Thermodynamics of adsorption of surfactants at solid–liquid interface

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ABSTRACT

Adsorption of surfactants at interfaces is determined by a number of forces involving electrostatic attraction, covalent bonding, hydrogen bonding, hydrophobic bonding and solvation and desolvation of various species. The extent and type of forces involved vary depending on the adsorbate and the adsorbent and also the composition and other characteristics of the solvent and dissolved components in it. The influence of such forces on the adsorption behavior is reviewed here from a thermodynamics point of view. Experimental results from micro calorimetric study of adsorbed layers of different surfactant systems at solid-liquid interface are also presented. It was found that the entropy effect was more pronounced for the adsorption of anionic-nonionic surfactant mixtures than for the anionic surfactant alone. High surface activity of the nonionics and its hydrophobic interaction with adsorbed anionic surfactants are considered to be the main mechanisms for the marked entropy effect in mixture adsorption. Calorimetric investigations of the effect of the position of sulfonate and methyl groups on the aromatic ring of isomerically pure alkylxylene sulfonates on their adsorption at solid/liquid interface showed the position of the sulfonate with respect to the alkyl chain to be more critical than that of the methyl groups in determining the adsorption behavior.

INTRODUCTION

Adsorption of surfactants on solids in contact with aqueous solutions is important for controlling a variety of interfacial processes (1,2,3)such as detergency, cleansing action of personal care products, flocculation and dispersion, enhanced oil recovery, mineral flotation and other solid liquid separations. An understanding of the mechanisms of adsorption is essential for improving the efficiency of such processes. Several factors, such as electrostatic attraction, covalent bonding, hydrogen bonding or non polar interaction between the adsorbate and interfacial species, lateral interactions between the adsorbed species, desolvation effects, interactions between dissolved species and surfactants and surface precipitation have been considered to contribute to the adsorption process(4). In real systems adsorption is therefore a complex process since the nature and extent of adsorption is dependent on properties of solids, solution ionic strength, surfactant composition, nature of solvent species, pH and temperature of the system as well as dissolved mineral and biological species. In this paper free energy of adsorption is considered in terms of contributions from such factors. The adsorption mechanisms are examined using adsorption and microcalorimetric results of different surfactant systems at solid-liquid interfaces.

THEORY

Adsorption is essentially selective partitioning of the adsorbate into the interfacial region. It results from the more energetically favorable interactions between the adsorbate species and the chemical species in the interfacial region than between the former and those in the bulk solution. If ΔG°_{bi} is the free energy term corresponding to transfer of the adsorbent species from the bulk(b) to the interfacial region (i), concentration in the interfacial region, C_i, can be expressed as

$$c_i = c_b \exp\frac{-\Delta G^{\circ}_{bi}}{RT} \tag{1}$$

whereas C_b is the bulk concentration in mol dm^{-3}, R is the gas constant and T is the absolute temperature. To express the adsorption in terms of mol/cm^2 the right hand side of equation is multiplied by the thickness of the adsorbed layer, τ.

$$\Gamma_i \quad \tau \, c_b \, \exp\frac{-\Delta G_{ads}}{RT} \tag{2}$$

$\Delta G°_{ads}$, is equal to $\Delta G°_{bi}$, and can be the result of electrostatic attraction, covalent bonding, hydrogen bonding or non-polar bonding between the adsorbate and adsorbent species, lateral interaction between the adsorbed species etc. In addition, desolvation or solvation of any species due to the adsorption process can also contribute towards the net free energy of adsorption. Another factor that is usually ignored arises from the variations in such physical properties as structure and dielectric constant of the medium from the bulk to the interfacial region. Thus $\Delta G°_{ads}$, the driving force for adsorption will be sum of a number of contributing forces mentioned above and can be written as:

$$\Delta G°_{ads} = \Delta G°_{elec} + \Delta G°_{chem} + \Delta G°_{c-c} + \Delta G°_{c-s} + \Delta G°_{H} + \Delta G°_{H_2O} \tag{3}$$

$\Delta G°_{elec}$ is the electrostatic interaction term and is equal to $zF\psi_\delta$ where z is the valency of the adsorbate species, F the Faraday constant and ψ_δ the potential *in the* δ plane (δ is the thickness of the compact part of the double layer), $\Delta G°_{chem}$ is the chemical term due to covalent bonding, $\Delta G°_{cc}$ is the lateral interaction term owing to the cohesive chain-chain interaction among adsorbed long chain surfactant species, $\Delta G°_{c-s}$ is similar interaction between the hydrocarbon chains and hydrophobic sites on the solid, $\Delta G°_{H}$ is the hydrogen bonding term and $\Delta G°_{H_2O}$ is the solvation or desolvation term owing to hydration of the adsorbate species or any species displaced from the interface due to adsorption.

Adsorption isotherms for certain surfactants such as alkylsulfonate on alumina have been found to undergo a marked increase in slope at a particular surfactant concentration(5). This has been attributed to the formation of two-dimensional lateral aggregates called solloids or hemimicelles between the adsorbed long chain surfactant species above a certain adsorption density. Such an association in the interfacial region is analogous to the micelle formation in bulk solution and results from favorable energetics of partial removal of the alkyl chains from the aqueous environment. Marked changes in a number of other interfacial properties such as flotation, suspension settling rate and contact angle have provided supporting evidence for such lateral associative interactions among adsorbed surfactant species.

The energy gained due to this aggregation can be estimated in a number of ways. For example, $\Delta G°_{ads}$ can be divided into two terms in equation (2), one corresponding to that of electrostatic forces and the other corresponding to that of the hemi-micellization:
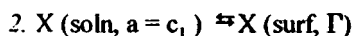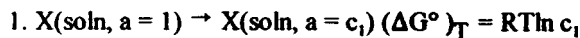
$$\Gamma_i = \tau \, c_b \, \exp\frac{-\Delta G°_{elec} - \Delta G°_{hm}}{RT} \tag{4}$$

Concentrations corresponding to hemimicelle formation (C_{HMC}) can be obtained from flotation and electrokinetic experiments. Substitution of C_{HMC} for C_b, and $n\phi_h$ for $\Delta G°_{hm}$, where n is the number of CH$_2$ and CH$_3$ groups in the chain and ϕ_h the average free energy of transfer of 1 mol of CH$_2$ groups from the aqueous environment into the hemi-micelles yields *(see* Fig. 1).

$$\ln C_{HMC} = \frac{n\phi_h}{RT} + \Delta G°_{elec} \ln\frac{\Gamma_i}{\tau} \tag{5}$$

Heat and standard entropy changes associated with the adsorption process can be calculated by considering the adsorption of the long-chain ions, X; as follows(6).
Consider the process of transfer of solute from solution to the surface to take place in two steps:

1. $X(soln, a = 1) \rightarrow X(soln, a = c_i)$ $(\Delta G^\circ)_T = RT \ln c_i$

2. $X(soln, a = c_i) \rightleftharpoons X(surf, \Gamma)$

$$\frac{\Delta G = 0}{}$$

$X(soln, a = 1) \rightarrow X(surf, \Gamma)$

$(\Delta G^\circ_{x_s})_T = RT_i \ln c_i$ (6)

c_i is the concentration of the sodium dodecylsulfonate in solution in mole per liter corresponding to an adsorption density of Γ mole per sq cm at temperature T, and $(\Delta G^\circ_{x_s})_T$ is the relative partial molar free energy of the absorbed ions at this temperature. Here we have considered a solute standard state for X in the solution such that the activity coefficient

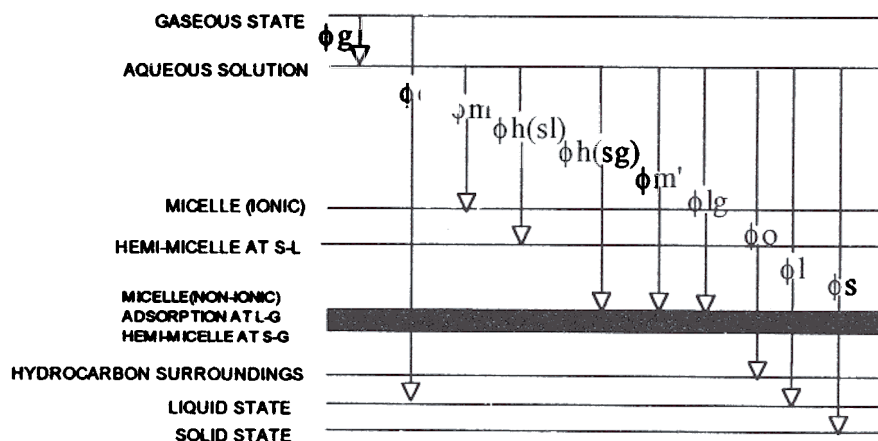$\gamma_{x_i} \rightarrow 1$ as $c \rightarrow 0$.

Fig 1. Schematic diagram for free energy of transfer of CH_2 groups from aqueous solutions to various environments [7].

The heat and entropy of adsorption calculated in the manner outlined above for dodecyl sulfonate adsorbed on alumina particles show marked changes at particular concentrations and are in general agreement with the postulate of interaction of surfactant ions to form two-dimensional solloidal aggregates. Most interestingly, the association was found to produce a net increase in the entropy of the system, suggesting a decrease, upon aggregation, in the ordering of the water molecules that were originally surrounded isolated surfactant chains (see Fig. 2).

EXPERIMENTAL RESULTS

The broad understanding of the free energy of adsorption is further used to analyze the thermodynamic data as revealed from micro calorimetry studies. Calorimetry has been used earlier to study the adsorption of surfactants at the solid/liquid interface (8, 9, 10, 11,12) and is an useful tool to understand the interactions of the surfactant with the solid and also cooperative interactions among surfactants on the solid surface. Two different surfactant systems were investigated. In one case, mechanisms of adsorption of an anionic surfactant and a nonionic surfactant, and their mixtures on alumina were studied. In another study, the effect of position of the sulfonate and also of the position of the methyl groups on the benzene ring on the adsorption of isomerically pure alkylxylenesulfonates on alumina was examined.
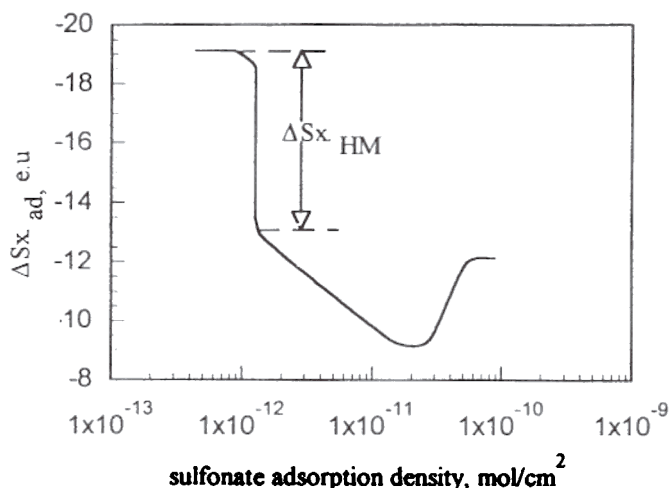
Fig. 2. Partial molar entropy of adsorption of sulfonate as a function of its adsorption density [6]

A. anionic surfactant sodium octylbenzenesulfonate ($C_8\phi S$) and dodecyloxyheptaethoxyethylalcohol ($C_{12}EO_8$) system

The adsorption isotherm and the heat of adsorption curve for 1:1 $C_8\phi S/C_{12}EO_8$ mixtures system are shown in Fig. 3. The shape of the heat curve mirrors that for adsorption, except for the absence of a maximum.
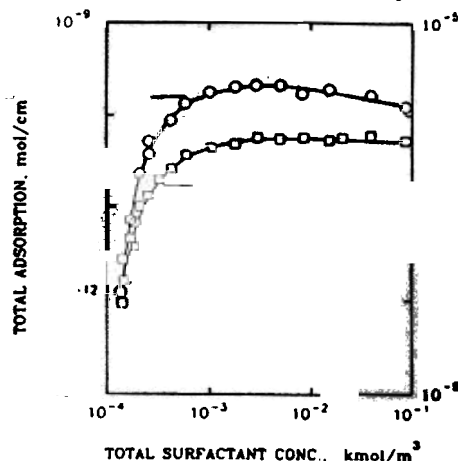

TOTAL SURFACTANT CONC., $kmol/m^3$

Fig. 3. Adsorption isotherms and heat of adsorption of 1:1 $C_8\phi S/C_{12}EO_8$ mixtures on alumina [11].

The adsorption enthalpy however was surprisingly constant as a function of adsorption density (Fig. 4). As compared to the adsorption of pure sulfonate, adsorption of surfactant mixtures on alumina is less exothermic although adsorption levels are significantly higher before the onset of plateau. These results clearly suggest a stronger entropy effect for mixture adsorption than for single sulfonate adsorption.

B. alkylxylenesulfonates system

In order to better understand the mechanisms of adsorption, the adsorption enthalpies of the three surfactants were measured using calorimetry. The differential enthalpy of adsorption of the three surfactants as a function of adsorption density is shown in Fig. 5.

The enthalpy of adsorption of the surfactants is exothermic at all adsorption densities. The enthalpy is constant and highly exothermic in a small range of low adsorption density. This can be interpreted as being due to the direct interaction between the ionic heads of the surfactant and the individual ionic sites of the surface. With increase in the adsorption density, the enthalpy decreases and finally attains a constant value. The adsorption

density at which the enthalpy starts to decrease corresponds to the onset of formation of solloids (hemimicelles) as inferred from the break in the adsorption isotherm; i.e., there is simultaneous interaction between the individual molecules and surface and between hydrophobic parts of the surfactant. Finally, when the adsorption proceeds purely due to hydrophobic interaction between the hydrocarbon tails, the enthalpy attains a constant value of about -4 kcal/mol, which is of the same order of magnitude as the enthalpy of micellization of the surfactants (~ - 1 kcal/ mol). This indicates that like the formation of micelles, the formation of solloids is also entropy driven. The error in the enthalpy at low adsorption densities (below 10^{-12} mol/ cm^2) is 14% and at high adsorption densities 3%.

The enthalpy of adsorption of the para-xylenesulfonates is higher than that of meta-xylenesulfonate at low adsorption densities suggesting greater attraction to the solid surface which results in their larger adsorption. This greater attraction is attributed to a combination of electrostatic and hydrophobic attraction of the surfactants to the interfacial region. These results confirmed the earlier finding (14) that adsorption of the two para-xylenesulfonates is higher than that of the metaxylenesulfonate in the premicellar region but is the same in the plateau region. The lower adsorption of the meta-xylenesulfonate in the hemimicellar region was attributed to

1. lower hydrophobicity of the alkyl chain due to higher inductive effect from the sulfonate, since it is closer to the alkyl chain in the case of meta-xylenesulfonate (15) , and

2. higher steric constraints arising from the position of the sulfonate and methyl groups to the packing of the surfactant molecules in solloids. Also it can be seen that the two para-xylenesulfonates have similar enthalpy of adsorption. This suggests that the position of the methyl groups does not play as important a role as the position of the sulfonate. Once the solloids form, the adsorption enthalpies of the surfactants are similar.
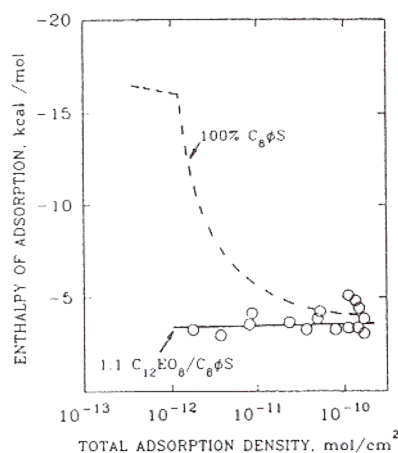

Fig. 4. Enthalpy of adsorption of 1:1 $C_8\phi S/C_{12}EO_8$ mixtures on alumina, 50° C, 0.03 M NaCl, pH 8.2 [13].
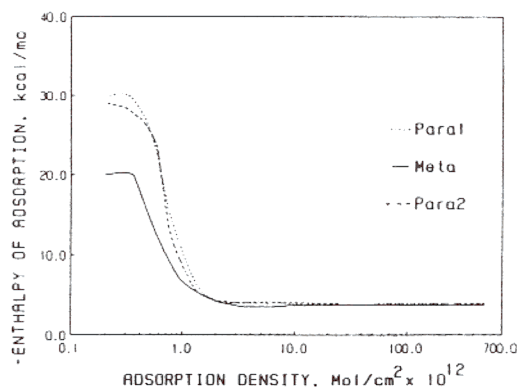

Fig. 5 Differential enthalpy of adsorption of 4C11 2,4-meta xylenesulfonate(Meta), 4C11 3,5-para-xylenesulfonate (Para 1), and 4C11 2,5-para-xylenesulfonate (Para 2) on alumina [14].

CONCLUDING REMARKS

It can be seen from the above discussion that adsorption is determined in addition to the interactions of the surfactant species and its complexes with the solid also by the nature of interaction forces between solvent species and surfactant species as well as the solid surface. Electrostatic interactions between surfactant molecules and the solid surface and the lateral chain-chain interactions between the adsorbed surfactant molecule play an important role in determining the adsorption behavior. As seen from the two experimental studies of surfactant system at solid/liquid interface, at low surfactant concentrations enthalpy is the main driving force for adsorption while the adsorption is entropy driven at higher surfactant concentrations. The entropic effects were more pronounced in the case of anionic-nonionic surfactant mixtures compared to the nonionic system alone. The nonionic surfactant, dodecyloxyheptaethoxyethylalcohol ($C_{12}EO_8$), is highly hydrophobic and its adsorption is strongly induced by the co-adsorbed anionic sodium octylbenzenesulfonate species ($C_8\phi S$) through hydrophobic chain-chain interactions at the alumina-water interface. The adsorbed $C_8\phi S$ molecules can be considered to serve as hydrophobic nucleation sites for the abstraction of the nonionic $C_{12}EO_8$ into the adsorbed layer. This adsorption process is strongly entropy driven since such a process is accompanied by the release of many water molecules from around each nonionic surfactant molecule.

Calorimetric data from alkylxylenesulfonates isomers showed that the position of the sulfonate and the methyl groups on the aromatic ring of alkylxylenesulfonates has a major effect on the energetics of their adsorption and the nature of their aggregation at the interface leading to a marked effect on the extent of adsorption. Systematic work on adsorption as well as desorption using absorbents and adsorbates of different structural and compositional characteristics will be required to develop a full understanding of the overall adsorption process.

REFERENCES

1.   K. L. Mittal (ed.), *Surface and Colloid Science in Computer Technology*, Plenum Press, New York, 1987.
2.   M. J. Rosen, *Surfactants in Emerging Technologies*, Marcel Dekker, New York, 1987.
3.   P. Somasundaran, *Energetics of Adsorption at interfaces*, in Thermodynamics and Kinetics of Metallurgical Processes, M. Mohan Rao *et. Al* (Eds.), The Indian Institute of Metals, Calcutta, 1985.
4.   E.D.Goddard and P. Somasundaran, *Croatia Chemica Acta*, 48,4,451, 1976.
5.   P. Somasundaran and D. W. Fuerstenau, J. *Phys. Chem.* 70, 90,1966.
6.   Somasundaran P and Fuerstenau D W *Trans. AIME 252* 215 1972
7.   I. J. Lin and P. Somasundaran ,*J. Colloid Interface Sci.*, 37, 731 1971
8.   L. A. Noll,, *Colloids Surf* ,26, 43, 1987.
9.   G. W. Woodbury, and L. A. Noll, *Colloids Surf.*, 33, 301,1988.
10.   S. Partyka, W. Rudzinski, B. Brun, and J. H. Clint, *Langmuir*, 5, 297, 1989.
11.   E. Fu, D.E.S. thesis, Columbia University, New York, 1987.
12.   R. Denoyel, F. Rouquerol, and J. Rouquerol, *Colloids Surf.*, 37, 295 (1989).
13.   E. Fu, P. Somasundaran and Qun Xu, *American Chemical Society*, 25,366,1992
14.   A. Sivakumar, P. Somasundaran and S. Thach, *Journal of Coll. And Interf. Sci.*,159,481,1993.
15.   P. Somasundaran, R. Middleton, and K. V. Viswanathan, *Structure/Performance Relationship in Surfactants*, *ACS Symp.. Ser.* 253,(ed. M. J. Rosen), *270*, 1984.