Hydrophobic hydration: a matter of the mean energetics of water

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The enthalpically favored hydration of hydrophobic entities, termed hydrophobic hydration, impacts the phase behavior of numerous amphiphiles in water. We show experimental evidence that hydrophobic hydration is determined by the mean energetics of the aqueous medium. We investigate the collapse and aggregation of an amphiphilic polymer, poly-N-isopropyl acrylamide (PNiPAM), in aqueous solutions containing small amounts of alcohol and find that the thermodynamic characteristics defining the phase transitions of PNiPAM evolve relative to the solvent composition at which the excess mixing enthalpy of the water/alcohol mixtures becomes minimal. Such correlation between solvent energetics and solution thermodynamics extends to other mixtures containing neutral organic solutes that are considered as kosmotropes to induce a strengthening of the hydrogen bonded water network. This denotes the energetics of water as a key parameter controlling the phase behavior of PNiPAM and identifies the excess mixing enthalpy of water/kosmotrope mixtures as a gauge of the kosmotropic effect on hydrophobic assemblies.