Thermodynamics of Water and Water Solutions – Questions, Myths and some Answers

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Water is the most important substance in the world; it covers two thirds of the Earth and our own cells include two thirds water by volume. Hundreds of books have been written about water and at the same time we know so little about it. In the words of Philip Ball, for many years consultant of *Nature*: "No one really understands water. It's still a mystery" [1]. Water has more than 50 exceptional physico-chemical (thermodynamic) properties which are considered "anomalous" in the sense that no other liquids behave that way (trends with temperature, pressure and composition). Among the most exciting ones are the maximum of density at 4 ºC (ice floats, lakes freeze from top to bottom), high values of heat capacity (thus stabilizing Earth's climate) and surface tension (small insects walk on water) and maxima and minima of many thermodynamic properties as function of temperature e.g. the minimum hydrocarbon solubility in water at room temperature (related to the hydrophobic effect) and the speed of sound.

What is the true reason for all these ? Presumably hydrogen bonding "in some form" and especially the hydrogen bonding structure and its changes are the prevailing explanations. But which hydrogen bonding structure?

Numerous theories for water structure have been presented but they are all up for debate. It is unclear whether liquid water maintains the tetrahedral structure (as we know it from ice) or whether it should best be described by a two-state model, where most molecules are in the form of rings or chains [3,10] and literature is full with heated discussions [1-2]. Effects of salts [7], surfaces and biomolecules on water structure are not well understood. Neither molecular simulation [4] or advanced experimental methods [5,6] have provided the full answer. Direct spectroscopic and other measurements could provide quantitative information on the degree of hydrogen bonding of water but they are not in good agreement with each other and these data can be interpreted in different ways [5,8]. Promising novel thermodynamic based theories have problems if an unclear picture of water is the input and it is not surprising that they cannot explain many of the anomalous properties of pure water and aqueous solutions [8]. Moreover, novel theories giving new insight have been presented, most recently the "exclusion zone" concept pioneered by G. Pollack [9].

Where is the truth ?

The purpose of this presentation is to illustrate some of the recent theories about water structure, their role in thermodynamics, try to answer some of the aforementioned questions and point out areas where further investigations are needed.

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