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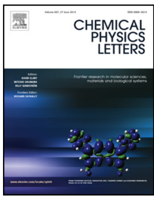

A study of the hydration of lysozyme in neat organic solvents using isothermal calorimetry: Effect of water solvation

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ABSTRACT

The interaction enthalpies of the dried and hydrated lysozyme with neat organic solvents (DMSO, formamide, ethylene glycol, and methanol) were obtained at 25 °C. These organic solvents represent a series of liquids in which the water solvation enthalpy is gradually changed over a wide range. The interaction enthalpies of the dried lysozyme with neat organic solvents are exothermic. At high water content, the interaction enthalpies are endothermic for formamide and exothermic for DMSO, methanol, and ethylene glycol. The dehydration enthalpies of lysozyme in organic liquids may be endothermic or exothermic depending on the initial water content and the water solvation enthalpy.

1. Introduction

It is well-known that the enzyme–water interactions play a crucial role in determining the stability, structure and functions of the enzyme molecules [1–6]. Knowledge of processes occurring upon the hydration of enzymes in neat organic solvents is also very important in biotechnological and pharmaceutical applications of enzymes such as their use as biocatalysts [7–11], biosensors [12,13], downstream protein processing in protein-dissolving organic solvents [14,15], transdermal delivery of pharmaceutical proteins [16]. However, it is still unclear which physicochemical parameters control the enzyme–water interactions in neat organic liquids.

Dordick and Gorman [17] studied the desorption of the enzyme-bound T_2O into nonaqueous organic liquids for chymotrypsin, subtilisin Carlsberg, and horseradish peroxidase. They showed that enzymes lost the enzyme-bound T_2O in organic solvents. Polar solvents resulted in the highest degree of T_2O desorption. However, no quantitative correlation was observed between the desorption ability of organic liquids and solvent polarity, hydrophobicity, and the saturated molar solubility of water in a given solvent.

The structure of the model enzyme lysozyme in water and neat organic solvents has been examined using ^{1}H NMR and circular dichroism spectroscopies [18]. No correlation has been observed between the conformational state of lysozyme in organic liquids and their physicochemical characteristics as dielectric constant, dipole moment, and Hildebrand solubility parameter.

Hence, there is a clear need for experimental and theoretical approaches by which the thermodynamic characteristics of the enzyme–water interactions in organic solvents may be determined.

Thermochemical studies have traditionally been very important in ascertaining a better understanding of the enzyme–water interactions. Enthalpy is an important thermodynamic quantity directly associated to the intensity of the intra- and intermolecular interactions in the above mentioned systems. Thus, particular, Smith et al. [19] calorimetrically measured the heats of pure water adsorption on lysozyme. They obtained both the water sorption isotherm and the enthalpy of hydration of the protein in the water content range 0–18% (g water/g enzyme) at 25 °C. The sorption calorimetry has been used to measure the adsorption isotherm of water on lysozyme and the corresponding heat effects in the water content range 0–50 wt% [20]. Our research group developed an experimental method for measuring the heat effects of hydration of proteins [21,22]. The most important observations of these calorimetric studies [19–22] can be summarized as follows:

(i) The hydration enthalpies vary strongly with the hydration level.
(ii) The hydration enthalpies are highly exothermic at low hydration level.
(iii) As the water content increases, the hydration enthalpies approach the enthalpy of condensation of pure water.

Thermochemical studies may be extremely pertinent to the understanding of the enzyme–water interactions in organic liquids. The interaction enthalpies of the dried α-chymotrypsin

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