



# The hydrophobic effect

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## ABSTRACT

This review is a brief discussion on the development of the understanding of hydrophobicity, or the hydrophobic effect. The hydrophobic effect is primarily discussed in terms of partitioning of hydrocarbons between a hydrophobic environment and water as well as solubility of hydrocarbons in water. Micellization of surfactants is only briefly reviewed.

It is emphasized that (i) the cause of the hydrophobic effect, e.g. the low solubility of a hydrocarbon in water, is to be found in the high internal energy of water resulting in a high energy to create a cavity in order to accommodate the hydrophobe, (ii) the “structuring” of water molecules around a hydrophobic compound increases the solubility of the hydrophobe. The “structuring” of water molecules around hydrophobic compounds is discussed in terms of recent spectroscopic findings. It is also emphasized that (iii) the lowering of entropy due to a structuring process must be accompanied by an enthalpy that is of the same order of magnitude as the  $T\Delta S$  for the process. Hence, there is an entropy–enthalpy compensation leading to a low free energy change for the structuring process. The assumption of a rapid decay of the entropy with temperature provides an explanation of the enthalpy–entropy compensation so often found in aqueous systems. It is also emphasized (iv) that the free energy obtained from partitioning, or solubility limits, needs to be corrected for molecular size differences between the solute and the solvent. The Flory–Huggins expression is a good first approximation for obtaining this correction. If the effect of different molecular sizes is not corrected for, this leads to erroneous conclusions regarding the thermodynamics of the hydrophobic effect. Finally, (v) micellization and adsorption of surfactants, as well as protein unfolding, are briefly discussed in terms of the hydrophobic effect.

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## 1. Introduction

The hydrophobic effect is manifested in a variety of situations involving amphiphilic compounds, such as the self-assembling into micelles in bulk and into monolayers at hydrophobic surfaces. It is also manifested in the unfolding of proteins and there are many other examples. The driving force is the poor interaction of hydrocarbons, or hydrocarbon moieties, with water, hence forcing the hydrocarbon moiety into a water-free environment. The cause of this poor interaction is the subject of this presentation.

## 2. Frank and Evans versus Shinoda and Hvidt

Back in 1945 Frank and Evans suggested that the low solubility of hydrocarbons in water is due to “iceberg formation” (or ordering) of water molecules around the hydrocarbon [1]. Experimentally it has been found that the entropy change upon transferring a hydrocarbon from a nonpolar environment into water,  $\Delta_o^w S$ , is large and negative. (Here the index o represents “oil” i.e. a hydrophobic environment. This could be the liquid phase of the hydrocarbon itself, the interior of

a micelle or some other hydrophobic environment, see below.) This large and negative entropy of transfer was attributed to structuring of water molecules around the hydrophobic moiety. Since the enthalpy change,  $\Delta_o^w H$ , for the same process, is negligible at room temperature there is a large and positive free energy change,  $\Delta_o^w G$ , when a hydrocarbon moiety is introduced into water:

$$\Delta_o^w G(\text{large and positive}) = \Delta_o^w H(\text{small or zero}) - T \Delta_o^w S(\text{large and negative}) \quad (1)$$

This large and positive free energy change implies a poor interaction of the hydrocarbon moiety with water. Frank and Evans therefore concluded that the poor interaction, or low solubility, of hydrocarbons with water is due to structuring of water (“iceberg formation”) around the hydrocarbon.

When interpreting the temperature dependence of micelle formation a similar picture evolves (but now with opposite signs), i.e. there is a large and positive entropy of micellization accompanied with a small, or zero, enthalpy of micellization, resulting in a large and negative free energy of micellization. Here the small enthalpy change on micelle formation is often interpreted in terms of interaction of the headgroups of the amphiphile [2].

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In the late 70's Shinoda [3,4], and later Hvidt [5], presented an alternative and astounding explanation of the low solubility of hydrocarbons in water. They showed that the formation of “icebergs” around a hydrocarbon moiety, i.e. water structuring, would increase the solubility in water and hence the low solubility needed an alternative explanation. Their analysis suggested that it is the high cohesive energy in liquid water that is the cause for the low solubility of hydrocarbons in water. The arguments are based on the graph shown in Fig. 1a, showing the solubility in water as a function of the inverse of temperature for three hydrocarbons. According to the van't Hoff equation the slope of the solubility versus  $1/T$  gives us the enthalpy,  $\Delta H$ , accompanied with the mixing of the two liquids:

$$\frac{d \ln x_2}{d(1/T)} = -\frac{\Delta H}{R} \quad (2)$$

where  $x_2$  is the solubility limit expressed in mole fraction.

This slope is normally a straight line (Fig. 1b) since the heat of solution does not change appreciably with temperature [6]. Indeed the solubility of hydrocarbons in water shows such a pattern, but only at high temperatures. The deviation from the straight line increases dramatically at lower temperatures and this deviation is attributed to the structuring of water around the hydrocarbon molecule (Fig. 1a). A conclusion from the figure is then that the structuring of water (iceberg formation) increases the solubility, as indicated with the arrows in the figure. Hence the cause of the poor solubility of hydrocarbons in water needs an alternative explanation.

### 3. On the terminology “water structure” or “ordering of water”

When Frank and Evans coined the term “iceberg”, they referred to a microscopic region around a hydrophobic molecule, in which “water molecules are tied together in a quasi-solid structure”. Later, the word “iceberg” began to be taken literally, i.e. water molecules were assumed to form ice-like (tetrahedrally ordered) structures around hydrophobic molecules. However, this picture is not supported by experiments: Neutron scattering shows that there is hardly any difference in the state of water molecules when a hydrophobe is introduced [7]. On the other hand molecular dynamics calculation indicate that the structural changes of water in the vicinity of small nonpolar solutes cannot be deduced from the water radial distribution functions, explaining why this increased ordering is not observed through neutron diffraction experiments. The molecular dynamics study shows a slower translational and re-orientational dynamics of water near hydrophobic groups, resembling water at low temperatures [8]. However, this issue is still under debate [9].

Femtosecond mid-infrared spectroscopy shows that hydrophobic groups are surrounded by water molecules that display much slower orientational dynamics than the bulk liquid and that are therefore effectively immobilized [10]. Bakulin [11] showed, using two-dimensional IR spectroscopy combined with molecular dynamics simulations, that water molecules in the hydrophobic solvation shell do not exhibit an increased tetrahedral ordering compared with the bulk. These water molecules are not ice-like frozen since they have librational degrees of freedom and can even rotate. However, the rate of the reorientation is dramatically decreased near the hydrophobic groups due to a substantial decrease in the water translational mobility. Hence, the hydrogen-bond network around hydrophobic groups is not more rigid, or ice-like, compared with the bulk but that the hydrogen bond dynamics is different. This slowdown has further been investigated through a combination of molecular dynamics simulations with mid-infrared pump-probe spectroscopy [12]. The authors show that H-bond breaks through two competing mechanisms: The first is switching through an associative partner exchange and the second through a dissociative breaking, characterized by an unbound state. The first mechanism is shown to occur less often near a hydrophobic surface, thus creating OH groups that do not switch, causing a distinct slower timescale in the reorientational dynamics.

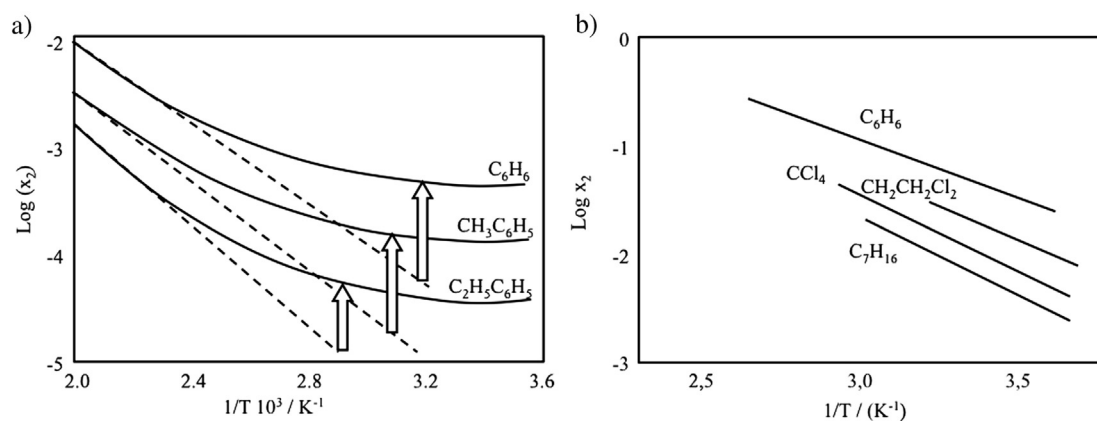
As will be discussed further below there are two issues that are fundamental for the hydrophobicity or the hydrophobic effect. The first is that the hydrophobic effect is proportional to the surface area of the hydrophobic moiety (see Fig 5c) and the second is that the entropy due to this “structuring” rapidly decreases with temperature (see Fig. 2a). We will here for the sake of simplicity use the terminology “water structuring” for the state of water with low entropy in the vicinity of a hydrophobic molecule, even though this is not defined here on a molecular level.

### 4. Ordering of the water leads to an enthalpy–entropy compensation

Patterson and Barbe [13] showed that a change in entropy due to any ordering, or structuring, process must be accompanied by a change in enthalpy. This is easily realized considering that a change in structuring should also be reflected by a change in the heat capacity. The relation between these three entities is:

$$-T \frac{d\Delta_0^{ws}}{dT} = \Delta_0^w C_p^{ws} = \frac{d\Delta_0^w H^{ws}}{dT} \quad (3)$$

Here the index ws stands for water structuring. If we make the plausible assumption that the structuring of water around a hydrophobic moiety decreases rapidly with temperature, and eventually vanishes



**Fig. 1.** (a) The solubility of three hydrocarbons, expressed as  $\log x_2$ , in water as a function of  $1/T$ , illustrating that only at high temperatures we obtain the expected straight line according to Eq. (1). At lower temperatures the structuring of water increases the solubility i.e. going from the dashed lines to the full drawn lines (redrawn from Ref. [3]). (b) Solubility of iodine in some solvents, expressed as  $\log x_2$ , versus the inverse of the temperature showing the expected straight line (redrawn from Ref. [6]).

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