THERMODYNAMICS AND HYDROPHOBIC HYDRATION OF SOME BIOCHEMICAL MODEL COMPOUNDS IN AQUEOUS AND MIXED AQUEOUS SOLUTIONS

A Thesis Submitted
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DOCTOR OF PHILOSOPHY

By
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to the

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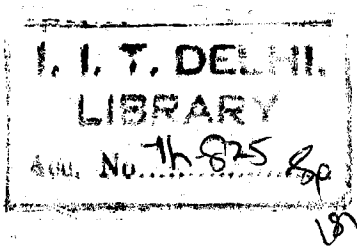

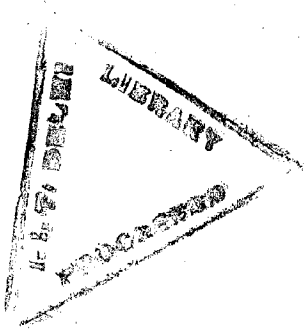

समर्पित -
पूज्य माँ और पिताजी के
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CERTIFICATE

This is to certify that the thesis entitled "THERMODYNAMICS AND HYDROPHOBIC HYDRATION OF SOME BIOCHEMICAL MODEL COMPOUNDS IN AQUEOUS AND MIXED AQUEOUS SOLUTIONS" being submitted by Mr. A.K. Mishra to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. Mishra has worked with my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge, has reached the requisite standard.

The results contained in this dissertation have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.

(J. C. Ahluwalia)
Professor
Department of Chemistry

I.I.T., Delhi
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A.K. Mishra

ABSTRACT

Investigation of small model compounds is known to be a very useful method for elucidating various solute-solvent and solute-solute interactions prevalent in the aqueous solutions of biological macromolecules. Thermodynamic investigations on some model compounds of proteins and polypeptides such as amino acids, N-acetyl amino acids, and peptides in water, aqueous alcohol, and aqueous urea solutions are described in this thesis. The nature of interactions of these solutes with water and mixed aqueous solvents has been deduced from the thermodynamic quantities such as enthalpy and heat capacity of dissolution and apparent molal volume of the solute. Enthalpies and heat capacities of dissolution are obtained by calorimetry and apparent molal volumes from density measurements.

Chapter 1 of the thesis describes briefly the 'water structure' -peculiar nature of which is supposed to be the origin of most of the typical solute-solvent and solute-solute interactions in aqueous solutions. A brief account of typical features of aqueous solutions and the techniques through which the thermodynamic data reveal the nature of molecular interactions in aqueous solutions are also incorporated in this Chapter.

Chapter 2 deals with the experimental set up of the isoperibol submarine calorimeter and the oscillating tube digital density meter and their operational procedure.

In Chapter 3, enthalpy, heat capacity, and apparent molal volume changes due to transfer of some amino acids from water to aqueous tert-butanol solutions are reported. Enthalpy of transfer of diglycine from water to aqueous tert-butanol and to aqueous ethanol solutions are also given in this Chapter. Entropies of transfer of a peptide backbone unit (CH_2CONH) and peptide group (CONH) from water to aqueous ethanol solutions were evaluated from the enthalpy of transfer data and the free energies of transfer of glycine, diglycine and α-alanine available in literature.

The thermodynamic transfer functions are discussed in terms of solute-solute interactions. Observed trends in the thermodynamic transfer functions of these model compounds have been also utilized to rationalize the effect of alcohols on the conformational stability of proteins and polypeptides.

Chapter 4 consists of the results of integral enthalpies of solution of sodium salts of some N-acetyl amino acids. Limiting partial molal heat capacity contributions of the peptide backbone unit (CH_2CONH) and the peptide group (CONH) are evaluated from the enthalpy of solution data and discussed in terms of the solute-solvent interactions.

The results of the apparent molal volume measurements of some amino acids, N-acetyl amino acids and peptides are described in Chapter 5. Group additivity relationships for the molal volumes and the effect of electrostriction in these series of compounds have been examined. Concentration dependence of the apparent molal volumes have been explained in terms of hydrophobic and hydrophilic interactions.

Limiting apparent molal volumes of these compounds are estimated from the van der Waals atomic volume increments and appropriate volume decrements due to hydrophilic hydration of polar (CONH and COOH) and zwitterionic (H_3N^+.....COO^-) groups.

Chapter 6 embodies the results of the limiting apparent molal volume changes due to transfer of some amino acids and peptides from water to aqueous urea solutions. The results have been interpreted in the framework of Friedman's cosphere overlap model.

Care has been taken to give proper credit for the investigations done by other workers. The author would like to apologize for any omission which might have occurred by oversight or error in judgement.

CONTENTS

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