Structural Relaxation or Modifications of Solvents

Introduction to the Microsymposium and on the Modulation of Thermodynamic Parameters Relative to Biomolecule–Solvent Interactions

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As a result of introducing a macromolecule in a solvent, changes in the structures of both solute and solvent are generally found. In this specific meaning we refer here to 'relaxation phenomena'.

The discussion will either concern or keep in view the case of biolomecules and to which extent these changes are involved in their thermodynamic stability or functional structure:

Dr. Ben-Naim will discuss hydrophobic interactions and structural changes in the solvent;

Dr. Wen will focus on thermodynamic properties of aqueous solutions of hydrophobic solutes;

Dr. Cordone, Dr. Fornili and myself shall discuss results of experiments concerning solutes of several types (proteins, polynucleotides, polysaccharides, and small planar molecules, useful as model systems for studying stacking interactions).

These have in common the strategy of modulating the solvent by (D–H) isotopic substitution, or by the addition of organic co-solvents, and arriving at corresponding modulations of the relevant thermodynamic parameters, or of biomolecular functions.

Net structural differences are reached through kinetics, which link time and temperature variables and are therefore capable of adding pertinent information. If for water these kinetics are too rapid, some transitions from one to another biomolecular conformation or states of aggregation (which can in turn be either functional or not) can be profitably followed up. Further, and under favorable circumstances, the path can be reversed so as to provide hints on the timescale of processes involving the solvent.

Thermodynamic Properties of Aqueous Solutions of Hydrophobic Solutes

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The existence of hydrophobic hydration is well established. Examples are found for aqueous systems containing purely nonpolar groups (*e.g.*, rare gases, alkanes and perfluoroalkanes), poly-functional solutes (*e.g.*, alcohols, ethers and ketones), and ionic solutes (*e.g.*, tetraalkylammonium and azoniaspiroalkane ions). Influence of solute shape on the surrounding water structure is subtle but of particular interest. The 'structure promotion' effect in dilute aqueous solutions of hydrophobic groups is now firmly established, but the quantitative details are still incompletely understood. Recent advance in understanding the nature of hydrophobic hydration is made by Frank who pointed out that the hydrophobic hydration is not the cause of the low solubility of nonpolar gases in water.

Hydrophobic bonding, which denotes the tendency of non polar groups in water to attract each other, is concentration dependent and not well characterized quantitatively. Several types of examples will be given in which the details of such interactions have been worked out.

Hydrophobic Interactions and Structural Changes in the Solvent

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Using a broad family of possible definitions of the concept of the 'structure of water' one can ask the following two relevant questions: *1*) For any specific process, say the dimerization of two simple solutes, how much structural change is involved in the solvent? *2*) Knowing the effect of the process on the structure of the water, to what extent do these structural changes affect the thermodynamics of the process?

An approximate answer to the first question may be given, based on one particular choice of a definition of the structure of water [1]. Regarding the second question, a quantitative answer may be given only for the standard free energy of the process. For all other thermodynamic properties only a qualitative answer is available at present. However, using a

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