

Theoretical description of surfactant aggregation at the solid/liquid interface – comparative study

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The comparison of two surfactant adsorption models is presented. In both models, the adsorbed phase is assumed to be a mixture of single monomers and aggregates of different shapes and sizes. These surface aggregates are assumed to behave as a 2D fluid of hard disks, i.e. only “excluded area” interactions are allowed in the adsorbed layer. The effects of surface heterogeneity on monomer adsorption are also taken into account. The main difference between the compared models lies in assuming different structures of the surface aggregates. In the first model the aggregates are assumed to be monolayered and symmetrical bilayered disks (hemimicellar and admicellar aggregates model HAM). In the second model the adsorbed surfactant molecules are assumed to form spherical and globular aggregates (SGM), similar to those in the bulk solution. The theoretical expressions for adsorption isotherms and heats of adsorption corresponding with these two models are compared with experimental data for three zwitterionic surfactants adsorbed on the silica surface. The advantages and faults of the two models are discussed.

1. INTRODUCTION

One of the characteristic features of the surfactants is their tendency to adsorb at the surface or interface. Surfactant adsorption at different interfaces is in practice used to facilitate detergency, control wetting and penetration of solutions, stabilise foams and emulsions, and collect minerals in flotation operations. To establish the optimal conditions for its application, it is important to obtain information not only on the adsorbed amount of surfactant as a function of its concentration, but also on the structure of the adsorbed layer.

Recently, significant effort has been directed towards acquiring better understanding of the adsorption nature of different surfactant molecules at solid surfaces. Using the AFM technique equilibrium surface aggregates of cationic [1, 2], anionic [3] and non-ionic [4] surfactants have been investigated and various equilibrium structures have been observed for the same surfactant on different substrates and for different surfactants on the same substrate. So far three distinct surface aggregate geometries have been observed depending upon the type of surfactant, the solution conditions and the surface properties. These are the sphere, the cylinder and the double flat sheet at the hydrophilic surfaces, and the corresponding half-structures: the hemisphere, the hemicylinder and the single flat sheet at hydrophobic ones.

Many theoretical models were proposed to describe adsorption of surfactants at the solid/liquid interface. The most sophisticated are those which take into account the formation of surface aggregates. Unfortunately, most of them assume the fixed structure of the adsorbed layer and do not go beyond the interpretation of adsorption isotherms. An exception is the model proposed by our group, which allows evolution of the adsorbed phase structure with the increasing adsorbed amount [5-8]. In our model we assumed that the adsorbed phase is a mixture of surfactant monomers and aggregates of various shapes and sizes. We considered two types of aggregate structure. In our earlier papers the surface aggregates were seen as monolayered and bilayered disk-like structures (the model of hemimicellar and admicellar aggregates – HAM). Recently, following the experimental findings, we modified our model by assuming that the surface aggregates have similar shapes to those formed in the bulk solution (the model of spherical and globular aggregates – SGM). We have used different experimental data such as isotherms, heats of adsorption, and electrophoretic mobilities to verify our theories. In this paper we present the comparison between our both aggregation models by applying them to the description of the same adsorption systems –the adsorption isotherms and the heats of adsorption of three zwitterionic surfactants adsorbed at the hydrophilic silica/solution interface.

2. THEORY

As it was mentioned before, in both versions of our model the surface layer is assumed to be a mixture of single dispersed surfactant molecules and aggregates of various sizes and shapes which are in the equilibrium with the surfactant monomers and micelles in the bulk phase.

In the case of HAM (hemimicelles and admicelles model) of all possible structures that aggregates may have, the most probable is the one characterised by the highest cohesive force. In the other model (SGM) for a given aggregation number the shape of aggregate (spherical or globular) is determined by the value

of the free energy of surface aggregation calculated according to the model proposed by Nagarajan et al. [9-11]. The surface species are assumed to interact via “excluded area” interactions. The schematic picture of the adsorbed phase corresponding to the two models is shown in Figure 1.

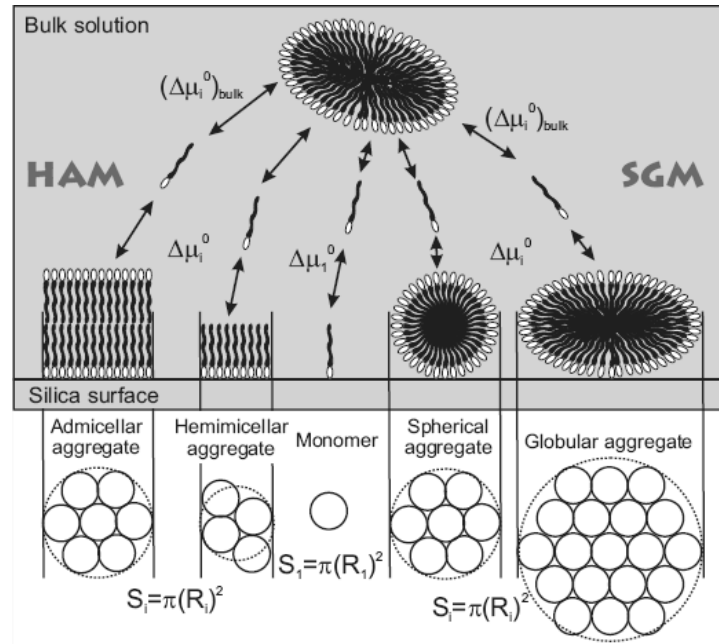


Fig. 1. Schematic representation of the structure of the surface aggregates: admicellar, hemimicellar, spherical or globular.

By applying the Scaled Particle Theory (STP) the equation system was obtained from which the individual adsorption isotherms can be calculated:

$$\Gamma_i = \frac{N_i S_i}{S} = K_i(x)^i (1 - \Theta) \exp \left\{ -r_i \frac{2A}{1 - \Theta} - s_i \left[\frac{\Gamma}{1 - \Theta} + \left(\frac{A}{1 - \Theta} \right)^2 \right] \right\}, \quad i = 1, \dots, i_{max} \quad (1)$$

In eq. (1) N_i is the number of surface aggregates of size i , S_i is the area excluded in the surface phase by a single surfactant molecule, S is the surface area of the adsorbent, x is the mole fraction of singly dispersed surfactant in the bulk solution and the other quantities in eq. (1) are defined as follows:

$$r_i = \frac{R_i}{R_1}, \quad s_i = \frac{S_i}{S_1}, \quad \Gamma = \sum_{i=1}^{i_{\max}} \Gamma_i, \quad A = \sum_{i=1}^{i_{\max}} \Gamma_i r_i, \quad \Theta = \sum_{i=1}^{i_{\max}} \Gamma_i s_i \quad (2)$$

Above, S_i is the cross section area of the i th disk and R_i is its radius. The relation between the theoretical quantities Γ_i and the experimentally measured adsorption Γ expressed usually in moles per unit of the surface area is given as follows:

$$\Gamma = \frac{1}{N_A S_1} \sum_i i \Gamma_i \quad (3)$$

where N_A is the Avogadro number.

The studies of experimental isotherms show that in the initial region of surface coverages, where mostly monomers are adsorbed, the double log-log plots of adsorption isotherms are linear, but their tangents are smaller than unity. In adsorption science such linear log-log Freundlich's plots indicate strong effects of surface heterogeneity. Taking into account the effect of surface energetic heterogeneity on monomer adsorption results into a certain modification of the equation system (1), in which the equation for monomer adsorption Γ_1 takes now the following form [5]:

$$\frac{\bar{\Gamma}_1}{1-\Theta} = \left\{ x \bar{K}_1 \exp \left\{ -r_1 \frac{2A}{1-\Theta} - s_1 \left[\frac{\Gamma}{1-\Theta} + \left(\frac{A}{1-\Theta} \right)^2 \right] \right\} \right\}^{\alpha kT} \quad (4)$$

where $0 < \alpha kT < 1$ and α is the heterogeneity parameter characterising the width of the energy distribution function. The constant \bar{K}_1 is defined as a mean value over the whole heterogeneous surface.

The constant K_i is related to the standard free energy change upon transfer of a surfactant monomer from the bulk phase to the surface aggregate of size i .

$$-kT \ln K_i = i \Delta \mu_i^0 \quad (5)$$

As the numerical calculations based on the above discussed approach have shown, the assumption, that the standard free energy changes per surfactant molecule is independent of i value, leads to a rapid two-dimensional condensation-like aggregation at a certain value of the bulk surfactant concentration. Formation of aggregates of finite dimensions occurred only when

we assumed that $\Delta\mu_i^0$ decreases with the increasing aggregate size. Because we do not know a priori how $\Delta\mu_i^0$ may decrease with i , in our publications dealing with the HAM model [5-7] we simply used the cut formal Taylor expansions to represent this unknown function. Retaining only the first two terms in this expansion leads to the following expression for K (HAM):

$$K_i = ai \exp(bi - ci^2) \quad (6)$$

where a , b and c are the compound parameters with no strict physical meaning.

Another way to represent $\Delta\mu_i^0$ is that proposed by Nagarajan et al. [9-11]. In a particular case of a weak interaction between the solid surface and the adsorbed surfactants the standard free energy of transfer of a surfactant from the bulk liquid to the surface may be treated as a perturbation of what is known in solution. $\Delta\mu_i^0$ is then considered as the sum of two terms

$$\Delta\mu_i^0 = (\Delta\mu_i^0)_{bulk} + (\Delta\mu_i^0)_{surf} \quad (7)$$

Each of these terms can be decomposed into a number of contributions on the basis of molecular considerations. According to Nagarajan et al. [9] for nonionic surfactants the following contributions should be included into the bulk term: the standard free energy change when the hydrophobic tail of the surfactant is transferred from its contact with water to the aliphatic core of an aggregate of size i , a contribution to the free energy stemming from the conformational constraints on the surfactant tails in the aggregate, a positive free energy contribution from residual contacts between the aliphatic core interface and water, a contribution coming from steric repulsion among the head groups located at the aggregate surface, a contribution accounting for the repulsive interactions between the dipoles of surfactant polar heads and a contribution due to partial dehydration of the polar head groups in the aggregate. The detailed expressions for each of the above contributions but the last one can be found in references [9-11].

For nonionic surfactants the surface contribution accounts for the free energy change associated with displacing water molecules by the surfactant head groups wherever aggregate – solid surface contact occurs. For spherical and globular surface aggregates Nagarajan et al. proposed to write this term in the following form:

$$(\Delta\mu_i^0)_{surf} = -\gamma a \quad (8)$$

where a is the surface area of aggregate per molecule being in contact with the solid surface and the displacement tension γ can be viewed as the difference between the water – solid and the aggregate head group – solid surface interfacial tensions. The latter tension represents various types of interactions involving uncharged surfaces, such as dipolar interactions, hydrogen bonding interactions, hydration interactions, etc.

In SGM the adsorption constant K takes the following form [8]:

$$K_i = \exp\left\{-i\left[(\Delta\mu_i^0)_{bulk} + (\Delta\mu_i^0)_{surf}\right]/kT\right\} \quad (9)$$

The overall differential heat of adsorption corresponding with the above models can be calculated from the expression:

$$Q_i = \sum_i Q_i \left(\frac{\partial i N_i}{\partial \mu_1^b} \right) / \sum_i \left(\frac{\partial i N_i}{\partial \mu_1^b} \right) \quad (10)$$

where Q_i ($i = 1, 2, \dots, i_{max}$) denotes the molar differential heat of adsorption of the aggregate of type i at a certain set of the surface coverages $\{\Gamma_i\}$ and can be calculated from the temperature dependence of K_i .

3. RESULTS AND DISCUSSION

The values of the model parameters found while fitting best the theoretical equations to the experimental data are collected in Table 1 (HAM) and Table 2 (SGM).

Tab. 1. The HAM best – fit parameters (only monomers and admicellar aggregates are considered).

Surfactant	S_1 (\AA^2)	a	b	c	h_1	h_2	αkT
C12N1C	30	$0.1 \cdot 10^{-6}$	23.0	0.11	0	-4.0	0.67
C12N3C	30	$0.1 \cdot 10^{-6}$	22.0	0.17	10	-2.0	0.42
C12N3S	29	$0.1 \cdot 10^{-6}$	21.8	0.07	-9	-2.9	0.71

In the above Table h_1 and h_2 are the parameters occurring in the equation for the molar differential heat of adsorption of the aggregate of type i [5].

Tab. 2. The SGM best – fit parameters.

Surfactant	a_p (Å ²)	d (Å)	d_0 (Å)	γ_{surf} (mJ/m ²)	$d\gamma_{surf}/dT$ (kJ/m ² K)	ΔQ_h (kJ/mol)	αkT
C12N1C	49	3.4	1.2	9.5	-0.110	-10.3	0.67
C12N3C	54	5.2	3.6	14.0	-0.107	-11.8	0.42
C12N3S	48	4.5	2.6	11.5	-0.080	-9.2	0.71

In Table 2 a_p represents the effective cross-section area of the polar head group, d is the distance separating the charges of the dipole, d_0 is the correction to the radius of the surface aggregate occurring in the equation for the area excluded by the aggregate “ i ”, $S_i = \pi(R_h + d - d_0)^2$ (R_h is the length of the hydrophobic chain) and ΔQ_h is the additional heat effect connected with the partial dehydration of head groups forming an aggregate (not considered in the Nagarajan et al. model). For more details please see reference [8].

The comparison of the theoretical curves with the experimental data is shown in Figures 2 and 3. The adsorption isotherms and the differential heats of adsorption of the three zwitterionic surfactants: dodecyldimethylammonioethanoate (C12N1C), dodecyldimethyl-ammoniobutanoate (C12N3C), dodecyldimethylammonio-1-propanosulfonate (C12N3S) adsorbed on the hydrophilic silica were measured in the CNRS Laboratory in Montpellier [12, 13]. One can see that the agreement of theory with experiment is good for both expressions representing K_i 's. For the HAM model the agreement is even better (smaller SQ deviation). It is probably due to the fact that the values of the HAM model parameters were found on merely best fit basis, whereas in the SGM model only four were found in this way, the others were taken from the independent surface tension measurements (a_p), or calculated from the molecular data (d).

The noticeable difference is observed in Figure 4 where the equilibrium distributions of areas occupied by the surface aggregates among their aggregation numbers are shown. The HAM and SGM approaches predict that the surface layer consists of single surfactant molecules which are in equilibrium with surface aggregates. For K_i given by eq. (6) the sharp minimum is observed on the curve $\Delta\mu_i^0(i)$ at low i values and the predicted surface aggregates are small. They are much smaller than those in the bulk phase ($i_{bulk} = 35-45$) [8]. For more sophisticated eq. (9) the minimum is wider and located at higher i values. This leads to formation of larger surface aggregates than those in the bulk phase.

It can be concluded that there is a strong effect of the shape of $\Delta\mu_i^0(i)$ function used in our calculations (Figure 5) on the predicted structure of the adsorbed phase. The more sophisticated expression for $\Delta\mu_i^0(i)$ used in the SGM

model leads to the more realistic picture of the adsorbed phase. Moreover, the SGM model contains only four adjustable parameters (γ_{surf} , d_0 , $d\gamma_{surf}/dT$, ΔQ_h) for simulating three kinds of experimental data: adsorption isotherms, heats of adsorption and heats of micellization, and all the other parameters involved in the model are the molecular constants or solvent and surface properties. In the HAM model the number of best fit parameters is larger and they are compound parameters with no strict physical meaning.

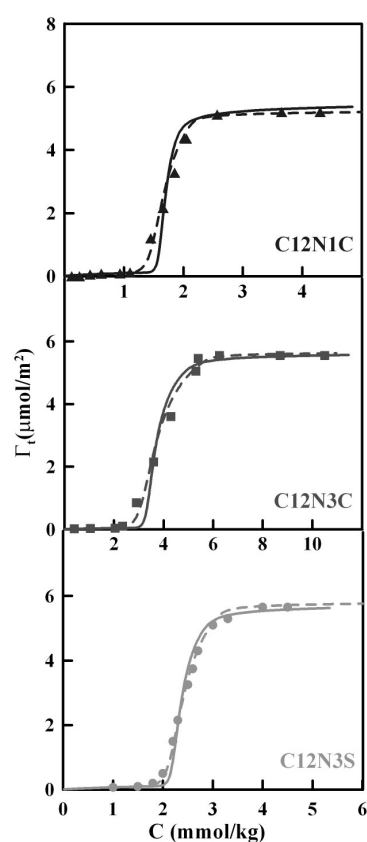


Fig. 2. The agreement of the theoretical HAM (dashed lines) and SGM (solid lines) adsorption isotherms with the experimental data (symbols) for C12N1C, C12N3C and C12N3S adsorbed on the silica at 298K.

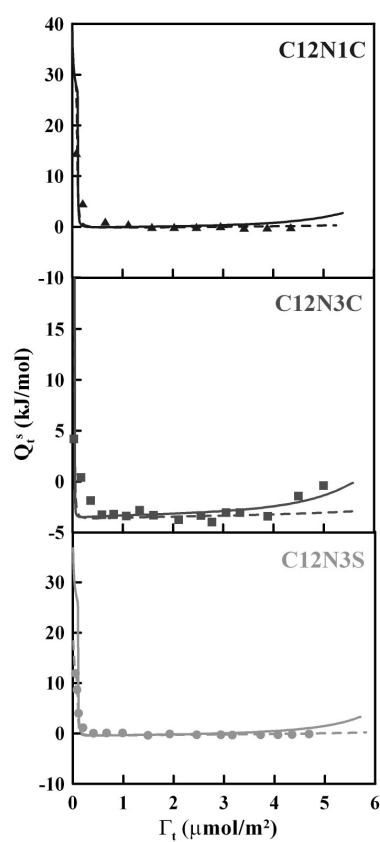


Fig. 3. The agreement of the theoretical HAM (dashed lines) and SGM (solid lines) heats of adsorption with the experimental data (symbols) for C12N1C, C12N3C and C12N3S adsorbed on the silica at 298K.

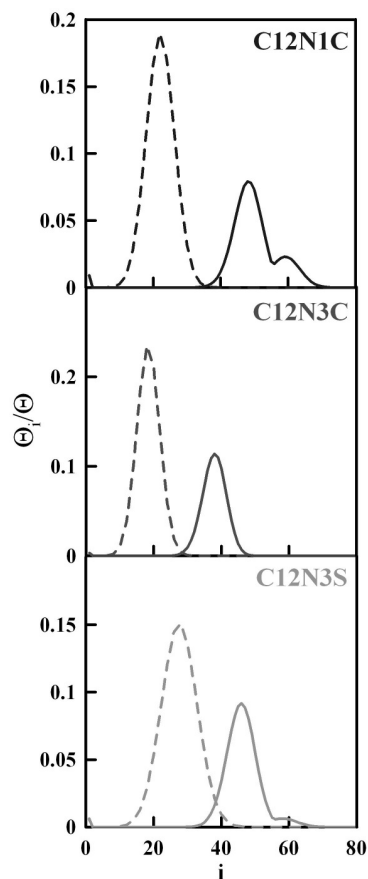


Fig. 4. The distribution of the surface areas occupied by surface aggregates among their aggregation numbers for C12N1C, C12N3C and C12N3S predicted by the two models: HAM (dashed lines) and SGM (solid lines).

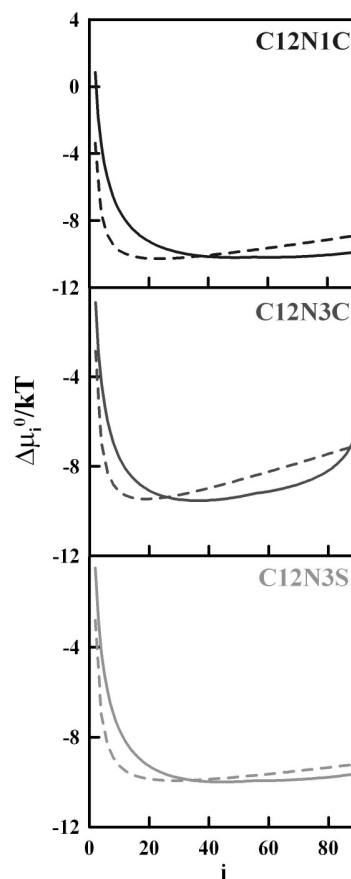


Fig. 5. The dependence of the standard free energy of surface aggregation of C12N1C, C12N3C and C12N3S calculated according to the HAM (dashed lines) and SGM (solid lines) theories.

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