THERMODYNAMIC STUDIES OF AQUEOUS AND MIXED AQUEOUS SOLUTIONS OF SOME BIOPOLYMER MODEL COMPOUNDS

A Thesis Submitted
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by

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to the

Department of Chemistry
INDIAN INSTITUTE OF TECHNOLOGY, DELHI

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TO

MY PARENTS AND TEACHERS

CERTIFICATE

This is to certify that the thesis entitled "THERMODYNAMIC STUDIES OF AQUEOUS AND MIXED AQUEOUS SOLUTIONS OF SOME BIOPOLYMER MODEL COMPOUNDS" being submitted by Mr. Rajiv Bhat 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. Bhat has worked under 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.

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RAJIV BHAT

ABSTRACT

The present work describes the thermodynamic investigations carried out on aqueous solutions of some amino acids, peptides, nucleic acid bases, nucleosides, and nucleotides. The thermodynamic parameters determined include the calorimetrically determined apparent molar heat capacities and the densitymetrically measured apparent molar volumes. Apparent molar heat capacities and volumes were measured using a Picker dynamic flow microcalorimeter and an Anton Paar DMA 60/602 digital density meter, respectively. From the apparent molar heat capacities and volumes, partial molar heat capacities ($\bar{C}^o_{p_2}$) and volumes ($\bar{V}^o_2$) at infinite dilution were derived by linear regression analysis.

Partial molar heat capacity and volume data for all the naturally occurring amino acids and peptides have been used to construct a hydrophobicity scale of the amino acid residues which is useful in predicting the stability of one protein as compared to the other. Combining our data with the heat capacity of denaturation data and volume results in denaturing solvents, it has been possible to evaluate the degree of exposure of proteins on denaturation and the volume associated with the voids and other specific interactions.

Partial molar heat capacities and volumes of transfer ($\bar{C}^{o}_{p_{2,tr}}$ and $\bar{V}^{o}_{2,tr}$, respectively) for homologous series of amino acids and peptides from water to aqueous solutions of sodium chloride and calcium chloride indicate that the favourable interaction of the salt ions with the peptide groups bring about the denaturation of proteins. A similar transfer to aqueous glucose and sucrose solutions shows that these additives owe their stabilizing effect of proteins due to having lesser magnitude of interactions with the peptide groups as is evident from the small transfer parameters.

$\bar{C}^{o}_{p_2}$ and $\bar{V}^{o}_{2}$ values for the nucleic acid bases adenine, thymine, cytosine, and uracil indicate that the presence of polar moieties in these compounds tends to reduce their hydrophobic character. Hence it is likely that the bases may not associate through hydrophobic interactions in the nucleic acids. From the $\bar{C}^{o}_{p_2}$ and $\bar{V}^{o}_{2}$ data on the bases, nucleosides, and nucleotides studied by us, it has also been possible to determine accurately the heat capacity and volume changes for the hydrolysis of various nucleosides and nucleotides, which are essential biochemical parameters.

Due acknowledgement has been made wherever the work described is based on the findings of other investigators. The author apologizes for any omission or mistake which might have creeped in due to oversight.

GLOSSARY OF SYMBOLS AND ABBREVIATIONS

A_pA	dinucleotide with adenine as the base.
5′-ADP	adenosine-5′-diphosphate.
5′-AMP	adenosine-5′-monophosphate.
5′-ATP	adenosine-5′-triphosphate.
c	concentration in units of mol dm^{-3} of solution.
CD	circular dichroism.
5′-CMP	cytidine-5′-monophosphate.
C_p	heat capacity of the solution.
C_p^o	heat capacity of the solvent.
C_p^*	heat capacity of the pure solute.
$\bar{C}^o_{p_2}$	partial molar heat capacity of the solute at infinite dilution.
$\bar{C}^o_{p_2,tr}$	partial molar heat capacity of transfer of the solute at infinite dilution.
$C_{p,A}$	heat capacity of the liquid A.
$C_{p,B}$	heat capacity of the liquid B.
ΔC_p	change in the heat capacity.
ΔC_p^o	heat capacity of dissolution at infinite dilution.
$\Delta \bar{C}_p^o$	change in the partial molar heat capacity at infinite dilution.
$\Delta C_{p,DN}$	heat capacity of denaturation.
$\Delta C_{p,tr}$	heat capacity of transfer.
d	density of solution.
d_o	density of solvent.

d_A	density of liquid A.
d_B	density of liquid B.
DNA	deoxyribo nucleic acid.
5′-GMP	guanosine-5′-monophosphate.
ΔG^o	standard Gibbs free energy change.
ΔG_{tr}	free energy of transfer.
ΔH	change in enthalpy.
ΔH^o	standard enthalpy change.
ΔH_s^o	integral enthalpy of solution at infinite dilution.
I_c	calibration current.
K	calibration constant.
m	molality.
M	molecular weight.
ORD	optical rotatory dispersion.
p	pressure in units of torr.
pK_a	$-\log_{10}(K_a)$.
ϕ_c	apparent molar heat capacity.
ϕ_v	apparent molar volume.
ϕ_c^o	apparent molar heat capacity at infinite dilution.
ϕ_v^o	apparent molar volume at infinite dilution.
poly(rA-rU)	polynucleotide with alternating sequences of adenine and uracil.
Ribo A_8	ribonucleotide with eight adenine units.
Ribo A_{10}	ribonucleotide with ten adenine units.
RNA	ribonucleic acid.
ΔS	change in the entropy.

ΔS^{o}	standard entropy change.
σ	standard deviation.
σ_A	heat capacity of liquid A in units of $J\ K^{-1} cm^{-3}$.
σ_B	heat capacity of liquid B in units of $J\ K^{-1} cm^{-3}$.
σ_s	shrinkage in volume
T	absolute temperature (in Kelvin).
T_m	transition temperature.
5′-UMP	uridine-5′-monophosphate.
5′-UDP	uridine-5′-diphosphate.
5′-UTP	uridine-5′-triphosphate.
V_f	free volume.
V_h	volume due to hydrophobic hydration.
V_s	shrinkage volume.
$V_{v.w.}$	van der Waals volume.
V_z	zener voltage.
$\overline{V}_2^{o}$	partial molar volume at infinite dilution.
ΔV	change in volume.
$\Delta \overline{V}^{o}$	change in the partial molar volume at infinite dilution.
ΔV_{ion}	volume of ionization.
$\overline{V}^{o}_{2,tr}$	partial molar volume of transfer of the solute at infinite dilution.
W_o	power input.
ΔW	change in power.

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