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Theoretical description of aggregation of cationic gemini surfactants in the bulk solution and on the silica surface

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Abstract A theory of cationic dimeric (gemini) surfactant adsorption onto negatively charged surface is presented. In the proposed model it is assumed that the adsorbed phase is a mixture of singly dispersed molecules of surfactant and spherical, globular and cylindrical aggregates of different dimensions. Only the "excluded area" interactions between the adsorbed species are considered and the effects of surface heterogeneity on monomer adsorption are taken into account. The aggregation behavior of gemini surfactants is based on the additive free energy model proposed by Camesano and Nagarajan (2000). The calculated surfactant adsorption isotherms and the differential molar enthalpies of micellisation and adsorption are compared with the experimental results obtained for a series of gemini surfactants depending on the length of a spacer, temperature or the presence of electrolyte. On the basis of theoretical results the evolution of adsorbed phase of gemini surfactants with the increasing adsorption is discussed. It is shown that the evaluated *cmc* values and the dimensions of surfactant aggregates are in a good agreement with experiment. Unfortunately, the theoretical model does not describe properly the temperature dependence of micellisation process.

Keywords Gemini surfactants · Surfactants adsorption · Surface aggregation

1 Introduction

Gemini surfactants, called also dimeric surfactants, represent a new class of surface active compounds. Most often they are built of two, at times three or more, monomers of conventional surfactants. Their molecules usually consist of two hydrophobic tails and two hydrophilic groups which are joined by a spacer—usually a hydrocarbon. The spacer can be rigid (e.g. aromatic ring) or flexible (e.g. alkyl chain). Despite the fact that gemini surfactants are relatively new compounds they found a huge application in numerous branches of industry and environmental protection. The success of gemini surfactants application has had a good reason. Namely, dimeric surface active agents are characterized by better interfacial properties than the corresponding monomeric conventional surfactants (i.e. surfactant molecules with the same single hydrophilic and hydrophobic groups). It should be mentioned that the critical micelle concentration (*cmc*) of geminis can be two orders of magnitude lower than the *cmc* of corresponding conventional surfactants (Atkin et al. 2003b; Menger and Keiper 2000; Hait and Moulik 2002). For instance, the *cmc* of dimeric surfactant 12-2-12 (ethanediyl-α,ω-bis (dodecyldimethylammonium bromide) equals 0.84 mM whereas the *cmc* of the corresponding monomeric form, DTAB (dodecyltrimethylammonium bromide), is 15.3 mM (Atkin et al. 2003b; Zana 2003). As the spacer becomes longer, the hydrophobicity of a molecule increases and surfactant molecules associate more readily in the bulk solution (*cmc* decreases). Gemini surfactants are also characterized by a significant surface activity (up to three times as large as conventional ones) (Rosen 1978). For example, the concentration which diminishes the surface tension by 20 mN/m (C_{20}) is only 0.13 mM for 12-2-12 whereas for DTAB it is 15.3 mM

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(Zana and Ed Holmberg 1998). Other noteworthy properties of gemini surfactants are their low Krafft temperature (Rosen 1993), higher than normal ability for solubilization (Dam et al. 1996) or bacteriocidal properties (Menger and Keiper 2000; Diz et al. 1994; Macian et al. 1996; Perez et al. 1996; Devinsky et al. 1985). The minimal inhibitory concentration (*mic*) for the conventional surfactant BDDAB is about 625 µM whereas for its dimeric form only 6 µM (Menger and Keiper 2000).

On account of popularity of these compounds in many fields a large interest was aroused in the scientific world. In the last decade plenty of papers dealing with the properties of surfactants of this type were published (Rosen 1978; Zana 2002). Having the complete experimental characterization of gemini surfactant systems (both in bulk solutions and at interfaces) our theory of surface aggregation was applied to describe theoretically the equilibrium at the solution/air and solid/solution interfaces.

Considering the images of gemini solutions (e. g. 12-2-12) made by means of Transmission Electron Microscopy at cryogenic temperature (cryo-TEM) it can be concluded that, depending on the surfactant concentration, aggregates of different shapes, such as spherical, globular and cylindrical are present (Bernheim-Groswasser et al. 2000; Zana 2002). The higher concentration, the bigger aggregates are created. The monomeric form of gemini surfactants of the type 12-s-12—DTAB mainly associates to spheroidal assemblies even in highly concentrated solutions or in the presence of simple salt (Candau et al. 1984; Ozeki and Ikeda 1982; Zana and Talmon 1993). Dimerization of DTAB gave new molecules the ability to form cylindrical aggregates which significantly changed the rheological properties of solutions. Further cryo-TEM research showed that the diameter of spheroidal endcap of rod-like aggregates is bigger than that of cylindrical part of the aggregate which is in agreement with theoretical predictions (Bernheim-Groswasser et al. 2000; Zana 2002).

According to Zana and Talmon (1993) the shape of gemini aggregates depends, among others, on the spacer length joining two surfactant monomers. The surfactant with the shortest spacer (12-2-12) forms the biggest rod-like micelles whereas in the solution of 12-4-12 (the longest joint) only spheroidal aggregates are present. In the case of the intermediate dimeric surfactant (12-3-12) both kinds of associates can be seen.

Molecular dynamics simulations of aqueous solutions of m-s-m gemini surfactants confirm that the change in the shape of micelles from spheroidal to rod-like one occurs as the length of a spacer increases (Karaborni et al. 1994), which can also be observed experimentally. Karaborni et al. (1994) showed that the most probable shape of an aggregate formed by a monomeric surfactant is spheroidal whereas its dimeric form—a worm-like one.

Similar conclusions can be drawn by analyzing AFM images of an adsorbent surface with a gemini surfactant adsorbed. Manne et al. (1997) took AFM pictures of three dimeric surfactants 18-3-1, 12-4-12 and 12-2-12 adsorbed onto the mica surface. In the case of the nonsymmetrical compound (18-3-1) spherical aggregates are present on the surface. In the next two cases the general trend is maintained: the fewer methyl groups in a spacer, the bigger aggregates are present. On the basis of AFM images of 12-2-12 adsorbed at the silica/solution interface Atkin et al. (2003a) claim that, surprisingly, this surfactant forms spherical aggregates on the silica surface. Thus, the questions are raised: Why aggregates of the same surfactant are so different in shapes: cylinders in the bulk solution, a bilayer at the mica surface and spheres at the silica surface? Is the kind of adsorbent the reason for the surfactant's behavior since the measurements were carried out under almost the same conditions?

Some time ago we proposed the theory of surface aggregation with which we were able to predict quantitatively the adsorption isotherms and differential heats of adsorption of nonionic and cationic surfactants. In this paper we will show that our theory can be also adapted to describe the 12-s-12 gemini surfactants adsorption on the hydrophilic silica surface.

2 Theory

2.1 Adsorption isotherm

Let us remind briefly the basis of our adsorption theory (Drach et al. 2005). We have assumed that the surface phase is a mixture of singly dispersed surfactant monomers, spherical and globular (i.e. ellipsoidal) aggregates of different aggregation numbers (i). By S_i let's denote the area (circle) excluded by the aggregate of size i. This area is equal to the cross-section area of the i-th aggregate. Surface associates are allowed to interact only via excluded area interactions. Consequently, the hard disk model of two dimensional gas can be applied and the expression for the chemical potential of the i-th surface aggregate can be written as follows:

$$\frac{\mu_i^s}{kT} = \frac{\mu_i^{s,0}}{kT} + \ln\left(\frac{\Gamma_i}{1-\Theta}\right) + r_i\left(\frac{2A}{1-\Theta}\right) + s_i\left[\frac{\Gamma}{1-\Theta} + \left(\frac{A}{1-\Theta}\right)^2\right] \tag{1}$$

The subscript i denotes the number of molecules in the aggregate whereas the superscript s refers to a given quantity in the surface phase. $\mu_i^{s,0}$ is a standard chemical potential of surface micelle of size i. Other symbols have the following meaning:

$$\Gamma_i = \frac{N_i^s S_1}{S}, \qquad r_i = \frac{R_i}{R_1}, \qquad s_i = \frac{S_i}{S_1} = \frac{\pi R_i^2}{\pi R_1^2} = r_i^2 \tag{2}$$

$$\Gamma = \sum_{i=1}^{i_{\max}} \Gamma_i, \qquad A = \sum_{i=1}^{i_{\max}} \Gamma_i r_i, \qquad \Theta = \sum_{i=1}^{i_{\max}} \Gamma_i s_i = \sum_{i=1}^{i_{\max}} \Theta_i \tag{3}$$

In the above equations R_1 and R_i are the radii of a monomer or an aggregate, respectively, S represents the total surface area and $i_{\max}$ is the maximal value of i.

Using the thermodynamic equilibrium condition $\mu_i^s(\{N_i^s\}, N^s, T) = i\mu_1^b(x_1^b, T)$, where $\{N_i^s\}$ is a set of numbers of aggregates of different sizes on the surface, μ_1^b is the chemical potential of monomer in the equilibrium bulk phase (superscript b), x_1^b is its mole fraction, and remembering that for the dilute surfactant solution μ_1^b can be written as $\mu_1^b = \mu_1^{b,0} + kT \ln x_1^b$ where $\mu_1^{b,0}$ denotes the standard chemical potential of a monomer in the bulk solution, the following equation system for the individual adsorption isotherms Γ_i was derived:

$$\Gamma_i = (x_1^b)^i K_i^s (1-\Theta) \times \exp\left\{-r_i \frac{2A}{1-\Theta} - s_i\left[\frac{\Gamma}{1-\Theta} + \left(\frac{A}{1-\Theta}\right)^2\right]\right\} \quad \text{for } i \le i_{\max} \tag{4}$$

In the above equation K_i^s represents the adsorption constant:

$$K_i^s = \exp\left(\frac{-i\Delta\mu_i^0}{kT}\right)$$

where $\Delta\mu_i^0$ denotes the standard free energy of transfer of a surfactant molecule from the bulk phase to the surface aggregate of i size ($\Delta\mu_i^0 = \mu_i^{s,0}/i - \mu_1^{b,0}$).

2.2 Energetic heterogeneity of the surface

The above considerations were based on the assumption of adsorption onto energetically homogenous adsorbent surface. To take the energetic heterogeneity of the surface into account we will assume, as in our previous paper (Drach et al. 2005), that the surface heterogeneity influences only the adsorption of monomers. From the monograph by Rudziński and Everett (1992) it follows that in the case of adsorption on a heterogeneous surface with random topography a possible modification of (4) for $i = 1$ might be

$$\frac{\overline{\Gamma}_1}{1-\Theta} = \left\{x_1 \overline{K}_1^s \exp\left\{-r_1 \frac{2A}{1-\Theta} - s_1\left[\frac{\Gamma}{1-\Theta} + \left(\frac{A}{1-\Theta}\right)^2\right]\right\}\right\}^{\alpha kT} \tag{5}$$

where α is the heterogeneity parameter characterizing the width of an energy distribution function. It satisfies the condition $0 < \alpha kT < 1$. $\overline{K}_1^s$ has a meaning of the most probable value of the constant K_1^s on a heterogeneous surface. Thus, taking into account the effect of surface heterogeneity on monomer adsorption, we replace the equation for Γ_1 in the equation system (4) by $\overline{\Gamma}_1$ given by (5).

2.3 Standard free energy of surface aggregation $\Delta\mu_i^0$

To calculate the adsorption isotherm first we have to estimate a value of the adsorption constant K_i^s and at the same time the standard free energy of transfer of a surfactant molecule from the bulk phase to the surface aggregate of i size $\Delta\mu_i^0$. We will take advantage of our previous work (Drach et al. 2005). There we treated $\Delta\mu_i^0$ as perturbation of what is known in solution and we wrote it as a sum of two terms:

$$\Delta\mu_i^0 = (\Delta\mu_i^0)_{bulk} + (\Delta\mu_i^0)_{surf} \tag{6}$$

Above the first term is related to the transfer of a surfactant monomer from the bulk solution to the bulk micelle of size i. The second one is a perturbation resulting from the surface presence. On the basis of molecular considerations and depending on the shape and size of a micelle each of these terms can be expressed as a set of various contributions. Pursuant to Camesano and Nagarajan (2000) approach the following contributions were taken into account in the bulk term:

$$(\Delta\mu_i^0)_{bulk} = (\Delta\mu_i^0)_{tr} + (\Delta\mu_i^0)_{def} + (\Delta\mu_i^0)_{pack} + (\Delta\mu_i^0)_{int} + (\Delta\mu_i^0)_{cov} + (\Delta\mu_i^0)_{st} + (\Delta\mu_i^0)_{ion} \tag{7}$$

where: $(\Delta\mu_i^0)_{tr}$ is the standard free energy of transfer of a surfactant hydrocarbon chain from the aqueous medium to the aliphatic core of a bulk micelle of size i, $(\Delta\mu_i^0)_{def}$ denotes the standard free energy of deformation of hydrophobic tail inside the micelle core, $(\Delta\mu_i^0)_{pack}$ represents the standard free energy of packing, $(\Delta\mu_i^0)_{int}$ is the standard free energy of formation of the micelle core–water interface, $(\Delta\mu_i^0)_{cov}$ describes the standard free energy coming from replacing the micelle core–water contact by the micelle core–spacer contact, $(\Delta\mu_i^0)_{st}$ and $(\Delta\mu_i^0)_{ion}$ are the standard free energies of steric and electrostatic interactions between polar heads, respectively. Some of these contributions are analogical to those for conventional surfactants. The detailed expressions for each kind of the above free energies can be found in reference (Camesano and Nagarajan 2000). The surface term in (6) takes into account interactions of surfactant molecules with the surface and can be expressed as follows:

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

where a is the surface area of aggregate/adsorbent contact per molecule and γ is the displacement tension which can be viewed as the difference between the water/solid and the aggregate head group/solid surface interfacial tension.

2.4 Differential heat of adsorption

The main source of information about the surfactant adsorption mechanism are usually adsorption isotherms and electrophoretic mobility data (Gu and Zhu 1990; Bijsterbosch 1974; Poirier and Cases 1991; Sobisch 1992; Ruthland and Pashley 1989). In recent years the microcalorimetry has become very popular and one of the most sensitive techniques used to study surfactant association both in bulk solutions and at solid/liquid interfaces. Calorimetric measurements allow a direct estimation of the enthalpy change during the aggregation and adsorption process.

Heats of adsorption yield much valuable information about the mechanism of surfactant adsorption which could not be concluded on the basis of adsorption isotherm analysis (Chandar et al. 1987; Zając et al. 1995, 1996, 1997; Trompette et al. 1994; Kiraly and Findenegg 2000; Kiraly et al. 1997; Fox et al. 1998; Narkiewicz-Michałek et al. 1993). In spite of the fact that research of micellization and adsorption of surfactants is often accompanied by calorimetric measurements, there have been only few papers published so far which dealt with a quantitative description of both the adsorption isotherms and the enthalpic effects of adsorption (Narkiewicz-Michałek et al. 1993; Łajtar et al. 1993, 1994; Drach et al. 1998; Woodbury and Noll 1987; Seidel et al. 1996; Partyka et al. 1989). In most of them the authors focused solely on the quantitative analysis of the adsorption isotherms, though it is well-known that only the simultaneous analysis of several independent characteristics of the system, e.g. experimental adsorption isotherms and heats of adsorption, allows estimation of the correctness of the proposed adsorption model (Drach et al. 1998, 2002).

The measured differential heat of adsorption is given by the formula

$$Q_t^s = \frac{dQ}{dN^s} = \frac{\sum_i Q_i^s(\partial i N_i^s/\partial \mu_1^b)}{\sum_i(\partial i N_i^s/\partial \mu_1^b)} \tag{9}$$

Above Q_i^s ($i = 1, 2, \ldots, i_{\max}$) denotes the heat of adsorption of the aggregate of size i per monomer at a certain set of the surface coverages $\{\Gamma_k\}$:

$$Q_i^s = -\frac{k}{i}\frac{\partial}{\partial(1/T)}\left(\frac{\mu_i^s - i\mu_1^b}{kT}\right)_{\{\Gamma_k\}} \tag{10}$$

It can be written as a sum of temperature derivatives of each contribution to the standard free energy of surface aggregation $\Delta\mu_i^0$:

$$\begin{aligned} Q_i^s &= Q_i^b + (Q_i)_{surf} \\ &= (Q_i)_{tr} + (Q_i)_{def} + (Q_i)_{pack} + (Q_i)_{int} + (Q_i)_{cov} \\ &\quad + (Q_i)_{st} + (Q_i)_{ion} + (Q_i)_{surf} \end{aligned} \tag{11}$$

where

$$(Q_i)_n = kT^2\frac{\partial((\Delta\mu_i^0)_n/kT)}{\partial T}, \qquad n = tr, def, pack, int, cov, st, ion, surf \tag{12}$$

The derivatives $(\partial i N_i^s/\partial \mu_1^b)$ can be estimated from the equation system (4).

3 Results and discussion

To test our theoretical model we used a set of experimental data (adsorption isotherms, enthalpies of micellisation and surface aggregation) obtained in CRNS laboratory in Montpellier for the three cationic gemini surfactants: 12-2-12, 2Br$^-$, 12-4-12, 2Br$^-$, 12-6-12, 2Br$^-$ adsorbed at the amorphous silica surface XOB015 (SilH) (Chorro et al. 1999; Prosser and Franses 2001; Grosmaire 2001; Grosmaire et al. 2001a, 2001b).

The strategy of calculations was the same as in our previous paper (Drach et al. 2005). We tried to model simultaneously the process of micellisation in the bulk solution and aggregation at the adsorbent surface together with the enthalpic effects accompanying them.

The surfactant solution was treated as a multi-component system consisting of water molecules, singly dispersed surfactant molecules and aggregates of various shapes and sizes. In the thermodynamic equilibrium state the chemical potential of a singly dispersed surfactant monomer is equal to the chemical potential of an aggregate per monomer.

$$\mu_i^{b,0} + kT\ln x_i^b = i(\mu_1^{b,0} + kT\ln x_1^b), \quad i = 1, 2, \ldots, i_{\max} \tag{13}$$

Rearranging the above equation we obtained the aggregate size distribution:

$$x_i^b = (x_1^b)^i \exp\left(\frac{-i(\Delta\mu_i^0)_{bulk}}{kT}\right) \tag{14}$$

and using it we calculated the critical micelle concentrations of the examined gemini surfactants:

$$x_1^b = \sum i x_i^b = x_{cmc} \tag{15}$$

and the average aggregation numbers:

$$\bar{i}_{bulk} = \sum_{i=1} i N_i^b \Big/ \sum_{i=1} N_i^b \tag{16}$$

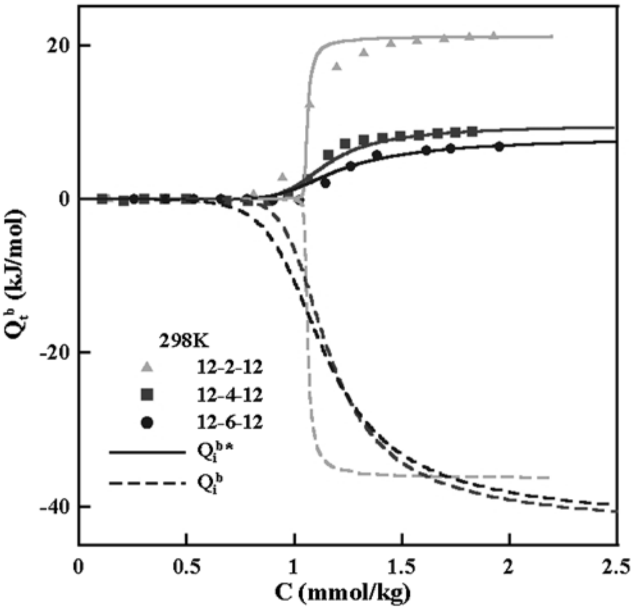

Fig. 1 The comparison of the experimental (*symbols*) and theoretical (*lines*) micellisation heats of: 12-2-12 (▲), 12-4-12 (■) and 12-6-12 (●). The *dashed* and *solid lines* were calculated using Q_i^b given by (17) and $Q_i^{b*} = Q_i^b + \Delta Q_h$, respectively

The size of aggregates in both phases was allowed to change as the surfactant concentration increased. First, we tried to reconstruct the surfactant solution properties such as the *cmc*, the average aggregation number ($\bar{i}_{bulk}$) and the isosteric heat of micellisation given by the formula:

$$Q_t^b = \sum_i Q_i^b \left(\frac{\partial i x_i^b}{\partial \mu_1^b}\right) \Big/ \sum_i \left(\frac{\partial i x_i^b}{\partial \mu_1^b}\right) \qquad (17)$$

where Q_i^b is the non-configurational heat of the bulk micelle formation defined analogically to Q_i^s (10, 11).

While calculating the standard free energy of micellisation, spherical, globular and spherocylindrical aggregates were considered. It was assumed that the change in a shape of an aggregate (e.g. from spherical to globular and then to cylindrical) occurs when the aggregate attains a certain dimension which corresponds to the minimum of the standard potential of bulk micellisation, $(\Delta\mu_i^0)_{bulk}$, for this particular shape. In our calculations of the heat of micellisation we used only one best-fit parameter. It was the hydrophobic core area per head group, a_p. We tried to find such a value of a_p that gave us an experimental *cmc* value of the gemini surfactant. Other parameters occurring in the detailed expressions of the free energy contributions were taken from literature (Camesano and Nagarajan 2000; Johnson and Nagarajan 2000; Nagarajan and Ruckenstein 1991).

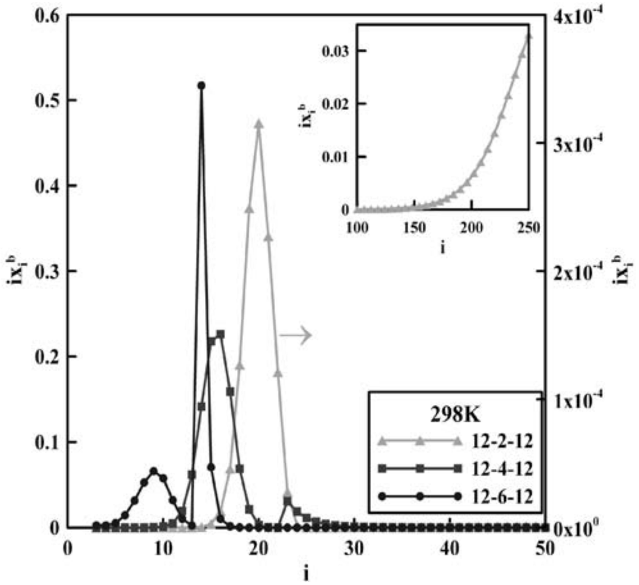

Fig. 2 The distribution of the surfactant molecules among the bulk aggregates of various sizes

Table 1 The parameters used to calculate the theoretical differential heats of micellisation

Surfactant	NaBr (mmol/kg)	T (K)	a_p (Å^2)	ΔQ_h (kJ/mol)
12-2-12,2Br$^-$	–	298	63.0	28.8
12-2-12,2Br$^-$	–	308	63.0	26.8
12-2-12,2Br$^-$	4.5	308	62.3	25.2
12-4-12,2Br$^-$	–	298	65.5	26.7
12-6-12,2Br$^-$	–	298	72.0	25.7

In Fig. 1 the theoretically calculated and experimentally measured differential heats of micellisation for the three gemini surfactants with various spacer lengths are compared. The values of parameters obtained while fitting best the theoretical heats of micellisation to the experimental ones are collected in Table 1.

In Fig. 1 the dashed lines indicate the heat of micellisation calculated by means of Camesano and Nagarajan (2000) approach (17). It is clearly seen that the *cmc* values are predicted correctly whereas the final thermal effect of the micellisation process is opposite to the real one. We faced the similar situation while fitting-best the micellisation heats of zwitterionic surfactants by applying the Nagarajan's expression for $(\Delta\mu_i^0)_{bulk}$ (Nagarajan and Ruckenstein 1991). By analogy, to reproduce quantitatively the experimental heats of gemini surfactant micellisation we had to introduce an additional contribution to the heat of micellisation—ΔQ_h (eq. for Q_i^b, $Q_i^{b*} = Q_i^b + \Delta Q_h$) and to treat it as a best-fit parameter. Analyzing the micellisation curves three regions can be distinguished:

1. The first plateau—the surfactant concentration is smaller than *cmc*. The micellisation still does not occur.

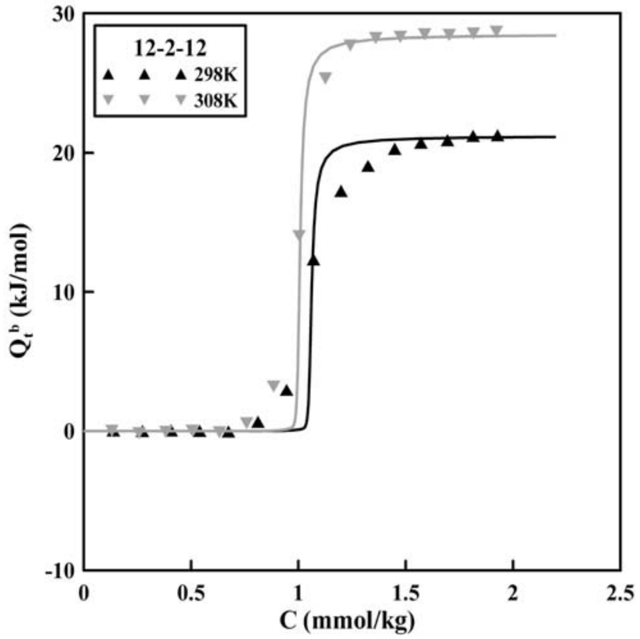

Fig. 3 The comparison of the experimental (*symbols*) and theoretical (*lines*) micellisation heats of 12-2-12 at 298 K (▲) and 308 K (▼)

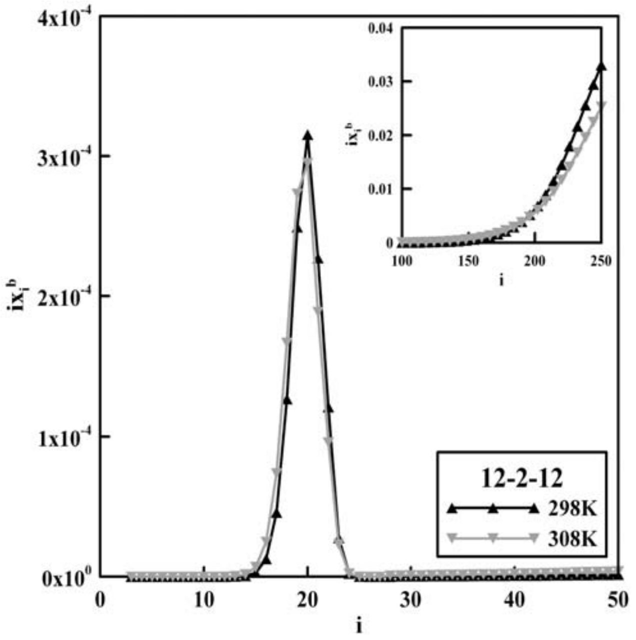

Fig. 4 The distribution of the surfactant molecules among the bulk aggregates of various sizes

2. Rapid growth of the heat effect—the surfactant concentration reaches the *cmc* value. In this region a sudden micelle formation occurs.
3. The second plateau—the concentration is above the *cmc*. The whole introduced surfactant associates so the heat remains constant.

As one can see in Fig. 1 the micellisation process is the most exothermic for the surfactant with the shortest spacer (12-2-12). It suggests that this surfactant aggregates the most readily.

In Fig. 2 the distributions of monomers among the bulk aggregates of different sizes are shown. These distributions were calculated from (14) and (16). For concentrations beyond the *cmc* all the examined gemini surfactants form spherical aggregates, some globular and spherocylindrical. The biggest micelles are formed by the surfactant with the shortest spacer (12-2-12) and the most favorable energetically shape of these associates is a rod-like one (small graph in the corner of Fig. 2). The maximum aggregation number in our calculations was set to $i_{\max} = 250$, and that is why the curves are cut at this value. An increase in a spacer length results in smaller aggregation numbers. They form spherical micelles (increasing part of the first peak), globules (decreasing part of the first peak) and small spherocylinders (the second peak). As one can see the sequence is in agreement with experiment (Johnson and Nagarajan 2000): the longer the spacer is, the smaller aggregates are.

In Figs. 3 and 4 the influence of temperature on the micellisation heat of 12-2-12 surfactant and the distribution of its aggregates in solution was shown. The increase of temperature from 298 to 308 K causes a slight reduction in *cmc* of cationic gemini surfactants which is confirmed by experiment (Johnson and Nagarajan 2000). In the case of the system at 308 K the micellisation process is more exothermic (the heat effect is more positive). Looking at the distributions of aggregates it can be easily seen that the temperature increase has a negligible effect on the dimensions of micelles.

In the next two figures (Figs. 5 and 6) the effect of salt concentration on the heat of micellisation and the distribution of aggregates of 12-2-12 are presented. The increase of sodium bromide concentration from 1 mmol/kg to 4.5 mmol/kg leads to a twofold drop of the surfactant *cmc* but it does not influence the size of aggregates.

To test our model of surface aggregation we used the experimental adsorption data and the heats of adsorption of 12-4-12 and 12-6-12 adsorbed on the silica surface (Chorro et al. 1999; Prosser and Franses 2001; Grosmaire 2001; Grosmaire et al. 2001a, 2001b). During the measurements the free-parameter procedure was used (i.e. such parameters as pH or ionic strength of the solution were allowed to change themselves). In Table 2 the parameters used for calculation of isotherms and heats of adsorption are collected.

Now let us discuss briefly the above parameters. The parameter αkT characterizes the energetic heterogeneity of the surface and can be estimated from the linear log-log plots of the initial part of the adsorption isotherms ($\ln \overline{\Gamma}_1 = \alpha kT \ln \overline{K}_1 + \alpha kT \ln x_1^b$) (Drach et al. 2005). S_1 denotes the surface area occupied by a monomer. We assumed that it is equal to $2a_p$ (a_p—the hydrophobic core area of the head group in the bulk micelles). The parameter d appears in the equation for the surface area of the aggregate/adsorbent contact, $a = S_i/i$, where $S_i = \pi(R_{ih} + d_{el} + d)^2$ (R_{ih}—the hydrophobic core radius, d_{el}—the thickness of a double layer). On account of electrostatic repulsions between aggregates the actual excluded surface area of the aggregate should be assumed slightly bigger than it can be estimated from its geometry. The parameter γ denotes the displacement tension, i.e. the difference between the water/solid surface interfacial tension and the aggregate head group/solid surface interfacial tension. Since we did not know the dependence of γ on the temperature, its derivative was treated as the best-fit parameter.

The last best-fit parameter of our adsorption model is the non-configurational heat of monomer adsorption $Q_1^{s,0}$ appearing in the equation for the differential heat of monomer adsorption $Q_1^s = Q_1^{s,0} - \frac{1}{\alpha}\ln\frac{\overline{\Gamma}_1}{1-\Theta}$ where $Q_1^{s,0} = k(\frac{\partial \ln \overline{K}_1}{\partial(1/T)})$.

The theoretically calculated and experimentally measured adsorption isotherms and heats of adsorption are compared in Figs. 7 and 8, respectively.

As one can see the theory reconstructs the experiment satisfactorily. Both isotherms have similar shapes but differ in maximum adsorption. For the surfactant with a shorter spacer separating the polar heads, the maximum adsorption is bigger. The shape of the isotherms suggests that the adsorption process occurs in two steps. In the first step monomers are mainly adsorbed. They remain at a certain distance from each other which prevents their hydrocarbon tails from interacting. When the surfactant concentration increases hydrophobic interactions start to play an important role which results in formation of surface aggregates and saturation of the adsorbent surface (plateau on the isotherm).

In Fig. 8 the agreement between the theoretical and experimental differential heats of adsorption was shown. Looking at the heat curve it becomes clear that the mechanism of adsorption is more complicated than it could be concluded from the adsorption isotherm curve. In the heat

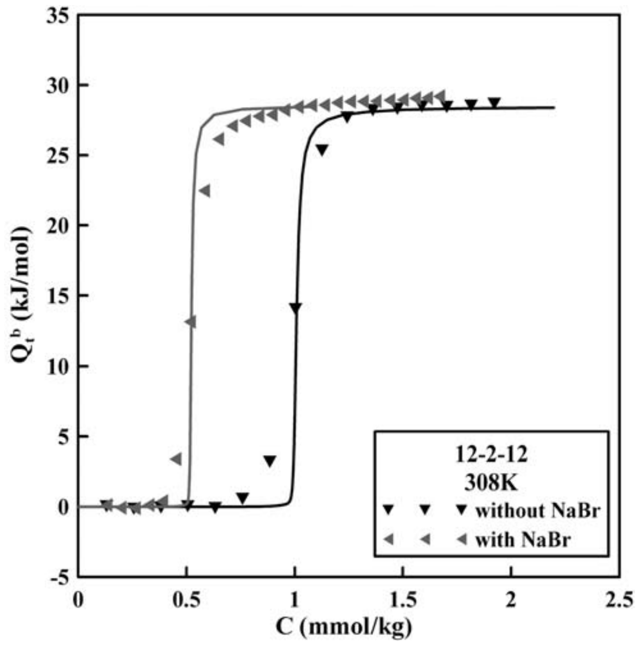

Fig. 5 The comparison of the experimental (*symbols*) and theoretical (*lines*) micellisation heats of 12-2-12 at 308 K in the absence (▼) and presence of NaBr (4.5 mmol/kg) (◀)

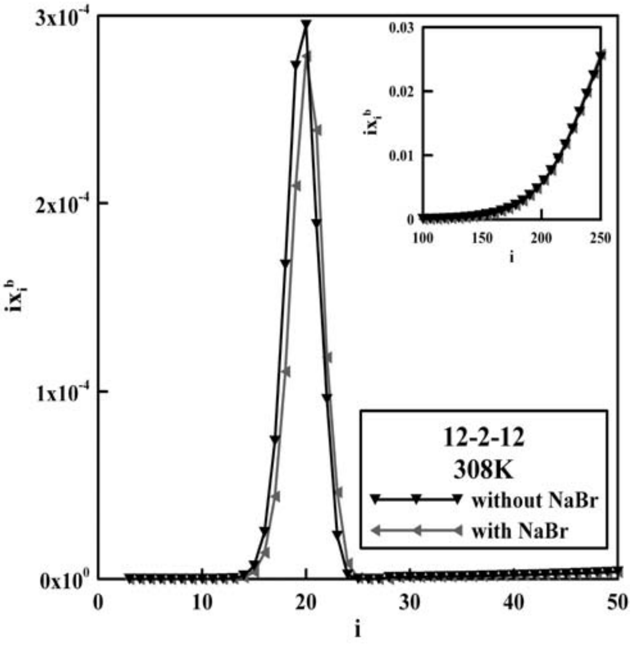

Fig. 6 The distribution of the surfactant molecules among the bulk aggregates of various sizes

Table 2 The parameters used to calculate the theoretical adsorption isotherms and heats of adsorption

Surfactant	T (K)	αkT	S_1 (Å^2)	d (Å)	γ (mJ/m^2)	$\frac{\partial\gamma}{\partial T}$ (mJ/m^{2}K)	$Q_1^{s,0}$ (kJ/mol)
12-4-12,2Br$^-$	298	0.33	131	0.8	9.0	−0.13	–
12-4-12,2Br$^-$	308	0.35	131	0.8	9.0	−0.13	−4.5
12-6-12,2Br$^-$	298	0.19	144	0.6	8.5	−0.12	–
12-6-12,2Br$^-$	308	0.20	144	0.6	8.5	−0.12	−4.3

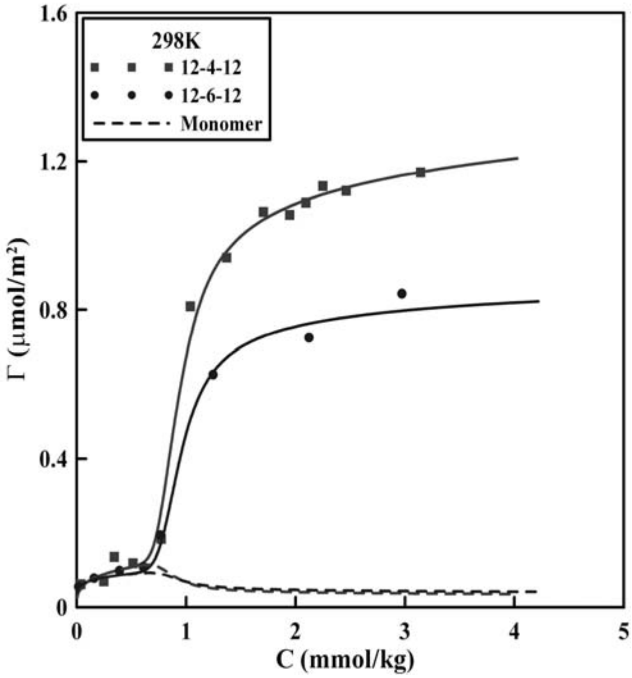

Fig. 7 The comparison of the experimental (*symbols*) and theoretical (*lines*) adsorption isotherms of 12-4-12 and 12-6-12 at 298 K calculated using the parameters collected in Table 2. The *dashed lines* denote the monomer adsorption contribution

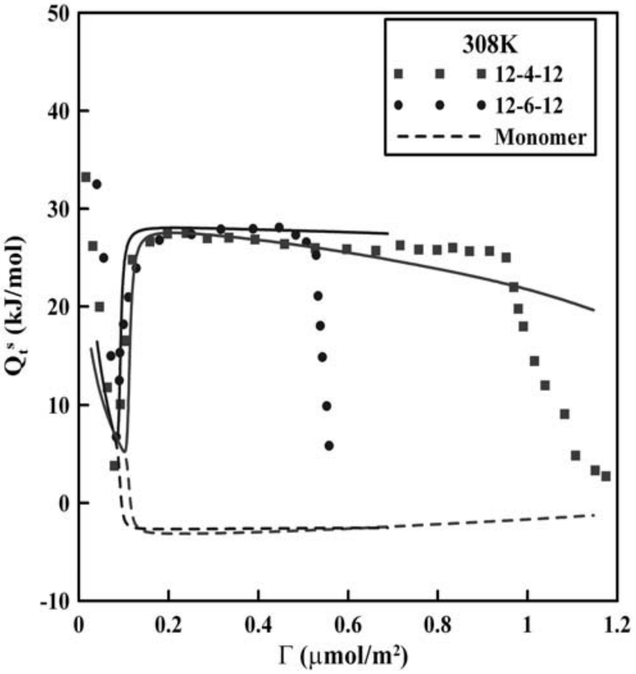

Fig. 8 The comparison of the experimental (*symbols*) and theoretical (*lines*) heats of adsorption of 12-4-12 and 12-6-12 at 308 K calculated using the parameters collected in Table 2. The *dashed lines* denote the adsorption heats of a monomer

curves we can distinguish four stages of adsorption for our cationic gemini surfactants onto silica surface:

1. The initial decrease of the heat with the increase of adsorbed amount corresponds to adsorption on the heterogeneous surface—adsorbing monomers occupy adsorption sites with lower and lower energy. The effects of surface heterogeneity on monomer adsorption were taken into account in our model and this region of the experimental data is reconstructed properly.
2. Growth of the heat after passing the minimum. In this stage hydrophobic interactions of tails are the driving force of the process.
3. The plateau region corresponds to the formation of surface aggregates. In this area the theoretical curves cover the experimental data semi-quantitatively.
4. The final step of adsorption—rapid heat decrease. As one can see our theory is not able to reproduce this stage of the adsorption process.

In Figs. 9 and 10 the distributions of the surface aggregates of the examined gemini surfactants are presented. As one can notice, when the adsorbed amount increases, the contribution of monomer adsorption diminishes whereas the number of aggregates increases. The aggregates formed by 12-4-12 surfactant are not only more numerous but also bigger in comparison with those formed by 12-6-12. In the case of the surfactant with a shorter spacer the size distribution for the surface aggregates is spread to higher aggregation numbers than that for the bulk solution. The surface distributions have two maxima on account of the allowed aggregate shapes (sphere–globule–spherocylinder).

4 Conclusions

In the present paper the model of spherical, globular and cylindrical aggregates has been applied for theoretical description of gemini surfactant aggregation in solution and at silica surface. The expression for the standard free energy change due to the transfer of a surfactant molecule from the dispersed state in solution to the micellar state proposed by Camesano and Nagarajan (2000) has been applied. As in our previous paper, the surface phase was treated as a mixture of hard disks of various sizes. The energetic heterogeneity of the surface has been taken into account with respect to monomer adsorption. The distributions of aggregate sizes, the adsorption isotherms and the differential enthalpies of micellisation and adsorption have been calculated and compared with the experimental data obtained for the three gemini surfactants: 12-2-12, 12-4-12, 12-6-12. Most of the model parameters have a strict physical meaning. They are molecular parameters or can be found from independent experiments. Comparing predictions of our theory with the experimental data, the following conclusions can be drawn:

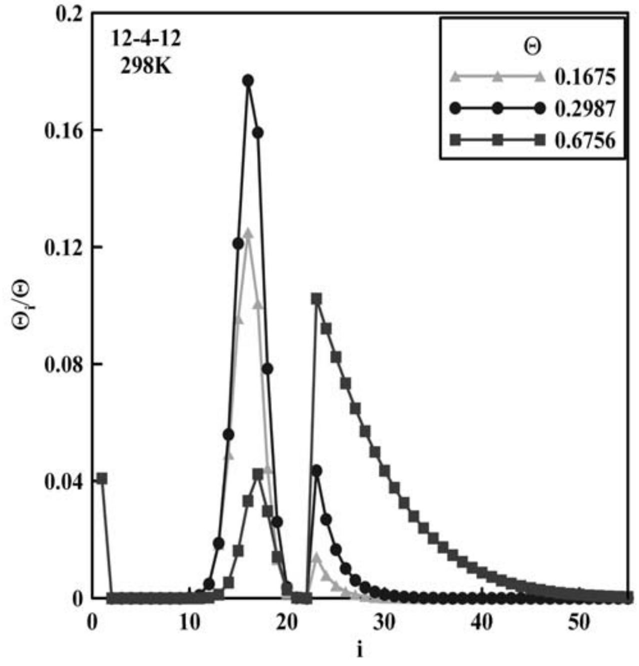

Fig. 9 The theoretically calculated surface aggregate distributions for various surface coverages of 12-4-12

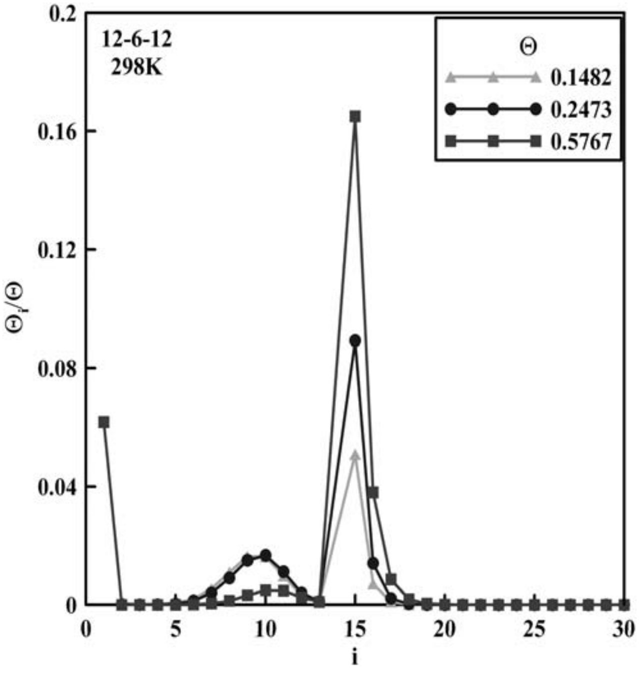

Fig. 10 The theoretically calculated surface aggregate distributions for various surface coverages of 12-6-12

1. The longer the spacer is, the smaller bulk and surface aggregates are formed.
2. A small addition of simple salt or an increase of temperature (10 K) does not cause the change in the amount and the size of micelles.
3. Surfactant monomers are present on the surface only in the range of initial concentrations.
4. Surface aggregates are formed close to the *cmc* and they are similar in shapes and sizes to bulk micelles which remains in agreement with the experimental findings.
5. Unfortunately, the bulk micellisation model does not describe the temperature dependence of this process properly (the same problem occurred when we tried to describe the behavior of zwitterionic surfactants micellisation).
6. The theory reproduces quite well the experimental adsorption isotherms and corresponding differential heats of adsorption of gemini surfactants.
7. Taking into account the energetic heterogeneity of the surface it was possible to reproduce the initial decrease of differential heat of adsorption.

It should be emphasized that our model is the first in literature to describe the process of surfactant aggregation and allows to predict with one set of parameters the bulk properties of surfactant solution, the equilibrium adsorption isotherms and the accompanying heats of adsorption.

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