Contents lists available at ScienceDirect



Journal of Molecular Liquids



CrossMark

© 2015 Elsevier B.V. All rights reserved.

journal homepage: www.elsevier.com/locate/molliq

Self-assembly inclusion of green solvent with oligosaccharides

Mahendra Nath Roy *, Kanak Roy, Koyeli Das, Biraj Kumar Barman

Department of Chemistry, University of North Bengal, Darjeeling 734013, India

ARTICLE INFO

ABSTRACT

efficient for β -CD than α -CD.

Article history: Received 30 October 2015 Accepted 24 December 2015 Available online 15 January 2016

Keywords: Green solvent Oligosaccharides Inclusion complex Hydrophobicity Formation constants

1. Introduction

The formation of cyclodextrin (CD) based inclusion complexes with wide variety of guest molecules are of great interest because of their extensive application in fields of bio-sensing and bio-imaging, drug and gene delivery, electronics, energy production and regenerative medicine [1–7]. Cyclodextrins (CDs) are obtained from the enzymatic degradation of one of the most essential polysaccharides, starch. The core of their structures contains dimensionally stable cavities that can trap or encapsulate other molecules through non-covalent interaction. The outer part of their cavities is hydrophilic in nature due to the large number of hydroxyl groups while the inner part of the cavities is lined with skeletal carbon and ethereal oxygen moieties of the glucose residues which make it relatively apolar and create a hydrophobic micro environment [8–10] (Scheme 1). On the other hand, Ionic liquids (ILs) (Scheme 2) with hydrophobic long chain have unique properties, such as "green" alternative to the conventional and environmentally detrimental volatile solvents, negligible vapor pressure, excellent thermal stability, strong ability to dissolve many chemicals, high electrical conductivity, large electrochemical window, and ability of repetitive utilization. All the unusual properties help IL to be broadly applied in material syntheses, chemical reactions, separations, electrochemistry and formation of ordered molecular assembly [11–12]. The term selfassembly refers to quite a fascinating phenomenon where unassociated, disorderly molecules come together in some fashion to form organized structures without any external stimuli [13].

In our previous work [14] we successfully addressed inclusion through hydrophilic–hydrophobic interaction of IL with β -CD. Herein,

* Corresponding author. *E-mail address*: mahendraroy2002@yahoo.co.in (M.N. Roy). we present a physicochemical and spectroscopic investigation for inclusion of the IL with α -CD and β -CD by easily available techniques.

2. Experimental section

This work has been focused on the characteristics of green solvent i.e. 1-butyl-4-methylpyridinium iodide and

some organic oligosaccharides, α - and β -cyclodextrins in aqueous media. In aqueous solution, hydrophobic

butyl side chain of the ionic liquid has been inserted into the hollow space of cyclodextrin. The selective forma-

tion of 1:1 inclusion complexes has been established here. Surface tension values, conductivity trends, and thermodynamic and spectroscopic study reveal that formations of inclusion complexes are more favorable and

2.1. Materials

The investigated compounds e.g., IL, α -CD and β -CD of puriss grade ware procured from Sigma-Aldrich, Germany and used as purchased. The mass fraction purity of IL, α -CD and β -CD were \geq 0.99, 0.99 and 0.98 respectively.

2.2. Apparatus and procedure

Solubility of the chosen compounds have been precisely checked and observed that the selected IL, α -CD and β -CD are freely soluble in triply distilled and degassed water (with a specific conductance of $1\times10^{-6}~S\cdot cm^{-1}$). Experimental solution of IL was prepared by mass (Mettler Toledo AG-285 with uncertainty \pm 0.0003 g), and then the working solutions were obtained by mass dilution at 298.15 K.

The surface tension experiments were done by platinum ring detachment method using a Tensiometer (K9, KRŰSS; Germany) at the studied temperature. The precision of the measurement was within $\pm 0.1 \text{ mN} \cdot \text{m}^{-1}$. Temperature of the system has been maintained circulating auto-thermostated water through a double-wall glass vessel containing the solution.

The conductance measurements were carried out in a Systronic-308 conductivity meter (accuracy $\pm 0.01\%$) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately (0.1 ± 0.001) cm⁻¹. Measurements were completed in a water bath maintained within $T = (298.15 \pm 0.01)$ K.



Scheme 1. Molecular structure and approximate geometric dimension of α -CD and β -CD.

The solution and solvent densities (ρ) were measured by means of vibrating u-tube Anton Paar digital density meter (DMA 4500M) with accuracy of \pm 0.00005 g cm⁻³ maintained at \pm 0.01 K of the experimental temperature. It was calibrated by passing doubly distilled, deionized, degassed water and dry air.

The viscosities (η) were measured using a Brookfield DV-III Ultra Programmable Rheometer with spindle size-42 fitted to a Brookfield digital bath TC-500.

3. Results and discussions

3.1. Surface tension

Surface tension (γ) measurements can be used to elucidate whether inclusion can happen or not but also to interpret the stoichiometry of inclusion complexes [15]. It was proved that no remarkable change occurs for the surface tension of pure water when α - and β -CD are added in water, indicating that α - and β -CD are almost surface inactive compounds in pure water mixtures [16]. γ value increase with addition of CDs are due to the fact that surface activity decreases with increasing no. of CD molecules into the IL (Schemes 3 and 4) solution. Each curve, Fig.1a and b, clearly shows a single break point in surface tension at a certain concentration, i.e., the γ value increase with the increase in concentration, reach a certain point (break point), and then become approximately steady, which obviously indicates the formation of selective 1:1 inclusion complex. By examining the details of γ -values (Table 1) it is understood that β -CD is more efficient for the formation of inclusion complexes than α -CD. This is evidently due to the fact that β -CD provides more workable feature (Scheme 1) for the formation of feasible inclusion complexes than α -CD. Also, we envisage the nonpolar tail group of the IL to be inserted via the wider rim through hydrophobic and hydrophilic interaction, so as to make maximum contact with the CD cavity (Schemes 3 & 4), while the charged polar head side remains either in the wider rim of CD or in the bulk solution through H-bonding.

3.2. Conductivity study

The selected IL is freely soluble in water. The solution conductivity of IL is markedly altered by the addition of CDs. The dependence of specific conductivity of IL, as reported earlier [17–18], with both



Scheme 2. The molecular structure of 1-butyl-4-methylpyridinium iodide.

CD concentrations at 298.15 K are depicted in Fig.1c & d. Through this method the stoichiometry of the inclusion complexes can be deduced from the breaks (Table 2) in the conductivity curves [19-20]. The remarkably decreasing specific conductivity with increasing CD concentrations indicates the inclusion complex formation between CD and the hydrophobic part of the IL one by one and hence movement of the IL is restricted and the free ions per unit volume is decreased; as a result the conductivity decreases. At a certain concentration of CDs, this linear decrease of specific conductance with IL concentration halted rather abruptly to show no or little further decrease with further CD additions and which represents the saturation point of inclusion. A distinct break in the conductivity curve occurred at a concentration of about 5.0 mmol L^{-1} for CDs, suggesting that the stoichiometry of the inclusion complex is equimolar [21]. This indicates that the principal inclusion complexes of CDs with IL in this range are of 1:1 ratio which indicates that the IL are almost totally in complexed form. This definitely illustrates that both the CDs have the favorable structures for the formation of selective inclusion complexes with the investigated IL. This is also supported by the above mentioned surface tension experiment.

3.3. Uv-Vis spectroscopic study

Absorption spectra used to confirm the formation of inclusion complex. In this study, absorption spectrum of the studied compound was taken into consideration [21–22]. Since α -CD and β -CD have almost



Scheme 3. The plausible stoichiometry inclusion ratio of host:guest molecules.



Scheme 4. The feasible and restricted inclusion.

Download English Version:

https://daneshyari.com/en/article/5409980

Download Persian Version:

https://daneshyari.com/article/5409980

Daneshyari.com