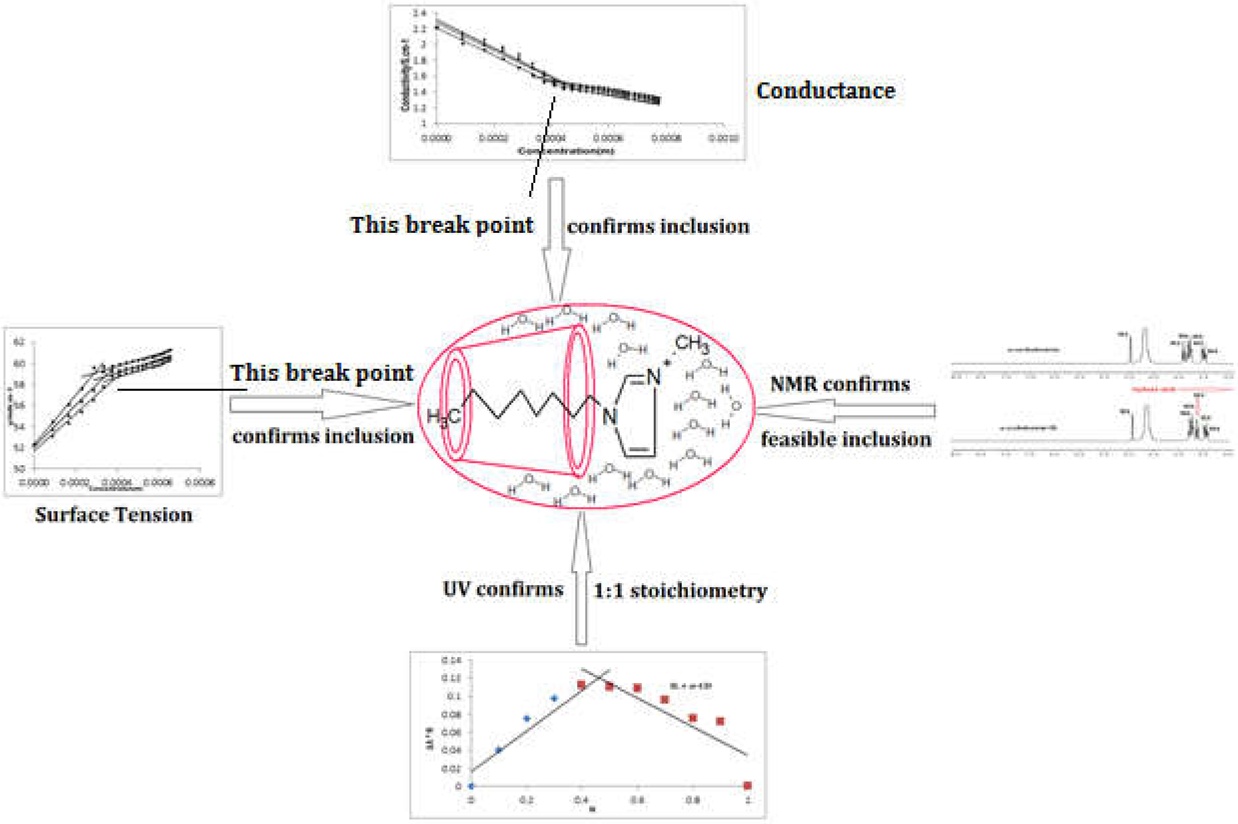


Scheme 5. (a) Stereo-chemical configuration of *α*-cyclodextrin, (b) truncated conical structure of *α*-cyclodextrin



Scheme 6. The feasible and restricted inclusion of host:guest molecule

One or two cyclodextrin molecules can entrap one or more IL molecules; therefore, the plausible host:guest ratio of the inclusion is 1:1, 1:2, 2:1, and 2:2, or even more complicated association complex (Scheme 3). However, the simplest and most common case of host:guest ratio is 1:1 by the core of molecular encapsulation by *α*-CD has been observed from surface tension and related studies discussed overhead.



Based on these α-cyclodextrin the selected IL can classically complex with aliphatic, aromatics side chains. Hence, the positive interfaces occurred to form the inclusion complex by

- The movement of polar water molecules from the apolar cavity of cyclodextrin.
- A reduction of the repulsive interactions between the hydrophobic group of IL and the aqueous environment.
- An increase in the hydrophobic-hydrophobic interactions as the inclusion of IL takes place into the apolar cavity of cyclodextrin.

Conclusion

Based on surface tension and conductance data it was supported that an inclusion complex between studied IL and α-CD was formed. In NMR study, the changes in the chemical shift corresponding to H^5 and H^3 protons of host and guestestablish the formation of IL–α-CD inclusion complex in aqueous solution. The Job plot of the UV-Vis spectrum proves also the inclusion complex formation in aqueous solution.The results point out that α -CD and IL finally form steady inclusion complex (IC) with a 1:1 stoichiometry. They both are promoting to each other owing to hydrophobic and hydrophilic interactions among them.

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