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ORIGINAL ARTICLE

Thermodynamic and spectroscopic studies of alanine and phenylalanine in aqueous β-cyclodextrin solutions

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Abstract Ultrasonic speed, u and density, ρ have been measured for DL-alanine (Ala) and L-phenylalanine (Phe) in aqueous β-cyclodextrin (β-CD) at 298.15, 303.15, 308.15, and 313.15 K. The complexation of Ala and Phe with β-CD has been studied by means of UV–vis and thermodynamic (ultrasonic speed and density) studies. Using the measured ultrasonic speed and density data the apparent molar compressibility ($\kappa_{S,\varphi}$), apparent molar volume (V_φ), limiting apparent molar compressibility ($\boldsymbol{\kappa}^0_{S,\varphi}$), limiting apparent molar volume (V^0_φ), their constants (S_K and S_v), and hydration number (n_H) have been obtained. The positive values of transfer properties at infinite dilution for Ala and Phe in β-CD is the outcome of the balance between released water molecules from β-CD cavity and hydrophobic groups of Ala and Phe that enter into the macrocycle β-CD cavity. The experimental results have also been discussed on the basis of UV–vis absorbance. The results indicate the formation of a more stable host–guest complex between Phe-β-CD than between Ala-β-CD.

1. Introduction

Cyclodextrins are cyclic oligosaccharides consisting of six to eight ($\alpha = 6$, $\beta = 7$, $\gamma = 8$) or more glucopyranose units linked by α-(1, 4) glycosidic bonds. They are also known as cycloamyloses, cyclomaltoses and Schardinger dextrins1, 2 [10,19,27]. The numerous and specific properties of β-CD (Fig. 1(I)) and its non-toxic character to humans have led to its use in clinical, food, cosmetics, environmental industries, pharmacy, [18,24,40,9,41] and textile industry [18,24,40,9,41, 38,27,16]. Interactions of cyclodextrin with unfolded proteins enhance protein stabilization [38] as well as solubilization [43,38] which affect the 3D-structure of proteins and inhibit their chemical and biological properties.

Due to the complex structure of proteins, the study of conformational stability and unfolding behaviour of globular proteins is a bit challenging [31]. Instead, the physicochemical [31,26] and thermodynamic [26] properties of amino acids, which are building blocks of proteins and peptides, in aqueous and mixed-aqueous solutions [26] are of significant interest. The properties of amino acids in aqueous cyclodextrin solutions are important for understanding the chemistry of drug carriers in drug delivery systems [38]. There have been a

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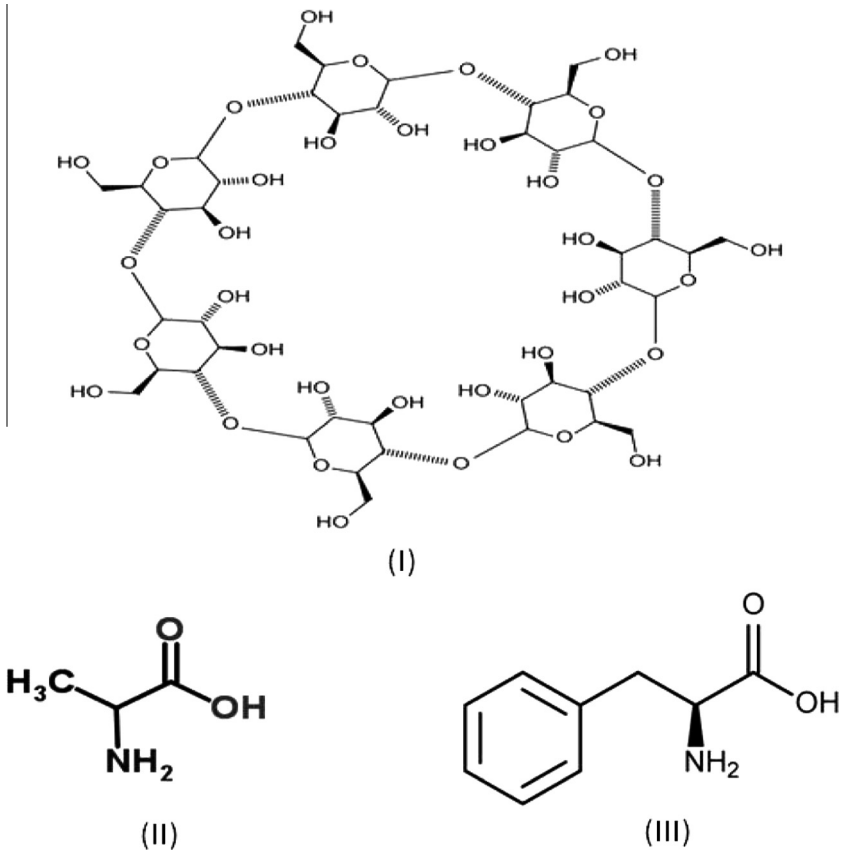

Figure 1 Chemical structures of (I) β-CD, (II) Ala, and (III) Phe.

number of physicochemical studies of some amino acids in pure water [15,4], in aqueous urea [5], in aqueous carbohydrates [1,26,35], in aqueous salts [39,17,31], and so on. Keeping this in mind, we decided to study Ala (Fig. 1(II)) and Phe (Fig. 1(III)) in aqueous β-CD to investigate amino acid–cyclodextrin interactions in aqueous medium. Ala is ambivalent and less hydrophobhic than Phe [21]. Due to the relative nonpolar character of the cavity of β-CD in comparison to the polar exterior, it can form inclusion complexes with a wide variety of guest molecules, predominantly due to hydrophobic interactions [33]. Although, the present study deals with the study of α-amino acids, Ala and Phe, it would be of great significance to outline the importance of unnatural α-amino acids. Unnatural α-amino acids when incorporated into biologically active peptides and proteins modify their stability, activity, bioavailability and binding specificity [29,30]. Moreover, incorporation of unnatural amino acids into various enzymes has been used to evaluate protein folding, its function and signal transduction [30]. The incorporated unnatural α-amino acids are capable of specifically restricting the rotation of N^{α}–C^{α}, C^{α}–C(O), C(O)–NH bonds and side-chain conformations by covalent or noncovalent steric interactions. The examples of such incorporation of α-amino acids range from simple α-methylated amino acids to proline mimetics and various unsaturated α, β-amino acids [29].

In the present work, estimated values of $V_{\varphi}^{0}, \kappa_{S,\varphi}^{0}$, transfer volume, transfer compressibility, hydration number and UV–vis spectra of Ala and Phe in aqueous solution of β-CD have been used to discuss host–guest and solute–solvent interactions prevailing in the systems under study.

2. Experimental

2.1. Materials and methods

DL-Alanine (Thomas Baker, (India), mass fraction >0.99) and L-phenylalanine (Loba, Mumbai (India), mass fraction >0.99) were used after recrystallizaton from ethanol–water mixture and were dried in vacuum over P_2O_5 at room temperature for about 72 h. β-Cyclodextrin (Hi Media Laboratories, Mumbai (India), mass fraction > 0.98) was used as such without any pretreatment. The aqueous solution of β-cyclodextrin of 0.008 m (mol kg^{-1}) was prepared using double distilled deionized water (conductivity $< 1.5 \times 10^{-6}$ S cm^{-1} at 298.15 K) and was used as solvent. The weighings were done using Precia XB220 (Swiss make) electronic balance precisely up to 10^{-4} g. The densities of the solutions were measured using a single-stem pycnometer made up of Borosil glass with a bulb capacity of 8×10^{-3} dm^3. The capillary had uniform bore with graduated marks and a well fitted glass cap. The calibration of the pycnometer was done using the procedure described in the literature [25,2]. The accuracy in density measurement was found to be ± 0.01 kg m^{-3}.

The ultrasonic speeds in solutions were measured at different temperatures using a single crystal variable path ultrasonic

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