



Study of inclusion complex of β -cyclodextrin and diphenylamine: Photophysical and electrochemical behaviors

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ABSTRACT

The photophysical, electrochemical and photoprototropic behaviors of diphenylamine (DPA) in aqueous β -cyclodextrin (β -CD) solution have been investigated using absorption spectroscopy and cyclic voltammetric techniques. Absorption of the neutral and cationic form of DPA is enhanced due to the formation of a 1:1 complex with β -CD. The formation of this complex has been confirmed by Benesi–Hildebrand plot and docking studies by RasMol tool methods. The solid complex of β -CD with DPA is investigated by FT-IR, XRD and AFM methods. The thermodynamic parameters (ΔG , ΔH and ΔS) of inclusion process are also determined. The pK_a values of neutral-monocation equilibria have been determined with absorption (conjugate acid–base) titrations. A mechanism is proposed to explain the inclusion process.

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1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides with internal cavities capable of forming complexes with hydrophobic organic molecules in aqueous solutions [1]. The inner diameters of the cavities are approximately 4.5 Å in α -CD, 7.0 Å in β -CD and 8.5 Å in γ -CD [2]. The CDs are capable of incorporating a high range of guest molecules based on hydrophobic and geometrical cavities (Scheme 1). They have a toroidal shape with an internal hydrophobic surface and an external hydrophilic surface (Scheme 1) and they are acting as a host molecule. These cyclodextrins are well known as they form stable host–guest inclusion complexes which have the interesting property of including organic, inorganic and biological molecules in their cavities [3,4]. Efforts have been made to modify CDs so as to enhance their catalytic powers [5,6]. The physical chemistry of complexation by CDs has been extensively studied [1–6].

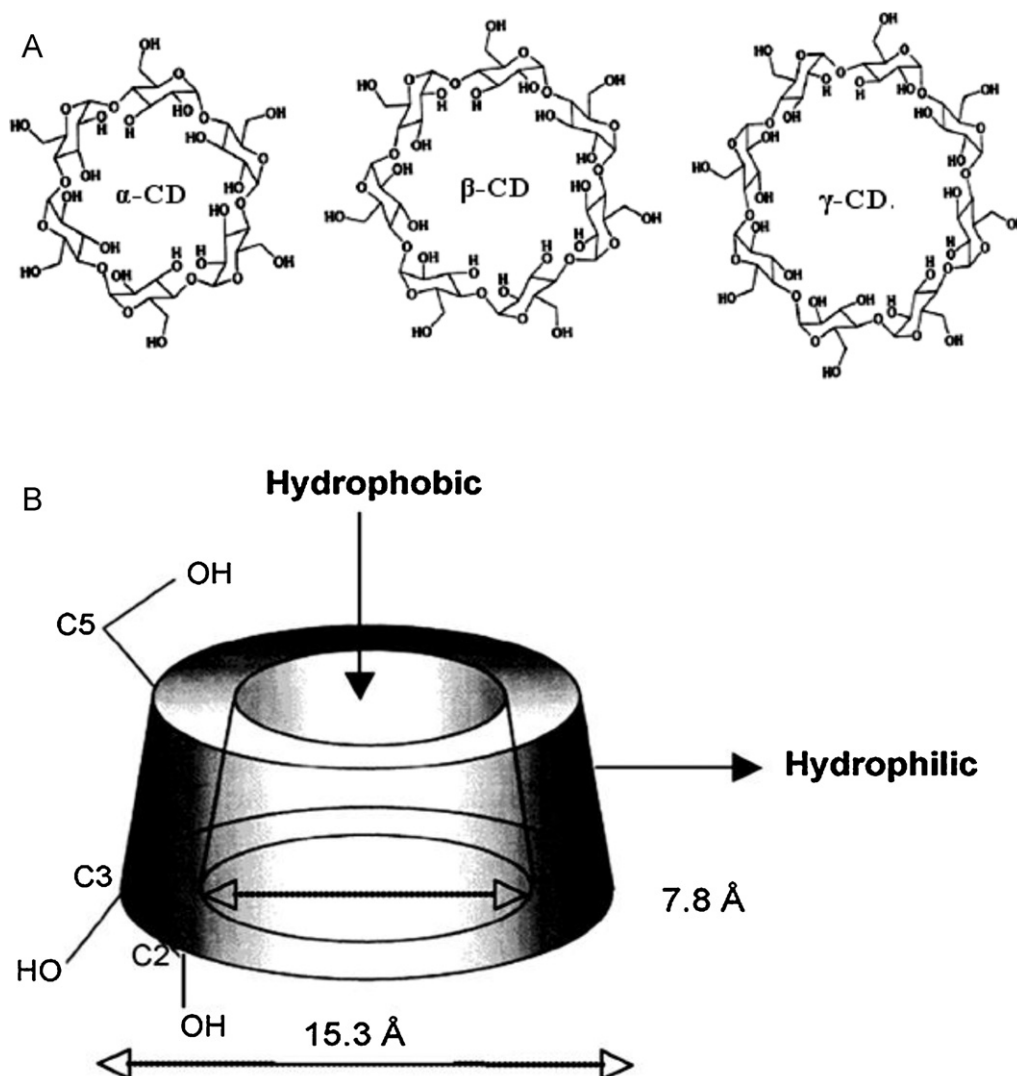
The chemical properties of cyclodextrins combined with their non-toxic character to humans have led to their use in pharmaceuticals, as food additives as well as in the environmental de-contamination procedures of wastewater, aquifer, air, and soil [7,8]. Particularly cyclodextrins and their derivatives have been used to remove contaminations by the formation of inclusion complexes or to enhance the solubility of several compounds [9–12].

Ramamurthy, Eaton, and Co-workers [13,14] have exploited the use of CDs as host to examine photochemical and photophysical processes that occur in molecules complexed within them and to compare their behavior in aqueous solutions and in the solid state. Their studies dealt mostly with intramolecular events, with only a single molecule present in the CD cavity. Furthermore, these studies seem to indicate differences in the extent of inter- and intramolecular hydrogen bond/intramolecular charge transfer for the molecules in aqueous solutions of cyclodextrins. Applications of cyclodextrins and their derivatives cover various areas of the chemistry, including the sensing of organic molecules and organic pollutants, analytical chemistry, pharmaceuticals, food and other industrial areas [15–17].

The inclusion of a guest in a β -CD cavity consists basically of a substitution of the included water molecules by the less polar guest [18]. The process is energetically favoured by the interactions of the guest molecule with the solvated hydrophobic cavity of the host. In this process entropy and enthalpy changes have an important role. In spite of the fact that the “driving force” of complexation is not yet completely understood, it seems that it is the result of various effects [18]; (a) substitution of the energetically unfavoured polar–apolar interactions (between the included water and the β -CD cavity on the one hand, and between water and the guest on the other) by the more favoured apolar–apolar interaction (between the guest and the cavity), and the polar–polar interaction (between bulk water and the released cavity–water molecules). (b) β -CD-ring strain release on complexation, (c) Van der Waals interactions and hydrogen bonds between host and guest molecules.

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Scheme 1. (A) Chemical structures of α -CD, β -CD and γ -CD. (B) The internal and external widths for β -cyclodextrin are noted in the figure and height of the cavity is presumed to be ~ 8 Å and width size is 15.3 Å.

In this study, we report the absorption characteristics of diphenylamine (DPA) in different β -cyclodextrin concentrations. For the past one decade, the corresponding author has largely been involved in studying the photophysical properties [19–25] and electrochemical properties [26] of various organic fluorophores. This molecule shows 1:1 inclusion with β -CD molecule, and is clearly confirmed by spectral analysis as well as docking method by RasMol tool [27]. This stimulated us to carry out a study on diphenylamine.

Diphenylamine (DPA) and its derivatives are most commonly used as stabilizers in nitrocellulose-containing explosives and propellants, in the perfumery, and as antioxidants in the rubber and elastomer industry. DPA is also widely used to prevent post-harvest deterioration of apple and pear crops. It is used for the production of dyes, pharmaceuticals, photography chemicals and further small-scale application [28]. First reports showed that DPA was found in soil and groundwater. Some ecotoxicological studies demonstrated the potential hazard of various diphenylamines to the aquatic environment and to bacteria and animals. Studies on the biodegradability of DPA and its derivatives are very sparse. Therefore, further investigation is required to determine the complete dimension of the potential environmental hazard [29] and to introduce possible (bio) remediation techniques for sites that are contaminated with this class of compounds.

Chattopadhyay et al. [30] have studied photochemical conversion of diphenylamine (DPA) to carbazole (CAZL) fluorometrically in aerated aqueous and aqueous β -CD environments. KothaiNayaki et al. [31] have studied the solvatochromism and prototropism of DPA in aqueous solution. The techniques of UV–Vis, FT-IR, XRD, AFM, CV and thermodynamic parameters have been used to examine the effects of β -cyclodextrin upon complexation of diphenylamine. And the formation constants of the complexes were calculated.

2. Experimental

2.1. Instruments

The absorption spectral (UV–vis spectrum) measurements were carried out with Shimadzu UV-2401PC double-beam spectrophotometer. The pH values in the range 2.0–12.0 were measured using Elico pH meter LI-120. Electrochemical studies were carried out using Auto lab electrochemical analyzer, it used to apply potential on the working electrode equipped with a three-electrode glassy carbon electrode (diameter: 1 mm) is served as a working electrode system. Reference electrode was saturated calomel electrode (SCE) and counter electrode was platinum wire. All experiments were carried out at 30 ± 1 °C. The working electrode was polished

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