J. Adv. Chem. Sci. - Volume 3 Issue 4 (2017) 510–514

Share Your Innovations through JACS Directory

Journal of Advanced Chemical Sciences

Visit Journal at http://www.jacsdirectory.com/jacs

ISSN: 2394-5311

Subsistence of Inclusion Complexes of Cyclodextrins with 1-Butyl-2, 3-Dimethylimidazolium Tetrafluoroborate Probed by Physicochemical Study

Kalipada Sarkar[1], Kanak Roy[2], Mahendra Nath Roy[2,*]

[1]Department of Chemistry, Islampur College, Islampur, Uttar Dinajpur – 733 202, West Bengal, India.
[2]Department of Chemistry, University of North Bengal, Darjeeling – 734 013, West Bengal, India.

ARTICLE DETAILS

Article history:
Received 17 August 2017
Accepted 31 August 2017
Available online 31 October 2017

Keywords:
Host-Guest Inclusion Complex
Ionic Liquid
Cyclodextrin

ABSTRACT

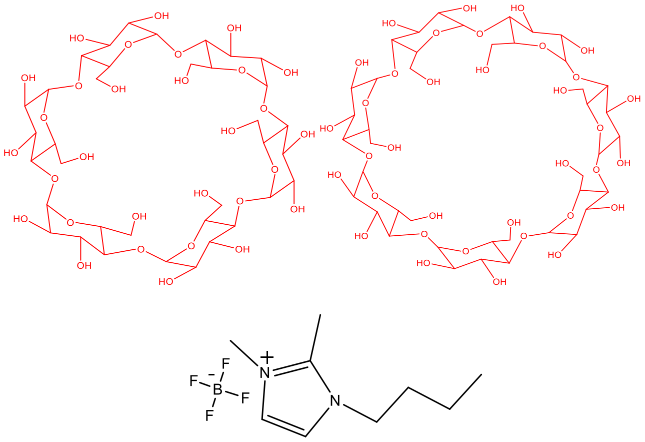
Inclusion complexes of ionic liquid, 1-butyl-2, 3-dimethylimidazolium tetrafluoroborate (BDMImBF$_4$) into cavity of hollow cylinder oligosaccharide, α- and β-cyclodextrins are manifested in aqueous medium. The inclusion phenomenon is confirmed with IR and 1HNMR spectroscopy whereas the stoichiometry of interfacial inclusion is proved with surface tension and conductance measurements. The interaction between cyclodextrin and ionic liquid is characterized by volumetric and viscometric studies.

1. Introduction

The hollow cylinder oligosaccharides α-, β- and γ-cyclodextrin contain six, seven and eight glucopyronose units are bound by α-(1–4) linkages and form truncated conical structures with inner cavity of the hydrophobic nature and the rim of hydrophilic nature [1]. The wider rim has all secondary hydroxyl groups and the narrow rim has all primary hydroxyl groups (1 and Scheme 2). This unique nature of cyclodextrin helps forming host-guest inclusion complexes with the hydrophobic part of any molecules [2]. The hydrophobic part the moiety is encapsulated into hydrophobic cavity of cyclodextrin. In aqueous solution the water molecules may occupy the cavity of α-, β- and γ-cyclodextrin which is very energetically unfavorable hence any appropriate molecule having a hydrophobic moiety replace the water molecule easily. This guest molecule along with the host cyclodextrin molecule forms the inclusion complex through host-guest interactions. Due to this special property, α-, β- and γ-cyclodextrin have been used widely in pharmaceuticals, pesticides, foodstuffs, toilet articles, and textile processing [3, 4]. In addition to these industrial applications, they are related to many interesting topics, such as molecular recognition, self-assembly, selectivity, molecular encapsulation, chemical stabilization, and intermolecular interactions [5, 6].

Ionic liquids (ILs) are nonvolatile, nonflammable and thermally stable solvents. They are used as alternative solvents in organic synthesis, chemical reactions, chemical separations, and material preparations [7]. They are considered to be green solvents as they do not produce any environmental hazards (8). ILs were designed as oriented solvents which could impact selectivity in reactions by ordering reactants. Cyclodextrin encapsulated IL can be used as stationary phase in chromatography. They are also used as heat transfer fluids for processing biomass and as electrically conductive liquids in electrochemistry (batteries and solar cells) [9–11].

In this paper we examined the formation of inclusion complexes of 1-butyl-2,3 dimethylimidazolium tetrafluoroborate (BDMImBF$_4$) insight into α-and β-cyclodextrin by different dependable methods such as 1H NMR, FT-IR, surface tension, conductivity, density and viscosity measurements. The structure of the IL, BDMImBF$_4$ is shown in Scheme 1.



1-butyl-2, 3-dimethylimidazolium tetrafluoroborate

Scheme 1 Structure of α-and β-cyclodextrin and (BDMImBF$_4$)

2. Experimental Methods

2.1 Materials

The studied IL, 1-butyl-2, 3-dimethylimidazolium tetrafluoroborate and α-and β-cyclodextrin of purist grade were procured from Sigma-Aldrich, Germany and used as purchased. The mass fraction purity of the IL and α-and β-cyclodextrin were >0.99, >0.98 and >0.98 respectively.

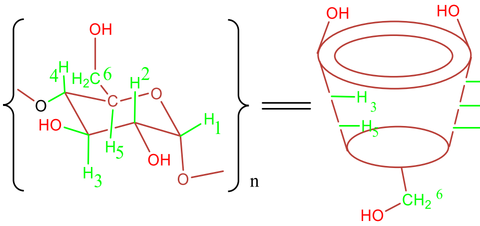
2.2 Apparatus and Procedure

The solubility of α-and β-cyclodextrins and that of the ionic liquid in triply distilled and degassed water was thoroughly checked before starting the experimental works. The solutions were prepared by adding known volume of water in airtight stoppered-bottle. Sufficient precautions were taken to minimize weight loss during mass measurements. The mass measurements were carried out on a Mettler AG-285 electronic balance with a precision of ±0.0003x10^{-3} kg. The conversion of molarity into molality was accomplished using experimental density values. The uncertainty in molality of solution is estimated to be ±0.0001 molkg^{-1}. All the solutions are prepared freshly before use.

---

*Corresponding Author
Email Address: mahendraroy2002@yahoo.co.in (Mahendra Nath Roy)

Cite this Article as: Kalipada Sarkar, Kanak Roy, Mahendra Nath Roy, Subsistence of inclusion complexes of cyclodextrins with 1-butyl-2, 3-dimethylimidazolium tetrafluoroborate probed by physicochemical study, J. Adv. Chem. Sci. 3(4) (2017) 510–514.



Scheme 2 Molecular structure of β-cyclodextrin

The surface tensions of the solutions were measured using a Tensiometer (K9, KRUSS; Germany) at the experimental temperature with a precision of 0.1 mNm^{-1}. The temperature of the system was kept constant by circulating thermostatic water through a double-wall glass vessel holding the solution. The platinum plates were thoroughly cleaned by washing with triply distilled and degassed water before each measurement. The vertically platinum plate was dipped into liquids to calculate the surface tension. The force needed to pull the ring, though the boundary was then expressed as the surface tension.

The density (ρ) was measured by means of vibrating-tube Anton Paar Density-Meter (DMA 4500M) with a precision of 0.00001×10^{-3} (kgm^{-3}). It was calibrated by double-distilled water and dry air [12]. The temperature was automatically kept constant within ±0.01 K.

The viscosity was determined with the aid of Brookfield DV-III Ultra Programmable Rheometer with spindle size-42 fitted to a Brookfield Digital Bath TC-500 calibrated at 298.15 K with doubly distilled water and purified methanol [13]. The uncertainty in viscosity measurements is within ±0.003 mPas.

The conductance measurements were done in a Systronic-308 conductivity meter (accuracy ± 0.01%) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately (0.1 ± 0.001) cm^{-1}. Measurements were made in a water bath maintained within T = (298.15 ± 0.01) K and the cells were calibrated by the method proposed by Lind et al [14]. The conductivity cell constant was calibrated using aqueous KCl (0.01 M and 0.1 M) solutions. The conductance data were reported at a frequency of 1 kHz and the accuracy was ±0.3%.

Fourier transform infrared (FT-IR) spectra were taken with a Perkin Elmer FT-IR. Samples were prepared as KBr disks with 1 mg of complex and 100 mg of KBr. The FTIR measurements were made in a scanning range of 4000–400 cm^{-1} at room temperature.

NMR spectra were taken in D_2O unless otherwise stated. ^1H NMR spectra were recorded at 400 MHz using Bruker ADVANCE 400 MHz instrument at 298.15 K. Signals are quoted as δ values in ppm using residual protonated solvent signals as internal standard (D_2O: d 4.79 ppm). Data are reported as chemical shift.

3. Results and Discussion

3.1 Surface Tension Study

Surface tension (γ) measurement gives important clue about formation of IC as well as stoichiometry of the host-guest assembly [15, 16]. Ionic liquid with long alkyl chain acts as a surface active compounds in its aqueous solution [17]. The addition of CD to pure water does not show any considerable change to the surface tension of water which is an indication that both cyclodextrins are almost surface inactive compounds.28. Here we measured the surface tension of the ionic liquid with increasing concentration of the α-and β-cyclodextrins and observed that the surface tension values increase with increasing concentration of α-and β-cyclodextrins up to a certain point and after that break point the surface tension become approximately steady (Fig. 1). This may be regarded as the formation of bigger micelle structure up to a certain concentration of cyclodextrinx. This phenomenon may be elucidated on the basis of inclusion complexes formation [18, 19].

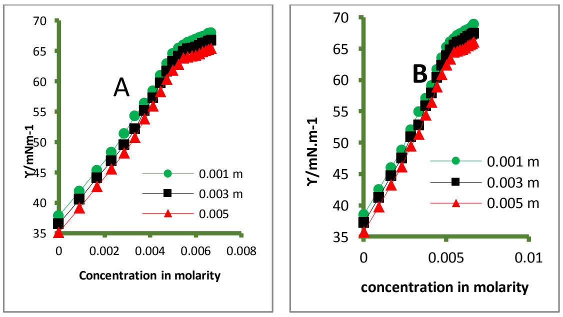
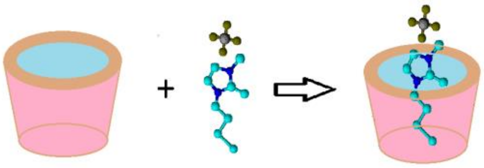


Fig. 1 Variation of surface tension of ionic liquid corresponding to the added concentration of aqeous (A) α-cyclodextrin and (B) β-cyclodextrin

The alkyl part of the IL penetrates into the hydrophobic cavity. The plot of surface tension against concentration of cyclodextrin gives only one break point which indicates 1:1 stoichiometric inclusion complex formation of IL in cyclodextrin cavity (Scheme 3). If there are two or more break points in graph of surface tension then the probable stoichiometries of inclusion complex will be 1:2 and 2:2 respectively [20]. The values of surface tension of different mass fraction of IL at the break point are listed in Table 1. In our present study the concentration ratio of CD and IL at the break point is 1:1. So the IL forms host-guest complexes with both α-and β-cyclodextrins of 1:1 stoichiometry. The γ value for β-CD is higher than that of α-CD which indicates that β-CD forms better complex than α-CD.

Table 1 Values for surface tension at the break point in different mass fractions of aqueous CDs at 298.15 K

Mass fraction of IL	Surface tension at break point for β-CD	Surface tension at break point for α-CD
w = 0.001	61.79	62.38
w = 0.003	63.19	63.81
w = 0.005	64.55	65.2



Scheme 3 Inclusion complex formation

3.2 Conductivity Study

The inclusion complex formation as well as stoichiometry of assembly may also be established by conductivity study [21, 22]. The conductivity of the IL is measured with the successive addition of CD. It is observed that the molar conductivity of the IL decreases with increasing concentration of CD up to a certain point after which no further decrease of conductivity is noted (Fig. 2). This observation also establishes the formation of inclusion complexes [23]. The hydrophobic part of the IL penetrates into the hydrophobic cavity of both the CDs. As a result the mobility of the encapsulated IL gets arrested. The remarkable decrease in conductivity with increasing concentration of CD continues till the process of inclusion complex formation completed. Values for conductance at the break point in different mass fractions of IL in aqueous CDs are shown in Table 2. After the break point no further decrease in conductance will be observed since the mobility of the free ions get arrested due to inclusion complexes formation. It is noticed that the break point occurs at equimolar addition of CD in aqueous solution of IL. This indicates that total inclusion complex formation takes place at 1:1 stoichiometry of IL and CD [24, 25]. If we compare the conductivity curves of the IL in α-and β-cyclodextrins, it is observed that the conductance at break point in case if α-CD is lower than that of β-CD which indicates that α-CD is more efficient than β-CD in the formation of inclusion complexes with the IL.

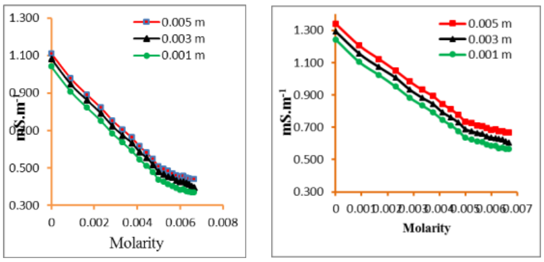


Fig. 2 Variation of conductance of ionic liquid corresponding to concentration of aqueous (A) α-cyclodextrin and (B) β-cyclodextrin

Table 2 Values for conductance at the break point in different mass fractions of aqueous CDs at 298.15 K

Mass fraction of IL	Conductance at break point for β-CD	Conductance at break point for α-CD
w = 0.001	0.636	0.437
w = 0.003	0.689	0.479
w = 0.005	0.736	0.508

3.3 Density Study: Interaction between Host and Guest

We may get valuable interactions between IL and cyclodextrin molecules from density study. The values of density (*ρ*), viscosity (*η*) of different mass fractions of aqueous *α* and *β*-cyclodextrin mixtures and of density (ρ) and viscosity (η) of the ionic liquid in different mass fractions

Cite this Article as: Kalipada Sarkar, Kanak Roy, Mahendra Nath Roy, Subsistence of inclusion complexes of cyclodextrins with 1-butyl-2, 3-dimethylimidazolium tetrafluoroborate probed by physicochemical study, J. Adv. Chem. Sci. 3(4) (2017) 510–514.

of aqueous α and β-cyclodextrin mixtures at 298.15 K are shown in Tables 3 and 4 respectively. We can calculate apparent molar volume, ϕ_V from densities of different molalities of IL in aqueous solution of α-and β-cyclodextrins of varying mole fraction (Table 5). The apparent molar volume can be considered to be the sum of the geometric volume of the solute molecule and changes in the solvent volume due to its interaction with the solute [26].

$$\phi_V = M / \rho - 1000 (\rho - \rho_0) / (m\rho\rho_0) \qquad (1)$$

The limiting apparent molar volume, ϕ_V^0 were obtained by a least-square treatment to the plots of ϕ_V versus $\sqrt{m}$ using the Masson equation [27].

$$\phi_V = \phi_V^0 + S_V^* \sqrt{m} \qquad (2)$$

Table 3 Experimental values of density (ρ), viscosity (η) of different mass fractions of aqueous α and β-cyclodextrin mixtures at 298.15 K

Aqueous solvent mixture	$\rho \times 10^{-3}$/kgm^{-3}	η/mPs
α-CD		
W_1=0.001	0.99745	1.2895
W_2 = 0.003	0.99808	1.2987
W_3 = 0.005	0.99828	1.3092
β-CD		
W_1=0.001	0.99771	1.2992
W_2 = 0.003	0.98816	1.3082
W_3 = 0.005	0.99887	1.3184

Table 4 Experimental values of density (ρ) and viscosity (η) of the ionic liquid in different mass fractions of aqueous α and β-cyclodextrin mixtures at 298.15 K

Molality Mol.kg-1	$\rho \times 10^{-3}$ kgm^{-3}	η mPs	Molality Molkg^{-1}	$\rho \times 10^{-3}$ kgm^{-3}	η mPs
W_1 = 0.001			W_2 = 0.001		
0.001	0.99789	1.3723	0.001	0.99815	1.383
0.002	0.99835	1.4178	0.002	0.99861	1.4281
0.004	0.99882	1.4913	0.004	0.99909	1.5038
W_1 = 0.003			W_2 = 0.003		
0.001	0.99852	1.3827	0.001	0.99860	1.3934
0.002	0.99898	1.4287	0.002	0.99907	1.4399
0.004	0.99946	1.5048	0.004	0.99955	1.5180
W_1 = 0.005			W_2 = 0.005		
0.001	0.99872	1.3943	0.001	0.99931	1.4047
0.002	0.99919	1.4413	0.002	0.99978	1.4518
0.004	0.99967	1.5192	0.004	1.00027	1.5320

W_1 and w_2 are mass fraction of IL in aqueous α and β-cyclodextrin respectively.

Table 5 Apparent molar volume (ϕ_V) and $(\eta_r-1)/\sqrt{m}$ of the ionic liquid in different mass fractions of aqueous α and β-cyclodextrin mixtures at 298.15 K

molalty molkg^{-1}	ϕ_V x 10^6 (m^{3}mol^{-1})	$(\eta / \eta_0 - 1) / \sqrt{m}$ (molkg^{-1})$^{-1/2}$	molalty molkg^{-1}	ϕ_V x 10^6 (m^{3}mol^{-1})	$(\eta / \eta_0 - 1) / \sqrt{m}$ (molkg^{-1})$^{-1/2}$
W_1 = 0.001			W_2 = 0.001		
0.001	196.5612	0.642	0.001	196.5100	0.645
0.002	195.6088	0.703	0.002	195.3574	0.701
0.004	194.8903	0.782	0.004	194.5054	0.786
W_1 = 0.001			W_2 = 0.001		
0.001	196.4372	0.647	0.001	196.4214	0.651
0.002	195.2849	0.708	0.002	195.1190	0.712
0.004	194.4333	0.793	0.004	194.0838	0.801
W_1 = 0.001			W_2 = 0.001		
0.001	196.3978	0.6502	0.001	196.2818	0.655
0.002	195.1457	0.7133	0.002	194.7801	0.715
0.004	194.0605	0.8011	0.004	193.6121	0.809

W_1 and w_2 are mass fraction of IL in aqueous α and β-cyclodextrin respectively

Table 6 Limiting apparent molar volume (ϕ_V^o), experimental slope (S_V^*), viscosity *A* and *B*-coefficient of ionic liquid in different mass fractions of aqueous α and β-cyclodextrin mixtures at 298.15 K

Mol fraction of IL	ϕ_V^0 x 10^6 (m^{3}mol^{-1})	S_V^* x 10^6 (m^{3}mol$^{-3/2}$ kg$^{1/2}$)	B (kg$^{1/2}$mol$^{-1/2}$)	A (kgmol^{-1})
α-CD				
W_1 = 0.001	198.8	-22.67	1.385	0.505
W_1 = 0.003	199.1	-27.21	1.451	0.502
W_1 = 0.005	199.8	-31.6400	1.504	0.5
β-CD				
W_2 = 0.001	199.2	-27.2200	1.412	0.503
W_2 = 0.003	199.6	-31.7000	1.493	0.501
W_2 = 0.005	199.9	36.2300	1.543	0.499

W_1 and w_2 are mass fraction of IL in aqueous α and β-cyclodextrin respectively

The ϕ_V^0 gives the idea about solute-solvent interaction. Here IL is the solute and aqueous solution of both α-and β-cyclodextrins act as co-solvent. The variation of limiting apparent molar volumes (ϕ_V^0) of IL in aqueous α-and β-cyclodextrins solutions with molality are reported in Table 6 and Fig. 3. In our present study, it is observed that ϕ_V^0 values increase with increasing concentration of IL as well as CDs which indicates that solute and co-solute interactions increase with increasing concentration of CDs (Table 6). In the present cases the positively charged N-atom interacts with the hydrophilic –OH groups of CDs giving rise to so called ion-hydrophilic interaction and there is also a hydrophobic-hydrophobic interaction between the alkyl group of the IL and the hydrophobic cavity of CDs. This hydrophobic-hydrophobic interaction is responsible for the formation of inclusion complexes [28]. It is also noticed that ϕ_V^0 values of the IL is higher in α-CD than β-CD which specify that the former is more efficient host than the latter in the formation of inclusion complexes .This may be explained on the fact that smaller cavity size of α-CD forms compact structure with the IL with hydrophobic-hydrophobic interaction compared with the relatively larger cavity size of β-CD.

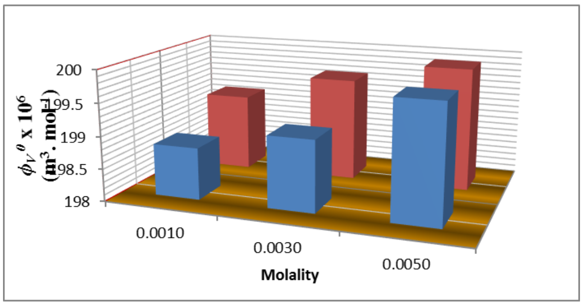


Fig. 3 Variation of limiting apparent molar volumes (ϕV0) of IL in aqueous α- and β-cyclodextrins solution with molality shown in red and blue column respectively

3.4 Viscosity Study

Viscosity study is also helpful for investigating the interaction between IL and CDs [29]. From the viscosities of the IL in different mass fraction of aqueous of CDs we can calculate the viscosity A and B coefficient using Jones-Does equation.

$$(\eta / \eta_0 - 1) / \sqrt{m} = A + B \sqrt{m} \qquad (6)$$

where, η_0 and η are the viscosities of the solvent mixture and solution, respectively. *A* and *B* values are the viscosity coefficients estimated by a least square method. The *A* and *B* values are obtained from the straight line by plotting $(\eta / \eta_0 - 1) / \sqrt{m}$ against $\sqrt{m}$. The $(\eta_r-1)/\sqrt{m}$ of the ionic liquid in different mass fractions of aqueous α and β-cyclodextrin mixtures at 298.15 K are reported in Table 5.

The viscosity B coefficient gives valuable information about the solute-solvent interaction [30, 31]. The viscosity B coefficient in our present study is positive and increases with increasing concentration of CDs (Table 6 and Fig. 4). This indicates that interaction between IL and the CD increases with increasing concentration of CD. The interaction is ion-hydrophilic and hydrophobic-hydrophobic in nature. The ion-hydrophilic interaction acts between positively charged N atom of the IL and –OH groups of CD whereas the hydrophobic-hydrophobic interaction acts between alkyl group of the IL and the hydrophobic cavity of CD. It is also important to note that the B coefficient value for α-CD is greater than that of than β-CD which again signifies that the former is more favorable than β-CD in forming ICs [32].

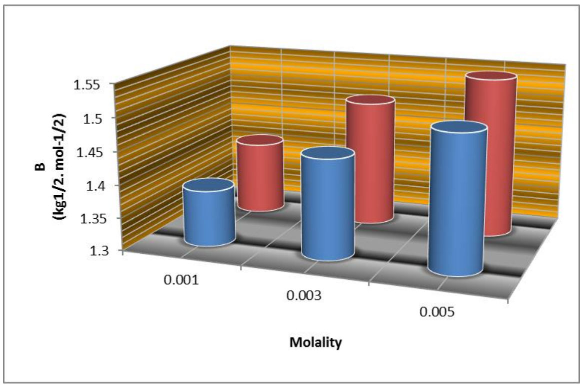


Fig. 4 Variation of viscosity B coefficient of IL in aqueous **α**- and β-cyclodextrins solution with molality shown in red and blue column respectively with molality

Cite this Article as: Kalipada Sarkar, Kanak Roy, Mahendra Nath Roy, Subsistence of inclusion complexes of cyclodextrins with 1-butyl-2, 3-dimethylimidazolium tetrafluoroborate probed by physicochemical study, J. Adv. Chem. Sci. 3(4) (2017) 510–514.

3.5 FT-IR Spectroscopy

Molecular interaction of the IC can be studied with the help of FT-IR spectroscopy [33-35]. The shift of the frequencies of IC from the IL and CDs indicate the formation of inclusion complexes [36, 37]. The FTIR spectra of α- and β-CD, IL and their ICs are shown in Figs. 5 and 6. The peaks of –C=N, -C-N and –C=C are present in the spectrum of the IL at about 1634.5 cm^{-1}, 1168 cm^{-1} and 1574.6 cm^{-1} respectively whereas the peak of –OH at about 3412.10 cm^{-1} and 3349.84 cm^{-1} are present in the spectrum of α- and β-CD.

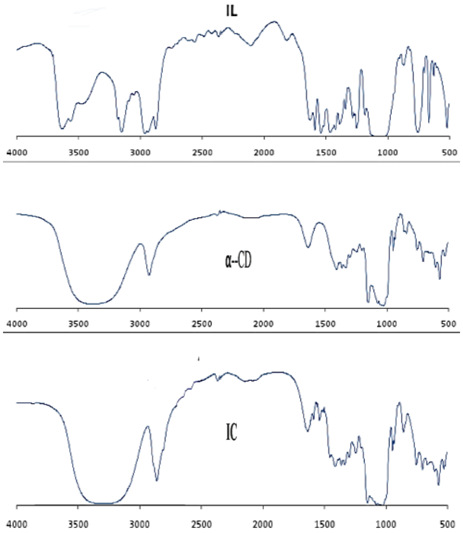


Fig. 5 FTIR spectra of α-CD, BDMImBF$_4$ and IC in D$_2$O at 298.15 K

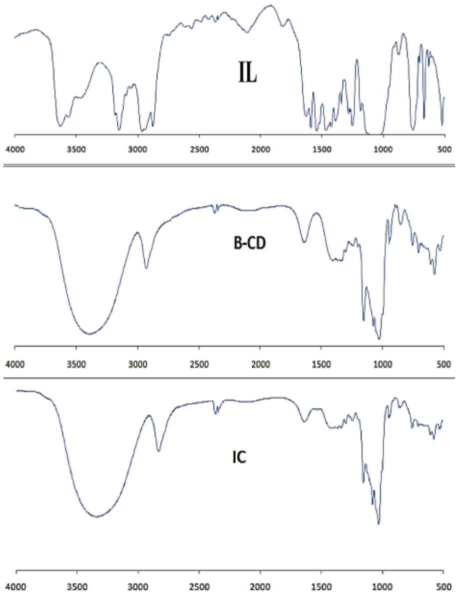
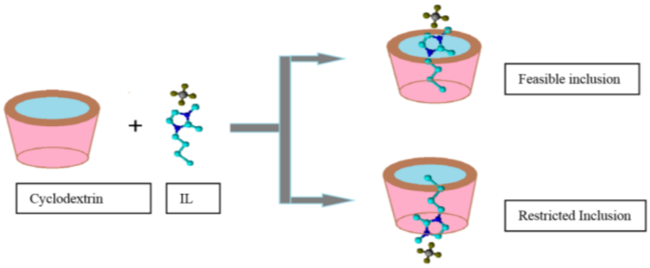


Fig. 6 FTIR spectra of α-CD, BDMImBF$_4$ and IC in D$_2$O at 298.15 K

The –O-H stretching frequencies of both the α- and β-CD have been shifted to lower energy of the spectrum of ICs possibly owing to the participation of H-bonding with the guest molecule. It is also observed that the peaks of –C=N and –C-N have not shifted which indicates that the immidazolium part of the IL stayed outside of the cavity of CDs and the hydrophobic part of the IL is encapsulated into the cavity of both the CDs.



Scheme 4 Feasibility and restricted inclusion complex formation of host-guest molecule

3.6 ^{1}H NMR Study Confirms the Inclusion Phenomenon

The chemical shift of the protons of the cyclodextrin molecule in the 1H NMR spectra is observed due the interaction of the host cyclodextrin with the guest IL molecule [38]. In this work we studied the ^{1}H NMR of the IL and the ICs of the IL with α- and β-CD. ^{1}H NMR spectra of α- and β-CD, IL and their ICs are shown in Figs. 7 and 8. There is a considerable chemical shift of proton of CD molecule due to inclusion complex formation revealed from spectral studies. In the structure of cyclodextrin the H$_3$ and H$_5$ hydrogens are positioned within the conical cavity, particularly, the H$_3$ are placed at the wider rim whereas H$_5$ are placed at the narrower rim of cyclodextrin molecule while the H$_1$, H$_2$ and H$_4$ protons are located at the periphery of the CD molecule (Scheme 2) [39, 40]. When a guest molecule enters into the cavity of CD then there should an up field chemical shift of H$_3$ and H$_5$ protons due to interaction with the alkyl group of the guest molecule which ascertain the formation of inclusion complex [41]. It is observed that the up field chemical shift for H$_3$ (located at wider rim of CD) is higher than that of H$_5$ (located at narrower rim) which proves that the IL enters through the wider rim of CD. The up field chemical shifts for all the protons of IC in case of α-CD is greater than that of β-CD which signify that α-CD binds strongly with IL than β-CD. Negligible chemical shifts for the other exterior protons are also detected due lesser interaction with the IL.

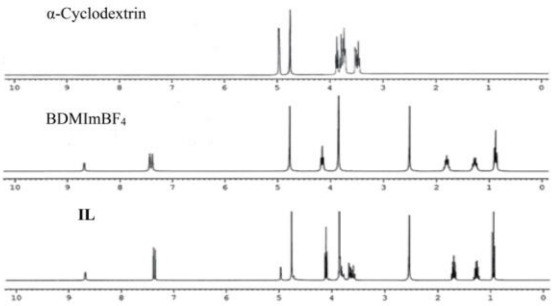


Fig. 7 ^{1}H NMR spectra of α-CD, BDMImBF$_4$ and IC in D$_2$O at 298.15 K

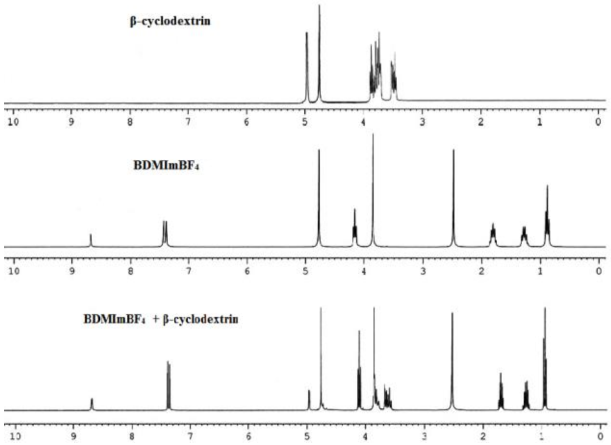


Fig. 8 ^{1}H NMR spectra of β-CD, BDMImBF$_4$ and IC in D2O at 298.15 K

3.7 Structural Influence of Cyclodextrins

The inclusion complex formation depends on the size of the guest molecule as well as the cavity diameter of the host molecule. The diameter of cavities of α- and β -CD are 4.7–5.3 Å and 6.0–6.5 Å respectively. Cyclodextrin molecule having hydrophobic cavity and hydrophilic rims provides a proper environment for the apolar part of an IL to reside inside the cavity, while the polar part makes association with the polar rims, thus stabilizing the whole inclusion complex [42]. Due to the formation of the inclusion complex, the water molecules from the hydrophobic cavity of CD are released into the bulk [43]. This is an energetically favorable process [28]. But, no covalent bonds are broken or formed during formation of the inclusion complex [44]. The insertion of the guest amino acid molecule is expected from the wider rim of the cyclodextrin molecule, so as to make maximum contact of the alkyl groups with the cyclodextrin cavity (Scheme 4), which is also supported by NMR data. The charged part of IL is projected outside the larger rim of CD in the aqueous environment and can make H-bonds with the –OH groups at both rims of the cyclodextrin molecule. Thus the inclusion complex is stabilized by the formation of H-bonds between the polar groups of IL and the primary as well as the secondary –OH groups at both the rims of a and CDs. It is observed that α -CD is more suitable than β -CD for the formation ICs with the IL possibly due to greater surface interaction, increasing the hydrophobic attractions which is in agreement with spectroscopic and physicochemical observations. The IC is of 1:1 stoichiometry possibly because of the difficulty for another molecule of IL to be trapped in the cavity of CD after the inclusion of the first.

4. Conclusion

The surface tension and conductance data reveal that the IL forms inclusion complex with α- and β –CD both in solution and the solid state. The chemical shift corresponding to H5 and H3 protons in NMR spectra also establish the inclusion of IL in the apolar cavity of both CD molecules. The CDs form steady inclusion complex (IC) with the IL with 1:1 stoichiometries however the IL is fitted more suitably with α–CD than β –CD. Density, viscosity data indicate the IL–CD interactions and also confirm the above results also. Solid state characterizations made by FT-IR confirm the existence of ICs in solid state also.

Acknowledgements

The authors are grateful to the UGC supported Major research project, Ref. No. RP/5032/FCS/2011 New Delhi for financial support in order to continue this research work. One of the authors, Prof. M.N. Roy is thankful to University Grant Commission, New Delhi, Government of India for being awarded one-time grant under Basic Scientific Research via the grant-in-Aid No. F.4-10/2010 (BSR) regarding his active service for augmenting of research facilities to facilitate further research work.

References

[1] M.L. Bender, M. Komiyama, Cyclodextrin chemistry, Springer Verlag, New York, 1978.

[2] Y. Liu, Z. Fan, H.Y. Zhang, C.H. Diao, Binding ability and self-assembly behavior of linear polymeric supramolecules formed by modified β-cyclodextrin, Org. Lett. 5 (2003) 251–254.

[3] K.A. Connors, The stability of cyclodextrin complexes in solution, Chem. Rev. 97 (1997) 1325-1357.

[4] W. Saenger, Cyclodextrin inclusion compounds in research and industry, Angew. Chem. Int. Ed. Engl. 19 (1980) 344–362.

[5] J. Dupont, R.F. De Souza, P. Suarez, Ionic Liquid (molten salt) phase organometallic catalysis, Chem. Rev. 102 (2002) 3667-3692.

[6] N.V. Plechkovaand, K.R. Seddon, Applications of ionic liquids in the chemical industry, Chem. Soc. Rev. 37 (2008) 123-150.

[7] T. Welton, Room-temperature ionic liquids, Solvents for Synthesis and Catalysis, Chem. Rev. 99 (1999) 2071–2084.

[8] A.P.S. Brogans, J.P. Halleet, Solubilizing and stabilizing proteins in anhydrous ionic liquids through formation of protein-polymer surfactant nanoconstructs, J. Am. Chem. Soc. 138 (2016) 4494–4501.

[9] H. Zhao, Protein stabilization and enzyme activation in ionic liquids: specific ion effects, J. Chem. Technol. Biotechnol. 91 (2016) 25–50.

[10] F. Endres, Z.S. El Abedin, Air and water stable ionic liquids in physical chemistry, Phys. Chem. Chem. Phys. 8 (2006) 2101–2116.

[11] N.V. Plechkova, K.R. Seddon, Applications of ionic liquids in the chemical industry, Chem. Soc. Rev. 37 (2008) 123–150.

[12] R. Gopal , M.A. Siddique, A study of ion-solvent interactions of some tetraalkyl-ammonium and common ions in N-methyl acetamide from apparent molar volume data, Jour. Phy. Chem. 72 (1969) 1814–1817.

[13] M.N. Roy, A. Jha, A. Choudhury, Densities, viscosities and adiabatic compressibilities of some mineral salts in water at different temperatures, Jour. Chem. Eng. Data 4 (2004) 291–296.

[14] H.M. Zerth, N.M. Leonard, R.S. Mohan, Synthesis of homoallyl ethers via allylation of acetals in ionic liquids catlyzed by trimethylsilyl trifluoromethanesulfonate, Org. Lett. 5 (2003) 55–57.

[15] M.N. Roy, D. Ekka, S. Saha, M.C. Roy, Host–guest inclusion complexes of α and β-cyclodextrins with α-amino acids, RSC Adv. 4 (2014) 42383–42390.

[16] A. Pineiro, X. Banquy, S. Perez-Casas, E. Tovar, A. Garcia, A. Villa, A. Amigo, A.E. Mark, M. Costas, On the characterization of host–guest complexes: surface tension, calorimetry, and molecular dynamics of cyclodextrins with a non-ionic surfactant, J. Phys. Chem. B 111 (2007) 4383–4392.

[17] S.D. Qi, S.Y. Cui, X. Chen, Z. Hu, Rapid and sensitive determination of anthraquinones in Chinese herb using 1-butyl-3-methylimidazolium-based ionic liquid with β-cyclodextrin as modifier in capillary zone electrophoresis, J. Chromat. A 1059 (2004) 191–198.

[18] S. Saha, T. Ray, S. Basak, M.N. Roy, NMR, surface tension and conductivity studies to determine the inclusion mechanism: thermodynamics of host–guest inclusion complexes of natural amino acids in aqueous cyclodextrins, New J. Chem. 40 (2016) 651–661.

[19] K. Roy, M.N. Roy, Study to explore inclusion complexes of ionic liquid with cyclic ethers in liquid systems, J. Adv. Chem. Sci. 3 (2017) 452–456.

[20] Y. Gao, X. Zhao, B. Dong, L. Zheng, N. Li, S. Zhang, Inclusion complexes of α-cyclodextrin with ionic liquid surfactants, J. Phys. Chem. B 110 (2006) 8576–8581.

[21] Y.A. Gao, Z.H. Li, J.M. Du, B.X. Han, G.Z. Li, W.G. Hou, et al., Preparation and characterization of inclusion complexes of β-cyclodextrin with ionic liquid, Chem. Eur. J. 11 (2005) 5875-5880.

[22] R. Palepu, J.E. Richardson, V.C. Reinsborough, Binding constants of beta-cyclodextrin/surfactant inclusion by conductivity measurements, Langmuir 5 (1989) 218-221.

[23] I.N. Topchieva, A.E. Tonelli, I.G. Panova, E.V. Matuchina, F.A. Kalashnikov, et al., Two-phase channel structures based on α-cyclodextrin-polythelene glycol inclusion complexes, Langmuir 20 (2004) 9036-9043.

[24] A. Apelblat, E. Manzurola, Z. Orekhova, Electrical conductance studies in aqueous solutions with glutamic ions, J. Sol. Chem. 36 (2007) 891–900.

[25] G. Law, P.R. Watson, Surface tension measurements of N-alkylimidazolium ionic liquids, Langmuir 17 (2001) 6138–6141.

[26] D. Ekka, M.N. Roy, 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 Adv. 4 (2014) 19831–19845.

[27] D.O. Masson, Solute molecular volumes in relation to the solvation and ionization, Philos. Mag. 8 (1929) 218–223.

[28] H. Shekaari, F. Jebali, Volumetric and conductometric studies of some amino acids in aqueous ionic liquid, 1-hexyl-3-methylimidazolium chloride solutions at 298.15 K, Phys. Chem. Liq. 49 (2011) 572–587.

[29] A. Roy, S. Saha, M.N. Roy, Study to explore host-guest inclusion complexes of cyclodextrins with biologically active molecules in aqueous environment, Fluid Phase Equilib. 425 (2016) 252–258.

[30] R.H. Stokes, R. Mills, Viscosity of electrolytes and related properties, International encyclopedia of physical chemistry and chemical physics, Pergamon, London, 1965.

[31] H.J.V. Tyrrell, M. Kennerley, Viscosity B-coefficients between 5° and 20° for glycolamide, glycine, and N-methylated glycines in aqueous solution, J. Chem. Soc. A (1968) 2724-2728.

[32] M.N. Roy, M.C. Roy, K. Roy, Investigation of an inclusion complex formed by ionic liquid and β-cyclodextrin through hydrophilic and hydrophobic interactions, RSC Adv. 5 (2015) 56717-56723.

[33] W. Zhang, X. Gong, Y. Cai, C. Zhang, X. Yu, J. Fan, G. Diao, Investigation of water-soluble inclusion complex of hypericin with β-cyclodextrin polymer, Carbohydr. Polym. 95 (2013) 366–370.

[34] S. Milovanovic, D. Markovic, K. Aksentijevic, D.B. Stojanovic, J. Ivanovic, I. Zizovic, Application of cellulose acetate for controlled release of thymol, Carbohydr. Polym. 147 (2016) 344–353.

[35] J.S. Negi, S. Singh, Spectroscopic investigation on the inclusion complex formation between amisulpride and γ-cyclodextrin, Carbohydr. Polym. 92 (2013) 1835–1843.

[36] N. Li, J. Liu, X.Y. Zhao, Y.A. Gao, L.Q. Zheng, J. Zhang, L. Yu, Complex formation of ionic liquid surfactant and β-cyclodextrin, Colloid Surf. A Physicochem. Eng. Aspects 292 (2007) 196-201.

[37] N. Khoddami, F. Shemirani, Preparation of carboxymethyl-α-cyclodextrin polymer grafted onto nano TiO_2 as a novel solid phase extraction sorbent based on a host–guest mechanism, Anal. Methods 7 (2015) 5338-5344.

[38] K.M. Makwana, R. Mahalakshmi, NMR analysis of tuning cross-strand Phe/Tyr/Trp-Trp interactions in designed β-hairpin peptides: terminal switch from L to D amino acid as a strategy for β-hairpin capping, J. Phys. Chem. B 119 (2015) 5376-85.

[39] V. Sindelar, M.A. Cejas, F.M. Raymo, W. Chen, S.E. Parker, A.E. Kaifer, Supramolecular assembly of 2,7-dimethyldiazapyrenium and cucurbit[8]uril: A new fluorescent host for detection of catechol and dopamine, Chem. Eur. J. 11 (2005) 7054–7059.

[40] T. Wang, M.D. Wang, C. Ding, J. Fu, Mono-benzimidazole functionalized β-cyclodextrins as supramolecular nanovalves for pH-triggered release of p-coumaric acid, Chem. Commun. 50 (2014) 12469–12472.

[41] J.V. Caso, L. Russo, M. Palmieri, G. Malgieri, S. Galdiero, A. Falanga, C. Isernia, Iacovino, Investigating the inclusion properties of aromatic amino acids complexing beta-cyclodextrins in model peptides, Amino Acids 47 (2015) 2215-2227.

[42] J. Szetjli, Introduction and general overview of cyclodextrin chemistry, Chem. Rev. 98 (1998) 1743–1754.

[43] A. Pineiro, X. Banquy, S Perez-Casas, E. Tovar, A. Garcia, et al., On the characterization of host-guest complexes: surface tension, calorimetry and molecular dynamics of cyclodextrins with a non-ionic surfactant, J. Phys. Chem. B 111 (2007) 4383-4392

[44] E. Schneiderman, A.M. Stalcup, Cyclodextrins: A versatile tool in separation science, J. Chromatogr. B 745 (2000) 83-102.

Cite this Article as: Kalipada Sarkar, Kanak Roy, Mahendra Nath Roy, Subsistence of inclusion complexes of cyclodextrins with 1-butyl-2, 3-dimethylimidazolium tetrafluoroborate probed by physicochemical study, J. Adv. Chem. Sci. 3(4) (2017) 510–514.