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Thermodynamics of the hydrophobic effect in surfactant solutions—micellization and adsorption

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Abstract: The thermodynamics of surfactant micellization and adsorption onto hydrophobic surfaces are examined. The ideal and the Flory-Huggins approximations for the combinatorial entropy of transfer are contrasted. Two main contributions for the Gibbs free energy of transfer from the aqueous solution to the micelle or the surface are considered. The first is the collapse of the water cavity left behind when the solute is transferred and the second is the destruction of the water structuring around the solute. It is the balance between these two contributions which causes the minimum in critical micelle concentration and the maximum in adsorption of ionic surfactants with temperature. Separation of these two contributions is achieved using a two-state model recently reported for water molecules around non-polar solutes.

The hydrophobic effect is the terminology commonly used to refer to processes where non-polar molecules, or non-polar parts of molecules, are spontaneously removed from water. Micellization of surfactants is an example of the hydrophobic effect. In the micellization there are two opposing forces at work. The first is the hydrophobicity of the hydrocarbon tail, favouring the formation of micelles and the second is the repulsion between the surfactant head groups. The mere fact that micelles are formed from ionic surfactants is an indication of the fact that the hydrophobic driving force is large enough to overcome the electrostatic repulsion arising from the surfactant head groups.

The hydrophobic effect also plays an important role in the process of adsorption of surfactants on solid surfaces from aqueous solution. Its thermodynamic analysis reveals that there are two driving forces (1): The first is the difference in interaction of the surfactant with the surface as compared to the interaction between the surface and water. The second contribution stems from the interaction of the surfactant with water. This is composed of the interactions of water with the surfactant head group and the hydrocarbon tail, where the latter is the cause of the hydrophobic effect. This latter driving force is therefore similar to that of micellization. Table I displays the micellization and adsorption Gibbs free energy of two surfactants for their adsorption on a polystyrene latex (2). The table reveals that for both surfactants their Gibbs free energies are very similar in size. The difference between them are attributed to the

interaction with the surface as indicated in the last column in the table. Thus, the hydrophobic contribution clearly dominates the Gibbs free energy of adsorption of surfactants on a hydrophobic surface.

TABLE 1. The contributions (divided by RT), calculated according to eqs (1) and (2), for the adsorption of two surfactants on polystyrene latex at 25°C. From ref (2).

Gibbs free energy of:	adsorption	micellization	interaction with surface
NP-EO10	15.4	13.6	1.8
SDS	11.3	9.1	2.2

One of the most important manifestations of the hydrophobic effect is the solubility limit of non-polar molecules in water. Here only two macroscopic phases are present and hence thermodynamic analysis is straightforward. Hence most work in the literature on the hydrophobic effect has dealt with solubility of hydrocarbons in water (3). The removal of a hydrocarbon molecule from water at room temperature is always associated with a large increase in entropy, an enthalpy of around zero and hence a large and negative Gibbs free energy. The increase in entropy is interpreted in terms of a release of structured water molecules in the vicinity of the surface of the hydrocarbon molecule. Thermodynamic analysis has shown that destructuring is accompanied by a strongly negative and temperature dependent heat capacity, reflected in a large temperature dependent positive entropy and enthalpy which compensate to give a small positive Gibbs free energy (4). Hence the structuring of water alone cannot be the cause for the hydrophobic effect, i.e. the small solubility of hydrocarbons in water. Besides the water structuring a second contribution is in effect and is due to the large energy released when the cavity holding the hydrocarbon molecule collapses. This contribution is assumed to be temperature independent. Thus the origin of the hydrophobic effect is to be found in the large energy required to form a cavity in the water for the hydrocarbon solute, i.e. water has a very high cohesion energy density. The origin of this high cohesion is of course a high hydrogen bonding density, which is a consequence of the small size of water molecules compared to ordinary organic molecules. The temperature dependence of the entropy and enthalpy of transfer is entirely determined by the water structuring since the contribution arising from the cavity formation is assumed to be temperature independent. It is the balance between these two contributions that is the cause of the minimum in cmc, maximum in adsorption with respect to temperature for ionic surfactant systems and minimum in solubility for non-polar molecules in water.

The first problem arising in assessing the hydrophobic effect is how to treat the experimental data in order to obtain relevant thermodynamic quantities. One problem is how to separate the structural entropy from the purely mixing or combinatorial entropy. The latter can be approximated by for example an ideal mixing entropy or by using the Flory-Huggins theory. The applicability of using Flory-Huggins theory for solutions of hydrocarbons in water is confirmed by the fact that the Gibbs free energy for the aqueous solubility of families of chemicals (alkanes, alkyl benzenes etc.) fall on parallel curves when (i) the Flory-Huggins combinatorics is used and (ii) when the Gibbs free energy is divided by the molecular surface area of the solute in the family (5). The second challenge is to separate the two contributions, water structuring and the cavity contribution, to the Gibbs free energy of the process. In what follows, we will discuss two possible approximations to the combinatorial entropy and the problem of evaluating the two contributions to the Gibbs free energy.

Analysis of the hydrophobic effect using an approximation for the combinatorial entropy.

The ideal entropy of mixing i.e. $\Delta S = -R [n_1 \ln x_1 + n_2 \ln x_2]$, where n is the number of moles and x is the mole fraction, has been used widely. Using the expression for the combinatorial entropy of mixing and ignoring the counterions of the ionic surfactants, we have the following expressions for the Gibbs free energy of micellization, $\Delta_w^{\text{micelle}} G$ (using the phase separation model), adsorption, $\Delta_w^{\text{ads}} G$ (using the Langmuir model) and transfer of a hydrocarbon from aqueous phase into pure hydrocarbon phase, $\Delta_w^{\text{hc}} G$ as obtained from the limit solubility in water:

$$\Delta_w^{\text{micelle}} G = RT \ln x_{\text{cmc}} , \quad (1)$$

$$\Delta_w^{\text{surface}} G = \Delta_w^{\text{ads}} G = -RT \ln K , \quad (2)$$

$$\Delta_w^{\text{hc}} G = RT \ln x , \quad (3)$$

where x is the mole fraction of the solute and K is the adsorption equilibrium constant obtained from the Langmuir equation, $\Gamma/\Gamma_{\text{max}} = Kx/(1+Kx)$. The enthalpy and entropy are obtained from the temperature dependence of eqs (1) - (3) using ordinary thermodynamics. These entropy and enthalpy functions are shown in Figure 1 for the following systems (a) micellization of dodecyl pyridinium bromide (DPBr) (6), (b) adsorption of dodecyl pyridinium chloride (DPC) onto kaolin (7) and (c) the transfer of toluene from water into its own liquid as obtained from solubility of toluene in water (8). All three systems show the same general behaviour, i.e. large and positive entropy which is decreasing with temperature, an enthalpy that is decreasing with temperature and is zero at around room temperature and finally a Gibbs free energy that is negative and increasing in magnitude with temperature.

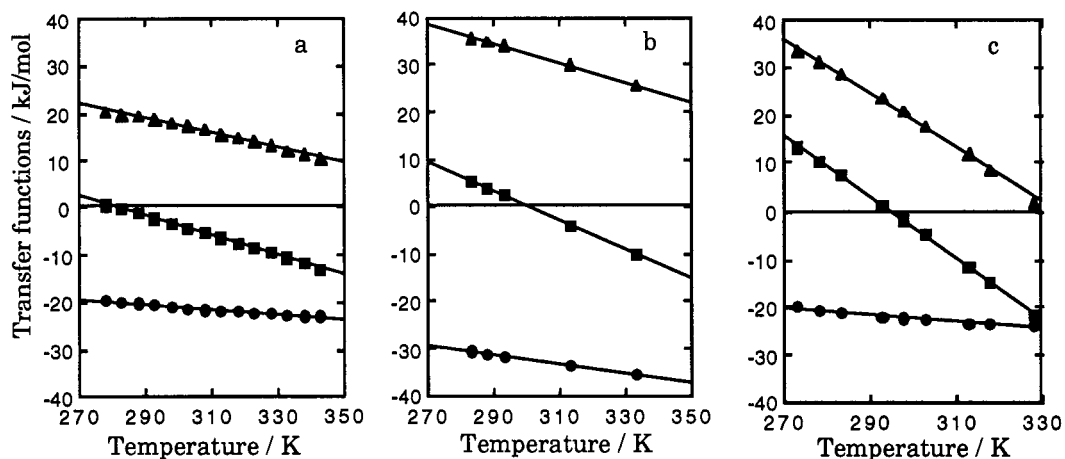


Figure 1: The Gibbs free energy(●), enthalpy (■) and entropy (▲) (times temperature) for the transfer from water to (a) micelles for DPBr, (b) kaolinite surface for DPC and (c) the pure liquid for toluene.

An estimation of the split-up between the water structure and cavity formation contribution can be found by making use of the fact that the water structuring terms become negligible at high temperature and that the cavity terms are assumed to be temperature independent. Thus, plotting ΔH versus ΔG and extrapolating to the $\Delta H = \Delta G$ line, i.e. where the structuring contributions to ΔG , ΔH and ΔS are effectively zero

gives us the $\Delta H_c = \Delta G_c$ originating from the cavity contribution (9). The contributions to the water structuring and cavity formation thus obtained are shown in Figure 2 a-c corresponding to the systems in Figure 1. In all systems the contribution originating from the cavity formation is large and negative and the entropy and enthalpy originating from the water structuring are large and positive and both decreasing with temperature. The Gibbs free energy originating from the water structuring is small and positive and decreasing with temperature. Figure 2 clearly shows that the cavity formation contribution is dominating in size and is the only negative contribution to the transfer from water to a hydrocarbon environment. Thus the contribution originating from the cavity formation is the only cause for the hydrophobic effect. We also conclude that the water structuring contribution is positive and hence counteracts the formation of micelles, the adsorption of surfactants and increases the solubility of hydrocarbons in water. We will in passing note that the above analysis is not directly applicable to aqueous solutions of non-ionic surfactants containing polyethylene oxide chains, since the temperature dependence of the polyethylene oxide-water interaction is dominating the behaviour of these surfactants (10).

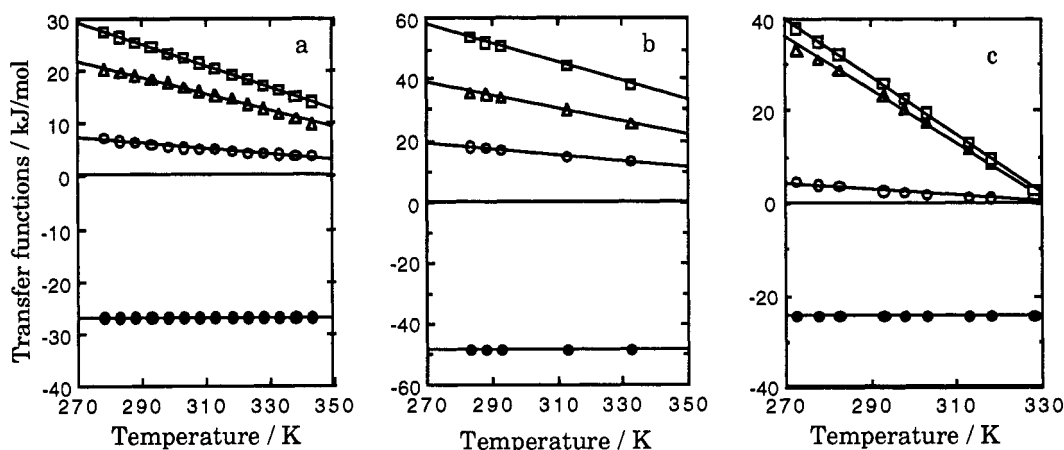


Figure 2: The Gibbs free energy and enthalpy originating from the cavity formation (●) and the Gibbs free energy (○), enthalpy (□) and entropy (times temperature) (△) originating from the water structuring for the transfer from water to (a) micelles for DPBr, (b) kaolinite surface for DPC and (c) the pure liquid for toluene.

Analysis of the hydrophobic effect using the Flory-Huggins expression for the combinatorial entropy.

A step further in the understanding of the hydrophobic effect is achieved if a better approximation for the combinatorial entropy is used than the ideal mixing expression. The Flory-Huggins theory offers an expression for the combinatorial entropy taking into account the fact that the molecules being mixed need not be of the same size. The Gibbs free energy, obtained from subtracting the Flory-Huggins combinatorial contribution from the experimentally obtained Gibbs free energy of transfer, is thus purely interactional in nature. Figure 3 shows a master plot obtained from the transfer of alkyl benzenes from water into its pure liquid as taken from ref. (5). The plot is obtained by first subtracting the Flory-Huggins combinatorial contribution from the experimental Gibbs free energy of transfer and then dividing by the molecular surface area of the alkyl benzene solute. The mere fact that a reduced master curve is obtained is an indication of (i) that the Flory-Huggins expression for the combinatorial contribution is a good approximation and (ii) the resulting interactional Gibbs free energy is proportional to the surface that the solute exposes to the water. These facts

have encouraged us to model the structuring of the water molecules in the vicinity of a non-polar molecule, using a simple two state model (relaxed or structured and unrelaxed or non-structured) (5). The model was used to understand the solubility minimum appearing in aqueous solutions of non-polar molecules. The expression of the Gibbs free energy for the relaxation, or structuring, of water in the vicinity of a non-polar molecule is according to the model (5),

$$\Delta G_s = NRT \ln(A/B) + N\Delta h [1-(1/B)] \quad (4)$$

where $A = 1 + \exp[\Delta h (\beta - \beta_m)]$, $B = 1 + \exp[\Delta h \beta_m]$, $\beta = 1/RT$ and $\beta_m = 1/RT_m$. N is the number of water molecules affected by the presence of the non-polar solute molecule, Δh is the energy difference between the two states and T_m is the temperature at which the populations of the two states are equal. Fitting to the transfer of alkyl benzenes from water to the pure liquid gives $\Delta h = 5320$ J/mol and $T_m = 220$ K. Note that these values only depend on the characteristics of water around a solute and hence they are the same for any non-polar solute; solute molecules differ only in that they have different molecular surface area being exposed to the aqueous solution, i.e. only the factor N in eq. (4) determines the size of the Gibbs free energy of transfer. In the 0 - 100°C range the model predicts an approximate linear dependence between the enthalpy and Gibbs free energy of structuring, supporting the procedure where experimental values of ΔH are plotted against ΔG in order to obtain a value for ΔG_c , i.e. the contribution originating from the cavity formation.

The model can also be used on the data from surfactant micellization. Here, we first need to correct the Gibbs free energy of micellization for the molecular size difference, i.e. we need to use the Flory-Huggins expression. Thus the Gibbs free energy of micellization is written as,

$$\Delta_w^{\text{micelle}} G_{\text{FH}} = RT \ln x_{\text{cmc}} + RT [\ln(V_s/V_w) + 1 - V_s/V_w] \quad (5)$$

where V_s and V_w are the molar volumes of the surfactant and water, respectively. The last term in eq (5) arises from the Flory-Huggins expression at infinite dilution of the surfactant. In order to get a complete description of the system we should also take into account the counterion binding to the system. This binding, however, has been shown to be relatively temperature independent (11) and it will therefore be ignored in this work. Thus, calculating the water structuring contribution to the Gibbs free energy of micellization and using eq (5) we obtain the thermodynamic contributions as depicted in Figure 4. Here we have assumed that ca 70% of the hydrocarbon tail is affected by the structured water, the remainder 30% is then under influence of the charge of the head group and should thus not be accounted for. This was assumed in order to obtain a temperature independent contribution originating from the cavity formation. The number of 70% is supported by experimental results (12). The figure reveals that the temperature independent contribution originating from the cavity formation and other factors, such as counter ion binding, is very large and negative, as expected. We also see that the Flory-Huggins correction term is of the same sign and same order of magnitude as the Gibbs free energy of transfer as calculated on a molar basis (eq (1)). This has also previously been found to be the case for the transfer of alkyl benzenes between an organic phase and water (5,13). Figure 5 depicts the resulting thermodynamic functions showing the same general picture as in Figure 2a, except for the absolute values of the transfer functions. Thus the simple two-state model can be used on most likely any physical phenomenon that is a reflection of the hydrophobic effect, provided that the entropy of the process is calculated properly.

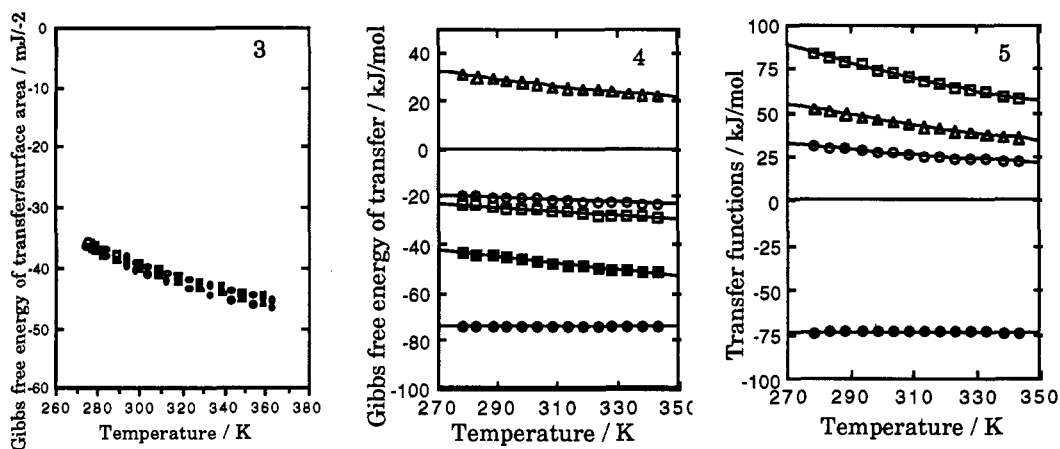


Figure 3: The non-combinatorial Gibbs free energy of transfer (expressed per unit surface area of the solute) of four alkyl benzenes (benzene to propyl benzene) from water to the pure liquid.

Figure 4: The different contributions to the Gibbs free energy of transfer of DPBr from water to micelle. (○) ΔG_X , (□) Flory-Huggins correction term, (■) ΔG_{FH} which is the sum of the two terms above, (Δ) ΔG_S from model calculation of the structuring of water in the vicinity of the hydrophobe, (●) ΔG_c contribution originating from the cavity formation in water.

Figure 5: The Gibbs free energy and enthalpy originating from the cavity formation (●) and the Gibbs free energy (○), enthalpy (□) and entropy (times temperature) (Δ) originating from the water structuring for the transfer from water to micelles for DPBr, as calculated using eqs (4) and (5), c.f. Fig 2a.

We conclude that the hydrophobic effect is a reflection of the solution properties of the non-polar moieties of the molecules. Thus, the temperature dependence of surfactant adsorption, or micellization, is akin to that of ordinary hydrocarbons in water. The minimum (cmc and solubility) and maximum (adsorption) with temperature is a consequence of a balance between the effects of water structuring and the formation of a cavity in the water in order to accommodate the solute.

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