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# Calorimetric investigations of gemini and conventional cationic surfactants at two silica-solution interfaces

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## Abstract

The importance of calorimetric methods in the study of colloidal phenomena is illustrated here by analysis of the enthalpies of adsorption, at 35°C, of two gemini and conventional cationic surfactants (12-2-12 and DTAB, respectively) on the surfaces of two silicas with different chemical properties. The values of the differential molar enthalpies of adsorption, corrected for the contribution of the dilution of the surfactant in solution, allow precise description of the adsorption process of the surfactants at the solid-solution interface. © 2001 Published by Elsevier Science B.V.

*Keywords:* Calorimetry; Adsorption; Cationic gemini surfactant; Silica

## 1. Introduction

The description of adsorption mechanisms at the solid–liquid interface requires determination of the various interactions among components of the system (solvent, solid and solute) [1]. Microcalorimetry gives the opportunity of directly studying these different types of interactions by measuring the enthalpies of adsorption [2]. The aim of this work is to detail the different steps that allow determination of the enthalpies of adsorption at the solid–liquid interface. First, are exposed the different problems which occur when determining these values. Afterwards, these problems are illustrated with some results obtained from different systems studied in particular. These systems include a cationic gemini surfactant: ethanediyl-1,2-bis(dodecyldimethylammonium bromide), called 12-2-12, and its monomeric counterpart: dodecyltrimethylammonium bromide (DTAB), and two silica supports. The silica XOB015 is used as received; it contains around 0.15% of sodium ions, and it was also used after an HCl-washing. This treatment eliminates the majority of sodium ions, only from the silica surface, by protonic substitution. These two supports will be respectively referred to by the abbreviations SiNa and SiH.

## 2. Materials

The amorphous silica XOB015 was supplied by Procatalyse S.A. (France). This material (SiNa), in its original state, contains a relatively large quantity of sodium ions and was used as received. It was also investigated after three washings with 5 N hydrochloric acid and continuous rinsing with distilled water until no chloride and sodium ions were detected by the value of the conductivity and the silver nitrate test.

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The treated silica is called SiH. Regardless of the treatment, the silica is macroporous (diameter of the pores >300 Å), the mean diameter of the particles is 40 μm and its specific surface area (BET/$N_2$) at 77 K is 29 $m^2\ g^{-1}$.

The conventional surfactant investigated, dodecyltrimethylammonium bromide (DTAB), is produced by Fluka. It was used as received (>98% purity). Its cmc is 15.6 mM at 35°C in water (Millipore Super Q System) [3].

The gemini surfactant studied, ethanediyl-1,2-bis(-dodecyldimethylammonium bromide) called 12-2-12, was synthesized in the laboratory [4]. This surfactant is made up of two identical amphiphilic moieties which are connected at the level of the polar heads by an alkyl chains (spacer s) with two carbon atoms; the hydrophobic tails are composed of twelve carbon atoms [5]. Its cmc in water at 35°C is 0.81 mM [4].

## 3. Description of the Calostar calorimeter

The Fig. 1 represents the calorimetric cell with devices for measuring the temperature, the controlled stirring and the addition of the reagents in use. The calorimetric device is placed into a metallic block where the temperature is controlled with a precision of $5 \times 10^{-4}$°C. The calorimeter is entirely run by computer. It takes about 15 min to return to the base line, the sensitivity of the detector is 0.5 μV $\mu W^{-1}$ and the

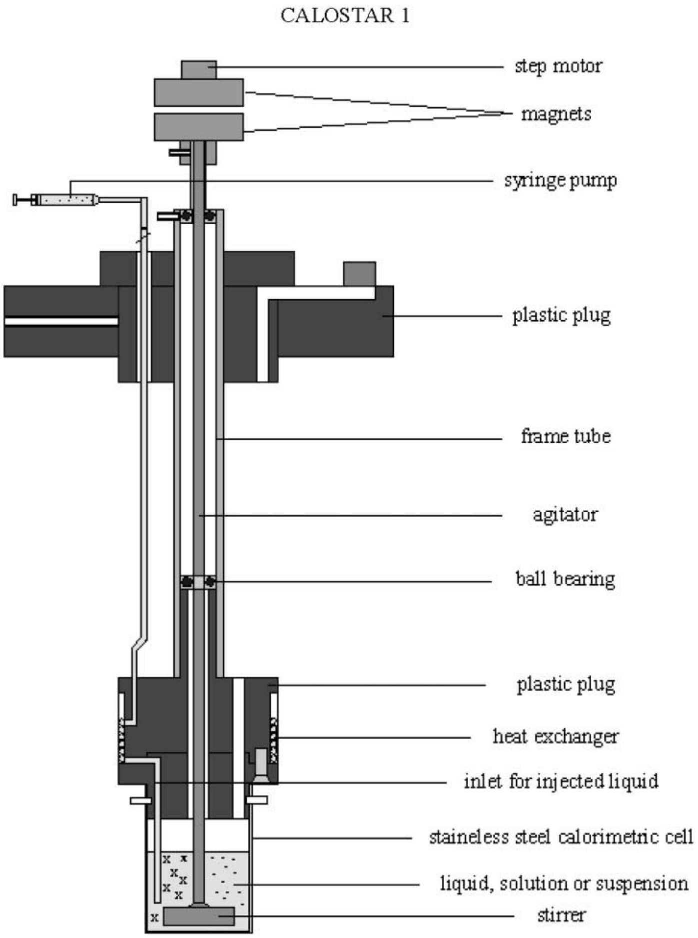

Fig. 1. Schematic representation of the Calostar microcalorimeter.

useful volume of the calorimetric cell goes from 5 to 15 cm$^3$. The Calostar microcalorimeter is perfectly adapted to studies on dilution, on adsorption and on micellisation. In the case of adsorption, the experimental procedure for measuring $\Delta H$ consists of filling up the calorimetric cell with an aqueous suspension of silica (about 8 g of water and 0.35 g of silica) and filling up the syringe with a micellar solution of surfactant. Once the calorimeter is equilibrated (around 12 h), one aliquot of the stock solution is injected into the suspension (from 5 to 100 μl). Adsorption equilibrium is attained almost instantaneously, when part of the solute molecule is adsorbed and the rest remains in the solution. The resulting thermal effect is recorded. After return to the base line, another injection is made.

>After having calculated the quantities adsorbed, from the adsorption isotherms, the dilution and adsorption enthalpies are determined by integration of the peaks which are obtained (Fig. 2) [6]. The differential molar enthalpies correspond to the variation of enthalpy between two injections per mole of surfactant.

For determination of the enthalpies of adsorption, the dilution enthalpies of the surfactant in solution are required. Indeed, when one aliquot of stock solution is introduced into the calorimetric cell, two phenomena are superposed: the dilution of the stock solution and the adsorption of the surfactant molecules onto the silica particles.

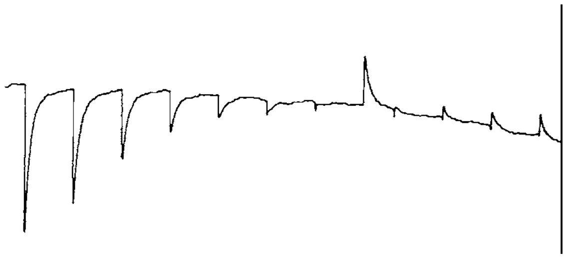

Fig. 2. Thermogramm.

### 3.1. Determination of the dilution enthalpies of the surfactant at 35°C

The enthalpies of dilution are determined using the same method, but, in that case, the calorimetric cell only contains the solvent. Dilution enthalpies were first determined in pure water (Fig. 3). The differential molar enthalpies of dilution of the studied surfactants was determined in surroundings equivalent to those observed during the adsorption. Indeed, the solution

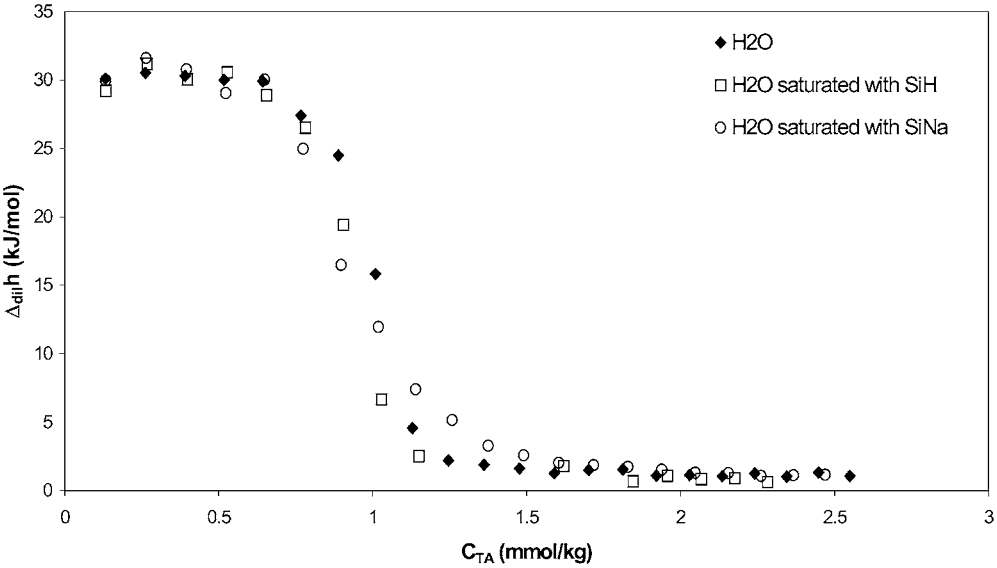

Fig. 3. Variation of the differential molar enthalpy of dilution of 12-2-12 in pure water and saturated with silica water at 35°C.

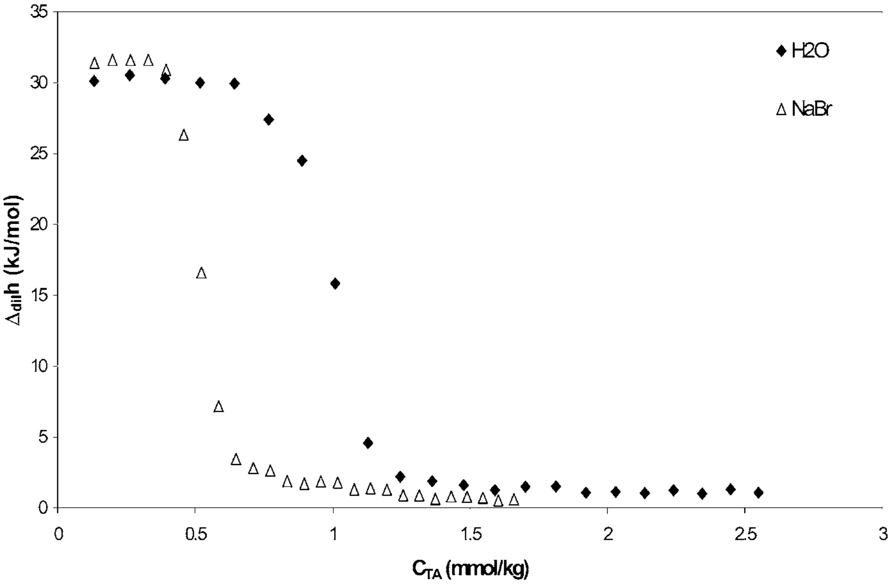

Fig. 4. Variation of the differential molar enthalpy of dilution of 12-2-12 as a function of the ionic strength at 35°C.

contains, then, sodium ions and protons released by the silica, and also bromide ions that are released by the adsorbed surfactant molecules. First, the dilution enthalpies of the studied surfactants were measured in water which was saturated with both solids. Indeed, initially, when the silica is in contact with water, it releases a specific quantity of sodium ions or protons, depending on the case. The results which are obtained are identical to those from the dilution in water (Fig. 3). Then, these modifications of composition of the solution do not influence the cmc. Secondly, in order to find again a ionic strength which is comparable with that obtained at the plateau of adsorption isotherm onto SiNa, the enthalpies of dilution were measured in a NaBr solution ($2.5 \times 10^{-3}$ M). The results shown in Fig. 4 show that, the enthalpy of micellisation is not modified, but that the cmc is shifted towards lower concentrations [7]. These results are confirmed by measurements of the conductivity of the surfactant solution in water, as well as of the supernatants collected after adsorption onto SiNa [3]. In order to determine the enthalpies of adsorption, the possible shift of that curve must also be considered. During adsorption on SiH, very few sodium ions are released, the pH has no effect on the micellisation and any correction become pointless.

### *3.2. Determination of the enthalpies of adsorption at 35°C*

The curve 1 in Figs. 5 and 6 represent the values of the enthalpies of adsorption obtained from the integration of the various thermograms [6]. Subtracting the enthalpy values obtained during the corresponding dilutions, the values of the differential molar enthalpies of adsorption are obtained (curve 2, Figs. 5 and 6). Depending on the chemical nature of the silica surface, a further correction may be necessary. In the case of SiH, the small quantity of sodium ions released into the solution scarcely changes the value of the cmc. However, for SiNa, the amount of bromide and sodium ions which are present in solution induces an appreciable shift of the cmc towards lower concentrations. If it is not taken in consideration, a very rapid increase of the exothermic values of the adsorption enthalpies is observed as the process is ending (curve 2, Fig. 6). Conductivity measurements taken during adsorption allows the shift of the cmc to be located and, thus, to make the corresponding correction [3]. Curve 3 (Fig. 6) is thus obtained, from which a drop of the exothermic values of the enthalpy is observed at the end of the adsorption process. Indeed, it corresponds to the dilution of the stock solution in a micellar

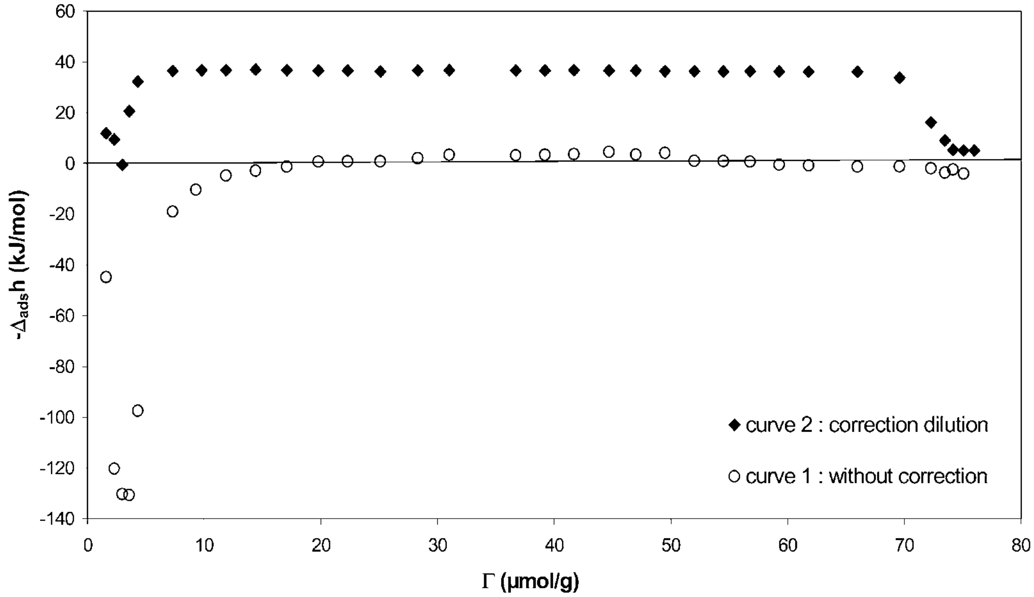

Fig. 5. Variation of the differential molar enthalpy of adsorption of 12-2-12 on to SiH at 35°C.

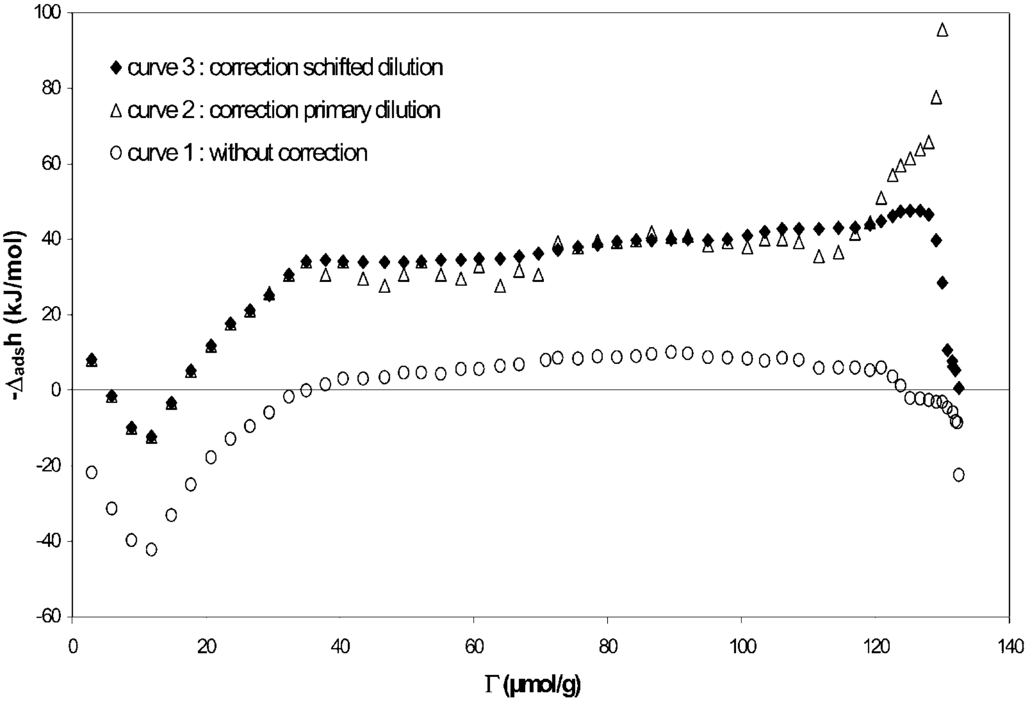

Fig. 6. Variation of the differential molar enthalpy of adsorption of 12-2-12 on to SiNa at 35°C.

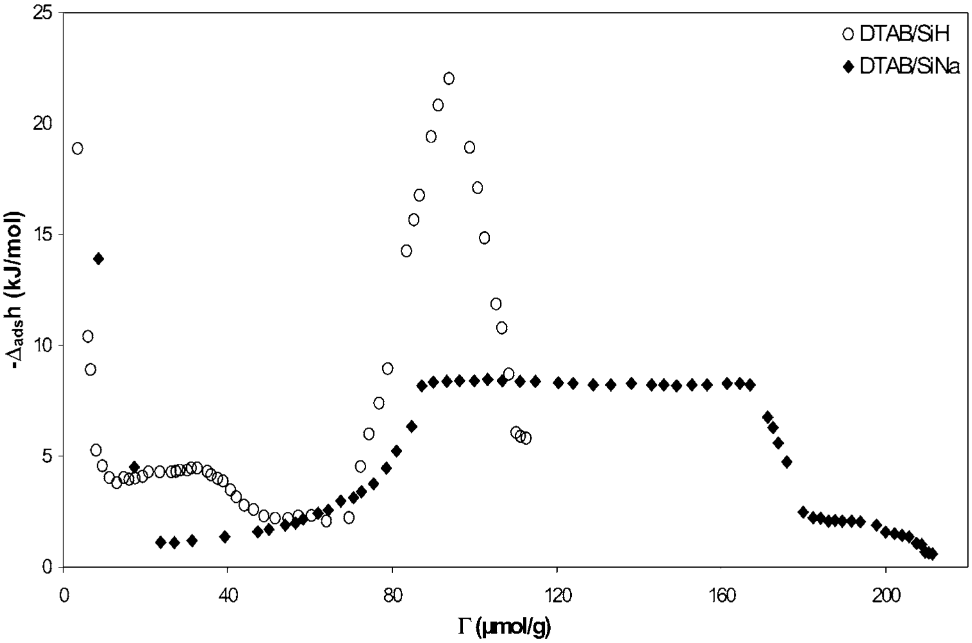

Fig. 7. Differential molar enthalpies of adsorption of DTAB/SiNa and DTAB/SiH at 35°C.

solution which appears in the calorimetric cell: athermic process as previously shown on the curves of the dilution enthalpies (Fig. 3).

## 4. Discussion

The values of the differential molar enthalpies of adsorption of DTAB and 12-2-12 on the two silica samples as a function of the amount of surfactant adsorbed *Γ* are shown in Figs. 7 and 8. An overall analysis of the curve profiles shows qualitative similarities concerning the evolution of the adsorption between the different systems studied. These curves clearly show three stages which describe the adsorption process of the cationic surfactants at the silica-solution interface.

The initial decrease of the exothermic values indicates direct adsorption of surfactant cations on to surface sites by the removal of sodium ions and/or protons. Successive additions of surfactant molecules into the water suspension of silica particles displace sodium ions and/or protons from the surface, and these become progressively more and more difficult to exchange. The exothermic values of the differential molar enthalpy of adsorption consequently decrease progressively. This is the consequence of a term due to the hydration of desorbed ions, constant and exothermic, and of a term associated with the exchange of the ions from the surface which itself becomes more and more endothermic, and reflects the heterogeneous distribution of the individual sites. After the minimum is reached, an increase of the exothermic values of the enthalpy is observed, corresponding to the predominance of hydrophobic interactions between alkyl chains of adsorbed molecules on the silica particles. This enthalpic effect is similar to that which is observed during micellisation and it indicates the beginning of interfacial aggregation. The stabilisation and subsequently a decrease of the exothermic values are then observed at higher amounts of adsorbed surfactant, which correspond to the growth and the reorganisation of the interfacial aggregate. For all the systems studied, an exothermic plateau is observed. The behaviour of DTAB onto SiH particular: after the initial decrease there is competition between individual and co-operative adsorption. The resulting thermic effects are opposed and give a pseudo-plateau.

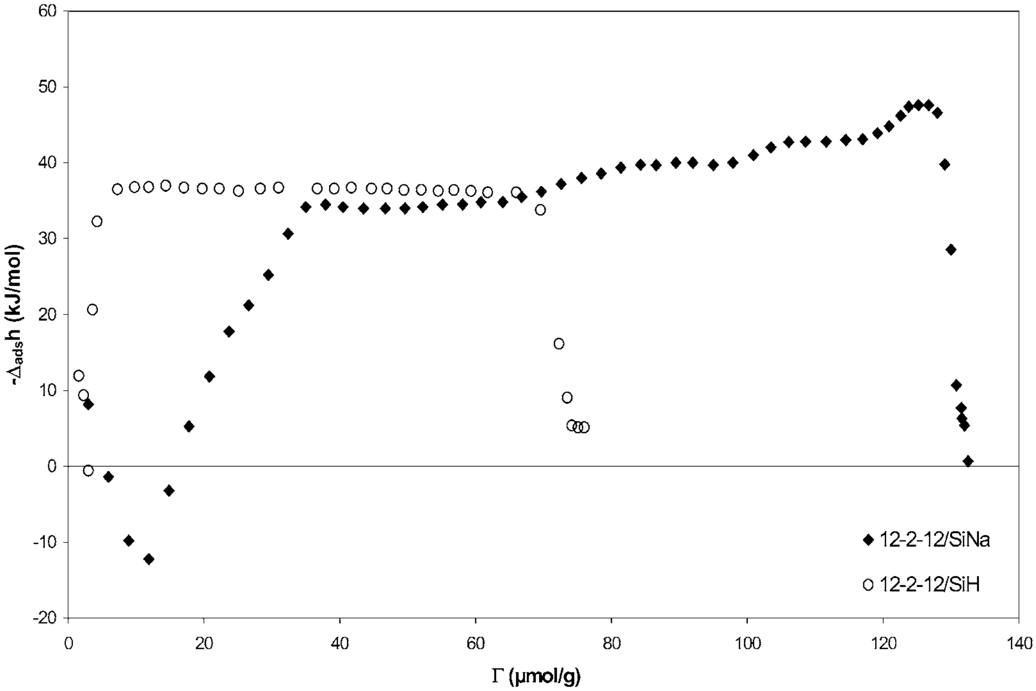

Fig. 8. Differential molar enthalpies of adsorption of 12-2-12/SiNa and 12-2-12/SiH at 35°C.

When the stage of individual adsorption is finished, then adsorption is only due to hydrophobic interactions and the system exhibits an exothermic peak (about $-23\ \mathrm{kJ\ mol^{-1}}$), which can be interpreted by the formation of an interfacial aggregate which grows around individually adsorbed surfactant molecules. This merging phenomenon (around $90\ \mu\mathrm{mol\ g^{-1}}$) leads to a large and compact interfacial aggregate.

The experimental results demonstrate that the variation of enthalpy which is necessary for the formation of an interfacial aggregate is more exothermic for the gemini than for the monomeric surfactant. It is possible to draw a parallel between these results and those observed during micellisation [8]. The enthalpic values of the micellisation process in bulk solution ($\Delta_{\mathrm{mic}}h = -29\ \mathrm{kJ\ mol^{-1}}$) are lower compared to those of the interfacial aggregation ($\Delta_{\mathrm{ag}}h = -47\ \mathrm{kJ\ mol^{-1}}$).

The chemical composition of the silica surface is very important. Indeed, the ionic strength of the equilibrium solution depends on the amount and on the nature of the ions provided by the silica surface. This induced ionic strength significantly contributes to the appearance of interfacial hydrophobic interactions at lower equilibrium concentrations. So, for the DTAB/SiH system, where the ionic strength is the lowest, the region of hydrophobic adsorption is characterised by a long plateau about $-4\ \mathrm{kJ\ mol^{-1}}$. Conversely, for the DTAB/SiNa system, where the ionic strength is significantly higher, the appearance of hydrophobic interactions rapidly leads to a regular increase of the exothermic values during adsorption.

## 5. Conclusion

The results presented here show the qualitative and quantitative contributions of calorimetric methods to our knowledge of adsorption phenomena. The determination of differential molar enthalpies of adsorption requires, at first, accurate knowledge of the dilution enthalpies of different surfactants in the same conditions as those of the adsorption. The values of the adsorption enthalpies, corrected by the real contribution of the dilution, give precise information on these processes and then reveal the importance of the chemical state of the silica surface for the adsorption. The results described show that the interfacial aggregate formed by the gemini surfactant is more compact than in the case of the corresponding monomeric surfactant.

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