



Research paper

The physical origin of hydrophobic effects



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ABSTRACT

From the structural studies on water and air/water interface, hydration free energy is derived, and used to investigate the origin of hydrophobic effects. As a solute is dissolved into water, hydration free energy increases, and is divided into initial and hydrophobic solvation processes. In the initial process, hydration free energy is dominated by hydrogen bonding in interfacial water (topmost water layer at solute/water interface). For hydrophobic process, hydration free energy is related to the hydrogen bonding in bulk and interfacial water. Therefore, hydrophobic effects originate from the structural competition between hydrogen bonding in bulk water and that in interfacial water.

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1. Introduction

Hydrophobic effects, describing the tendency of non-polar molecules or molecular surfaces to aggregate in an aqueous solution, are involved in many important chemical and biological processes including receptor–ligand interactions, protein folding and molecular assembly, as well as interactions in lipid membranes. To explain the fundamentals of biophysics and biochemistry, as well as to engineer new materials, many works have been carried out to investigate the mechanism of hydrophobic effects. However, a deep and quantitative understanding of the origin and nature of hydrophobic interactions remains elusive.

Historically, the concept of hydrophobicity arose in the context of the low solubility of non-polar solutes in water. The classical mechanism for hydrophobicity, proposed by Frank and Evans [1], and advanced by Kauzmann [2] and many others, predicts that, when a solute being smaller than a nanometer (or concentrations below the onset of solute aggregation), the water immediately surrounding the hydrophobic group is more “ordered” than in bulk water. This is termed as “iceberg” formation (or clathrate structure) around the hydrophobic hydrocarbon [1]. Another explanation is based on the application of scaled-particle theory (SPT) [3] to study the hydrophobic effects. In fact, SPT was originally developed for deriving the equation of the state for hard-sphere fluids. Similar concepts can be used to predict the free energy of cavity formation in any bulk system. According to the SPT model [4], the process of forming an empty spherical cavity in water is equivalent to that of inserting a hard sphere into water. In particular, a

recent theory by Lum, Chandler and Weeks [5] highlights the different physical mechanisms of the solvation of small and large hydrophobic solutes in water, which arises from the different manner in which they affect the structure of water. Based on their theory of hydrophobic solvation (LCW) [5], they predicted that the crossover between small and large regime occurs on the nanometer length scale. This suggests that the crossover arises from the change in the physical mechanism, from an entropy-dominated to an enthalpy-dominated mechanism [6]. Thermodynamically, the overall hydration free energy changes from growing linearly with the solvated volume to growing linearly with the solvated surface area [7].

Experimentally, hydrophobic interactions can be investigated through the direct measurement of the forces between hydrophobic surfaces, such as with surface forces apparatus (SFA) and the atomic force microscopy (AFM). The first direct force measurements between two hydrophobic surfaces was conducted by Israelachvili and Pashley [8] using SFA, which indicated that the hydrophobic attraction was longer-ranged, stronger than van der Waals interactions, and decayed approximately exponentially with a decay length of 1 nm [8]. Since then, many experimental measurements have been carried out to investigate the characteristics of hydrophobic interactions [9–13]. In Hammer et al. study [10], the effective range of the hydrophobic attraction can be detected up to several micrometers.

In principle, the free energy has two primary components, $\Delta G = \Delta H - T\Delta S$, where ΔH and ΔS are the enthalpic and entropic changes incurred during solvation. The enthalpic part is a measure of the average potential energy of interactions between molecules, and the entropic part is a measure of the order or intermolecular

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correlations. When hydrophobic solutes are dissolved in water, the thermodynamic functions may contain solute–solute, solute–solvent and solvent–solvent interaction energies. However, the strength of hydrogen bonding in water is stronger than that of van der Waals interactions, water should play an important role in the process of hydrophobic effects.

Hydrophobic interactions depend on the temperature, pressure, solute size and shape, type, and concentration of the additives as well as the proximity to interfaces. However, the tendency for hydrophobic particles to cluster in water is one of the most fascinating aspects, which is readily understood in terms of the dependence of hydration free energy on the solute size. In this study, according to the structural studies on water and air/water interface, hydration free energy is derived, and used to investigate the behavior of dissolved hydrophobic solutes.

2. Hydration free energy

The physical nature of hydrogen bonding has been extensively investigated by various theoretical calculations, such as symmetry-adapted perturbation theory (SAPT and SAPT-DFT) [14,15]. From the theoretical calculations on a water dimer [16], besides van der Waals interactions, there also exists obvious electrostatic interactions between the water molecules. Therefore, hydrogen bonding is closely related to the electrostatic interactions between neighboring water molecules.

The formation of hydrogen bonding leads to the electronic transfer between neighboring water molecules, which shortens the O···O distance, but weakens the O–H covalent bond. In comparison with a single H₂O molecule, the formation of hydrogen bonding leads to the OH vibration frequency moving to low wavenumbers. Therefore, the OH vibrations are sensitive to hydrogen-bonded networks, which are widely employed to investigate the structure of liquid water.

In recent years, many experimental and theoretical studies have been conducted on water molecular clusters, (H₂O)_n. In fact, this provides an approach to investigate the dependence of OH vibrations on hydrogen bonding. Based on our recent studies [17,18], when three-dimensional hydrogen-bonded networks appear ($n \geq 6$), various OH vibrational frequencies correspond to different hydrogen-bonded networks in the first shell of a water molecule (local hydrogen bonding). This indicates that OH vibrations are mainly dependent on the local hydrogen bonding of a water molecule, and the effects of hydrogen bonding beyond the first shell on OH vibrations are weak.

Because OH vibration is mainly dependent on the local hydrogen-bonded networks of a water molecule, different OH stretching frequencies can reasonably be ascribed to OH vibrations engaged in various local hydrogen-bonded networks. In principle, a water molecule interacts with neighboring water molecules to form hydrogen bonds either as proton donor (D), proton acceptor (A), or their combinations. At ambient conditions, the local hydrogen-bonded networks for a water molecule can be expected to be DDAA (double donor–double acceptor), DDA (double donor–single acceptor), DAA (single donor–double acceptor), and DA (single donor–single acceptor) [17,18]. Therefore, the Raman OH stretching band of ambient water can be fitted into five subbands, and are ascribed to OH vibrations engaged in DDAA, DDA, DAA, DA and free OH symmetric stretching vibrations, respectively [17–19].

Many works have been devoted to investigate the structure of liquid water, which can roughly be partitioned into two categories: (a) mixture models and (b) continuum models [20]. Based on our recent Raman spectroscopic studies on water structure [17–19], a water molecule interacts with neighboring water molecules (in

the first shell) through various local hydrogen-bonded networks. Additionally, the changes of temperature, pressure, dissolved salt, and confined environments undoubtedly affect the hydrogen-bonded networks of a water molecule, which will be rearranged to oppose these changes.

From the Raman spectral studies on ambient water [19], the DDAA–OH vibration is ascribed to OH vibration engaged in tetrahedral (DDAA) hydrogen bonding or an “unbroken” hydrogen bond, and free–OH vibration is assigned to the free OH symmetric stretching vibration. Therefore, based on the van’t Hoff equation, $\ln(I_{\text{free-OH}}/I_{\text{DDAA-OH}})$ versus $1/T$ can be applied to determine the thermodynamic characteristics of tetrahedral hydrogen bonding,

$$\ln I_{\text{free-OH}}/I_{\text{DDAA-OH}} = -\Delta H/RT + \Delta S/R \quad (1)$$

According to our recent studies [18], the enthalpy (ΔH) and entropy (ΔS) from DDAA (tetrahedral) hydrogen bonding to free water can be determined to be 11.35 kJ/mol and 29.66 J/mol, respectively.

As a hydrophobic solute is dissolved in water, an interface appears between the solute and water. Therefore, it is necessary to investigate the effects of solute/water interface on the water structure. The OH vibrational frequency is mainly dependent on the local hydrogen bonding of a water molecule; therefore, the solute mainly affects the structure of topmost water layer at the interface (interfacial water) (Fig. 1). Therefore, it is necessary to investigate the structure of interfacial water (topmost water layer at the interface).

In principle, vibrational sum frequency generation (SFG) spectroscopy is an interface selective technique, and has been applied to investigate the air/water interface [21–24]. Recently, phase-sensitive sum-frequency generation (PS-SFG) spectroscopy has also been developed by Shen et al. [25–27] to study the air/water interface. From PS-SFG, $\text{Im}\chi^{(2)}$ can directly be obtained from the experimental measurements. According to our recent study on the air/water interface [24], an obvious structural difference can be expected across the air/water interface, and no DDAA (tetrahedral) hydrogen bonding has been found in the interfacial water.

When a solute is dissolved in water, the solute mainly affects the hydrogen bonding in interfacial water (the topmost water layer) (Fig. 1). Additionally, in reference to bulk water, it can be expected that the interfacial formation should be related to the loss of DDAA hydrogen bonding in interfacial water. Therefore, after the ratio of the interfacial water layer to volume is determined, this can be used to calculate the loss of DDAA hydrogen bonding, and applied to determine the Gibbs energy of interfacial water,

$$\Delta G_{\text{Solute/water interface}} = \Delta G_{\text{DDAA}} \cdot R_{\text{Interfacial water/volume}} \cdot n_{\text{HB}} \quad (2)$$

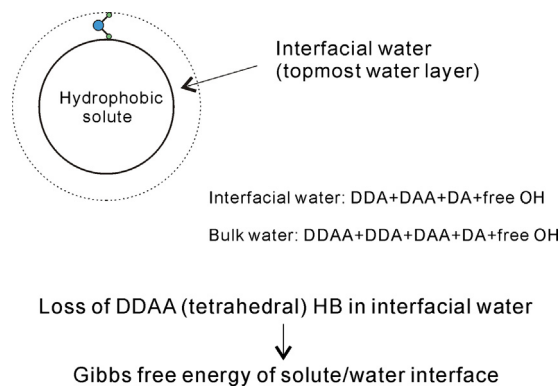


Fig. 1. Structural changes across the solute/water interface. As a hydrophobic solute is dissolved in water, the solute mainly affects the structure of interfacial water (topmost water layer at the interface).

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