Role of the solvent-excluded volume effect in molecular recognition processes

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Molecular recognition processes are fundamental for life and are fascinating because, notwithstanding the lack of eyes, two different protein molecules, for instance, are able to stick together with high affinity and selectivity [1,2]. The mystery of molecular recognition events is also increased by their occurrence in aqueous solutions. It should be important to shed light on the physico-chemical grounds of these processes. A basic fundamental concept is represented by the solvent-excluded volume effect. In a condensed state of the matter such as a liquid, it is necessary to create a cavity to host the solute [3]. Cavity creation is a theoretical construction to account for the volume that each molecule possesses and that no other molecule can occupy. Therefore, insertion of a solute reduces the configurational space available to solvent molecules, causing a decrease in their translational entropy. A correct measure of this solvent-excluded volume effect in water is given by the water accessible surface area, WASA, of the solute molecule (i.e., of the cavity suitable to host the solute). When two different molecules recognize each other and form a complex in water or aqueous solution, there is a marked WASA decrease [1,2] that, in turn, leads to marked gain in translational entropy for water molecules [4,5]. This water entropy gain is a general entropic driving force for molecular recognition events occurring in water and aqueous solutions. A statistical thermodynamic treatment will be provided and it will be applied to some relevant examples.

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