J. Chem. Thermodynamics 45 (2012) 122–136

Contents lists available at SciVerse ScienceDirect

J. Chem. Thermodynamics

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

Thermodynamic contributions of peptide backbone unit from water to biocompatible ionic liquids at $T = 298.15$ K

T. Vasantha [a], Pankaj Attri [b], Pannuru Venkatesu [b,*], R.S. Rama Devi [a]

[a] Department of Chemistry, Sri Padmavathi Women's Degree and Post Graduate College, Tirupati 517 502, India
[b] Department of Chemistry, University of Delhi, Delhi 110 007, India

ARTICLE INFO

Article history:
Received 17 August 2011
Received in revised form 16 September 2011
Accepted 21 September 2011
Available online 29 September 2011

Keywords:
Model compounds
Biocompatible ionic liquids
Solubilities
Transfer free energies
UV–vis spectroscopic studies

ABSTRACT

To quantify the biomolecular interactions of protein functional groups with biocompatible ionic liquids (ILs), transfer free energies ($\Delta G'_{tr}$) of model compounds from water to aqueous ILs solutions have been determined from the solubility measurements, as a function of ILs concentration at $T = 298.15$ K under atmospheric pressure. The aqueous systems investigated contain amino acids of zwitterionic glycine peptides: glycine (Gly), diglycine (Gly_2), and cyclic glycylglycine (c(GG)) with ILs of diethylammonium acetate ($[Et_2NH][CH_3COO]$, DEAA), triethylammonium acetate ($[Et_3NH][CH_3COO]$, TEAA), and trimethylammonium acetate ($[Me_3NH][CH_3COO]$, TMAA). It was found that the solubility of model compounds in aqueous IL solutions decreases with increasing IL concentration (salting-out effect). We observed positive values of $\Delta G'_{tr}$ for Gly, Gly_2, and c(GG) from water to ILs, indicating that the interactions between ILs and protein surface are unfavourable, which leads to stabilization of the native structure of amino acids. Moreover, our experimental data is used to determine transfer free energies ($\Delta g'_{tr}$) of the peptide backbone unit ($-CH_2C{=}ONH-$) from water to IL solutions. These results explicitly elucidate that all alkyl ammonium ILs acted as stabilizers for tested model compounds through the exclusion of ILs from surface of model compounds and also reflect the effect of alkyl chain on the stability of protein model compounds. To obtain the mechanism events of the ILs role in enhancing the stability of the model compounds structure, we further studied the UV–vis spectrum analysis.

1. Introduction

Proteins are polymers made up of specific sequences of model compounds linked together by covalent peptide bonds. The nature and the arrangement of the amino acid side chain along the protein backbone are responsible for the individual characteristics of the biomolecules, and it has been recognised that all of the information pertaining to the proteins is implicit in the amino acid sequence. In a protein, the peptide bond is very stable and has unusual conformational properties [1]. Basically, these bonds are influenced by the aqueous solutions therefore, it is very much important to have a clear idea on the solubility, stability, and thermodynamic properties of these molecules in aqueous solution. It has long been known that dramatic changes in the physical and functional properties of proteins are due to the addition of co-solvents. Their structural and chemical properties have been extensively investigated by both theoretical and experimental techniques thereby providing valuable insights into the chemistry of peptides [1–3]. Understanding of the protein–solvent interactions is of considerable importance in the development of biotechnologies and industrial processes.

The effects of co-solvents on the solubility and conformational stability of proteins have been of intense interest for decades. Obviously, the stability of biomolecules under co-solvent conditions is dependent on the nature of the co-solvent; which can alter a protein's properties and structural effects through biomolecular interactions between its functional groups and the co-solvent particles [4–7]. During the past decade, ionic liquids (ILs), a class of environmental friendly solvents, has been used for a wide range of industrial and pharmaceutical applications [8–13]. Ionic liquids represent a rather diverse class of co-solvents that are combinations of different ions, which are liquids at or close to room temperature [9,14–16]. The ILs are a relatively new class of compounds, they appear to be replacements for volatile organic compounds (VOCs). Due to the ionic nature of the materials, ILs have essentially negligible vapour pressure and so can be envisioned as being useful in a variety of applications [5,7]. The ILs pose a new option for an excellent co-solvent, not only for preserving proteins stability [17–21] but also as a refolding additive for the biomolecules from a quenched thermal unfolded structure [21,22].

Virtually, there are rapid physiological stresses inside the biomolecules, therefore the biomolecule needs to maintain its

* Corresponding author. Tel.: +91 11 27666646 142; fax: +91 11 2766 6605.
E-mail addresses: venkatesup@hotmail.com, pvenkatesu@chemistry.du.ac.in (P. Venkatesu).

0021-9614/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jct.2011.09.017