

Calorimetric investigation of the adsorption of cationic dimeric surfactants with a hydrophilic spacer group onto silica

A. Bendjeriou, G. Derrien, C. Charnay*, C. Chorro, S. Partyka

*Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques, UMR 5072, CC15, Université Montpellier II,
Place E. Bataillon, 34095 Montpellier Cedex 5, France*

Received 10 January 2005; accepted 10 January 2005

Available online 10 February 2005

Abstract

The adsorption of dimeric cationic surfactants, made up of two ammonium species linked via a hydrophilic spacer group, i.e. $\text{Br}^-n\text{-C}_{12}\text{H}_{25}\text{N}^+\text{Me}_2\text{-CH}_2(\text{CH}_2\text{OCH}_2)_x\text{CH}_2\text{N}^+\text{Me}_2\text{-}n\text{-C}_{12}\text{H}_{25}\text{Br}^-$, referred to as 12-EO_x-12, onto silica has been studied in aqueous solution at 298 K and free pH.

The effect of the molecular structure on the adsorption of these cationic surfactants onto raw silica (SiNa) and HCl-treated (SiH) silica was investigated. For this purpose, batch microcalorimetry measurements of the differential molar enthalpy of dilution and that of adsorption were performed at 298 K. The enthalpy data were supplemented by the classical observations such as the adsorption isotherms.

The microcalorimetry results show that the adsorption mechanism and the aggregation at the solid–liquid interface do not depend on the spacer group length. Then, important quantitative differences are observed between the two silica surfaces. The investigated surfactants provide useful molecular probes for the characterization of the surface active sites onto treated and raw silicas. The amounts adsorbed allow the surface sites present in SiNa and SiH to be quantified.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Adsorption; Gemini surfactants; Silica; Calorimetry

1. Introduction

The identification of active sites on solid surfaces remains an important task for researchers and engineers working on the formulation of solid–liquid dispersions. The development of modern surfactants has been in rapid progress over the last two decades. Amongst the surfactant series that have received considerable attention are gemini molecules that contain more than one hydrophobic tail and hydrophilic head. The 12-*s*-12 type surfactants with *s* referring to a polymethylene spacer are good examples of geminis [1].

A previous study [2] has shown that these dimeric surfactants may be used as molecular rulers to probe the distribution of charged surface sites in silica. According to our interest in the understanding of adsorption

mechanism, a new surfactant series made up of two hydrophobic chains and two polar head groups connected covalently through a hydrophilic polyoxyethylene spacer, $\text{Br}^-n\text{-C}_{12}\text{H}_{25}\text{N}^+\text{Me}_2\text{-CH}_2(\text{CH}_2\text{OCH}_2)_x\text{CH}_2\text{N}^+\text{Me}_2\text{-}n\text{-C}_{12}\text{-H}_{25}\text{Br}^-$, was developed. These surfactants are referred to as 12-EO_x-12 with *x*=1,3,6-oxyethylene moieties. The aggregation properties of this new class of surfactants were recently reported [3,4] for the smallest spacer groups *x*=1–3.

This study deals further with the thermodynamics of adsorption of such cationic surfactants onto silica. The detailed description of the adsorption onto solids involves the knowledge of the mutual interactions amongst all components (i.e. solid, solution, and solvent) in the bulk solution and at the interface. Calorimetry measurements offer the opportunity of studying directly the different types of interaction in the system. This method allows the measurements of the differential molar enthalpy of micellization in the bulk solution and the

* Corresponding author. Tel.: +1 9467143243; fax: +1 9467143304.

E-mail address: charnay@univ-montp2.fr (C. Charnay).

differential molar enthalpy of adsorption onto divided solids in suspension.

The main purpose of the present investigation is to gain some thermodynamic insight into the adsorption mechanism of gemini cationics 12-EO_x-12 on two silica surfaces: a raw silica with a relatively high quantity of sodium ions at the surface (SiNa), and the same sample washed with HCl (SiH).

2. Experimental

2.1. Materials

The amorphous silica XOBO15 was supplied by Procatalyse S.A. (France) and used as received. The original material (SiNa) contains a relatively large quantity of sodium ions. It was also investigated after triple washing with hydrochloric acid (5N) and continuous rinsing with distilled water until no chloride and sodium ions were detected in the conductivity and silver nitrate test. The treated silica is called SiH. The specific surface area of the sample was determined by the BET method at 77 K and found to be 30 m² g⁻¹ independently of the treatment.

The gemini surfactants studied here, i.e. (oligooxa) alkanediyl- α,ω -bis(dimethyldodecylammonium bromide) called 12-EO_x-12 (with $x=1,3,6$), were synthesized in the laboratory. They are made up of two identical dimethyldodecylammonium moieties, linked at the level of the polar heads, via a hydrophilic spacer group. The various members of the homologue series differ in the number of ethylene oxide (EO) units in the spacer: $x=1,3,6$.

The water used throughout the experiments was deionized and purified with a Millipore Super Q System. Its pH was about 6 and its conductivity was about 5 $\mu\text{S m}^{-1}$.

2.2. Methods

2.2.1. Calorimetric experimental procedures

The calorimetric measurements were performed at 298 K using a batch microcalorimeter “Calostar” [5]. The

calorimeter contains a calorimetric cell, a magnet stirring system, and a syringe pump, which allows the reagents to be introduced into the cell at a given time and in given quantities. The homogeneity of the solution or suspension is ensured by a horizontal stirrer in the calorimetric cell and directly connected to the external part of the calorimeter. The thermistors, calibration coil, and injection inlet are immersed in the water solution or suspension. The calorimetric device is placed into a calorimetric metallic block, where the temperature is controlled with a precision of $\pm 5 \times 10^{-4}$ °C. The time of return to the baseline (after one aliquot injection) is about 30 min; the detector (thermistor) sensitivity is 0.05 $\mu\text{V } \mu\text{W}^{-1}$. The experimental procedure for measuring $\Delta_{\text{exp}}H$ consists of filling up the calorimetric cell with an aqueous suspension of silica, the quantity of water and the mass of silica introduced in the cell being, respectively, about 8 and 0.35 g (≈ 10.5 m²), and filling up the syringe with a micellar stock solution of the surfactant. When the thermal equilibrium in the calorimeter is attained (after 12 h), small amounts of the stock solution are injected into the suspension.

The surfactant micelles in the stock solution injected in the adsorption experiment are first destroyed by dilution in the calorimeter cell and then some of the resulting monomers are adsorbed at the solid-solution interface. Therefore, the determination of the differential molar enthalpy of adsorption requires the knowledge of the enthalpy of the surfactant dilution in pure water, under condition similar to those used in measuring the adsorption isotherm [5]. The calorimetric experiments of dilution of the stock solution were carried out in water saturated with either SiNa or SiH. For this purpose, the distilled water was brought into contact with a silica sample for several hours, and then the supernatant was collected.

2.2.2. Adsorption isotherms

Adsorption isotherms were determined according to the previously described method, known as the solution

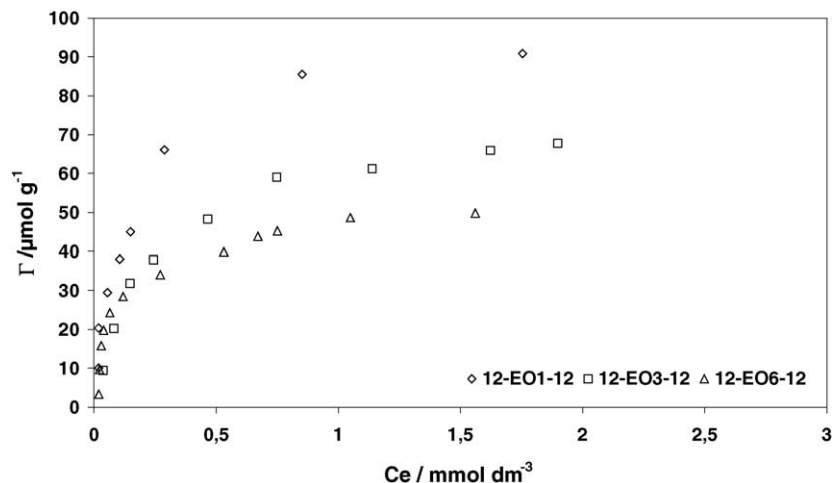


Fig. 1. Adsorption isotherms of 12-EO_x-12 onto SiNa at 298 K with Ce referring to the equilibrium surfactant concentration.

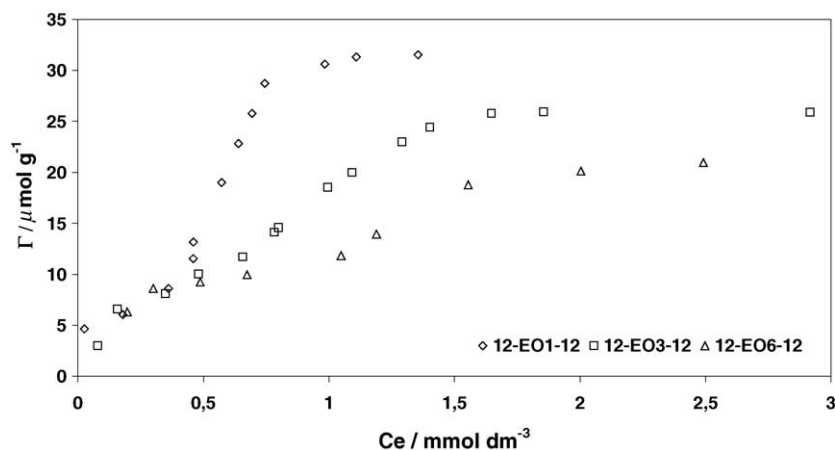


Fig. 2. Adsorption isotherms of 12-EO_x-12 onto SiH at 298 K with Ce referring to the equilibrium surfactant concentration.

depletion procedure [5]. The surfactant concentration in the supernatant was determined using a total carbon content analyser, Shimadzu TOC 5000.

3. Results

3.1. Adsorption isotherms

The adsorption isotherms of 12-EO_x-12 surfactants onto SiNa and SiH are represented in Figs. 1 and 2. It seems that both type of adsorption curves are quite similar. Three successive adsorption steps can be observed for low and moderate concentrations and a saturation plateau appears after the cmc is reached in the supernatant solution. For the three surfactants studied, the amount adsorbed onto SiNa is almost three times higher than that onto SiH (i.e. 91, 68, and 48 μmol g⁻¹ and 31.5, 25.9, and 20 μmol g⁻¹). These differences illustrate the effect of the chemical state of the silica surface on the quantity of surfactant adsorption and the dependence of the amount adsorbed upon the nature of the surfactant. In

fact, when the length of the spacer is higher, the adsorption quantity Γ is lower and this effect is the same for both silicas. The above results are similar to those obtained for the gemini cationic surfactants with a hydrophobic spacer, referred to as 12-*s*-12 [2].

3.2. Calorimetry

The main contribution of the present work is a calorimetric description of gemini surfactant adsorption onto two chemically different silica surfaces. The differential molar enthalpy of adsorption ($\Delta_{\text{ads}}H$) is determined from the thermal effect of the successive injections of the stock solution into the calorimetric cell containing silica particles in water suspension. During the introduction of n moles of surfactant into the cell, two phenomena occur: dilution of the stock solution and adsorption of the surfactant onto silica particles. The determination of the differential molar enthalpy of adsorption, therefore, needs precise dilution data (Fig. 3). All enthalpy curves of dilution present three particular regions, as previously reported [5,6].

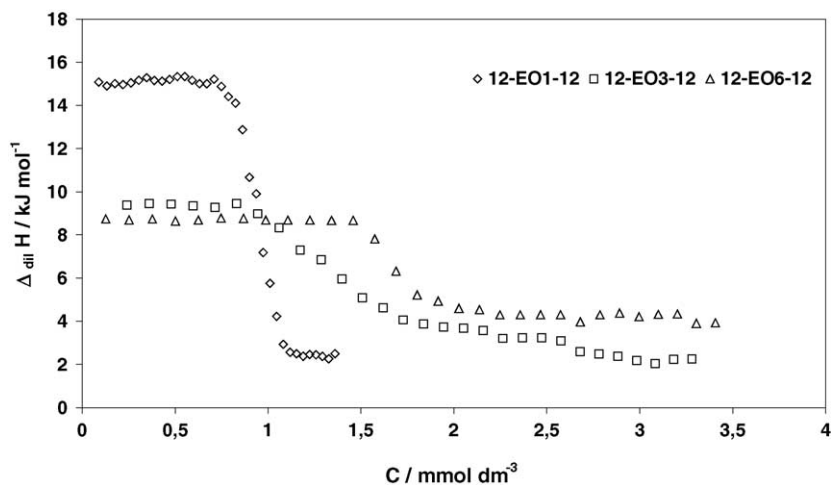


Fig. 3. Differential molar enthalpies of dilution for 12-EO_x-12 in water at 298 K.

Table 1

Amount adsorbed in the adsorption plateau region, enthalpies of micellization for the gemini surfactants adsorbed onto SiNa and SiH at 298 K

Surfactants	$\Gamma_{\max}/\text{SiNa}$ ($\mu\text{mol g}^{-1}$)	Γ_{\max}/SiH ($\mu\text{mol g}^{-1}$)	$\Delta_{\text{mic}}H^0$ (kJ mol^{-1})
12-EO ₁ -12	91	31.5	-12.6
12-EO ₃ -12	67.7	25.9	-6.9
12-EO ₆ -12	48	20.12	-4.5

The difference between the differential molar enthalpy values for the first and the second plateaux (respectively, monomeric and micellized states of the surfactant) allows a direct measurement of the enthalpy of micellization ($\Delta_{\text{mic}}H$) of 12-EO_x-12. All $\Delta_{\text{mic}}H$ values collected in Table 1 are negative, indicating that micelle formation is an exothermic, energetically favourable, process. Its sign is opposite to the dilution effect corresponding to micelle destruction and dilution of the resulting monomers. For all surfactants studied, the drastic decrease in $\Delta_{\text{dil}}H$ corresponds to the cmc. Comparison of the enthalpies of micellization for the investigated surfactants shows that surfactant self-assembly becomes less exothermic with increasing number of EO units in the spacer.

The curve 1 in Fig. 4 shows the variation of the differential enthalpy of adsorption for the 12-EO₁-12/SiNa system obtained from the integration of the experimental thermograms. The curve 2 represents the variation of the differential enthalpy of adsorption after the correction for the thermal dilution effect. The values of the differential molar enthalpy of adsorption ($\Delta_{\text{ads}}H$) of 12-EO_x-12 onto both silica samples are displayed in Figs. 5 and 6. As it was already observed for the 12-*s*-12 series [6], the enthalpy curves exhibit four steps which describe the adsorption process at the silica-solution interface:

- a decrease in the exothermic value of $\Delta_{\text{ads}}H$ at very low amounts adsorbed;
- an increase in the exothermic value of $\Delta_{\text{ads}}H$ after an enthalpy minimum;
- an exothermic plateau;
- a decrease in $\Delta_{\text{ads}}H$ at the end of the adsorption range.

4. Discussion

4.1. 12-EO_x-12/SiNa system (Fig. 5)

All enthalpic curves (Fig. 5) for the surfactants investigated in the present work have the same general shape. At the beginning of the adsorption range, exothermic enthalpy values are observed and then they become slightly endothermic at a coverage ratio of about 0.1 for the shorter spacers. This endothermic minimum appears at higher coverages when the number of EO groups increases.

The first adsorption step (presumably ion exchange), which involves electrostatic interaction between surfactant cation and negative sites of the silica surface, is strongly influenced by the spacer length and by the hydrophilic character of the spacer group. For 12-EO₁-12 (shortest spacer), the extremum value is more positive than those obtained with 12-EO₃-12 and 12-EO₆-12 (longer spacers). The enthalpic effect in this first step may be ascribed to the following phenomena:

- the destruction of the interfacial water, which gives rise to an endothermic effect.
- the ion exchange of sodium cations with dimeric surfactant ions, which involves the release of sodium from the surface and then their rehydration (exothermic effect) and a partial dehydration of bromide counter-ions binding to one or two cationic heads of the surfactant (endothermic effect). This latter effect depends on the spacer length and on the stoichiometry of the exchange between sodium and dimeric surfactant ions.

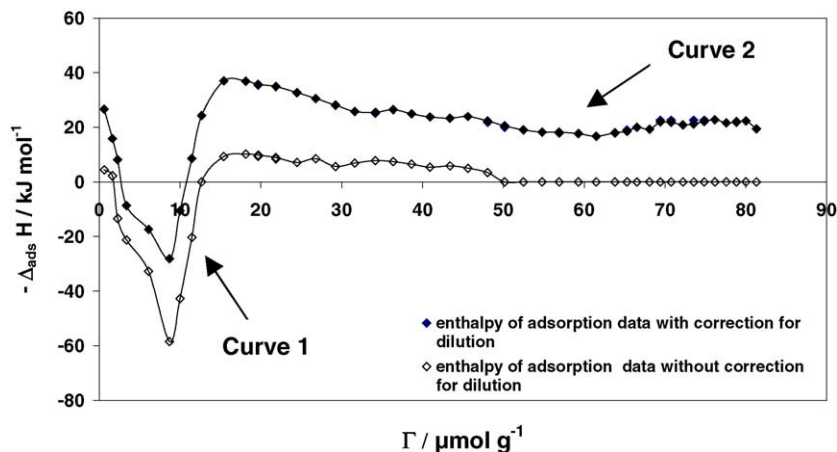


Fig. 4. Variation of the differential molar enthalpy of 12-EO₁-12 onto SiNa at 298 K.

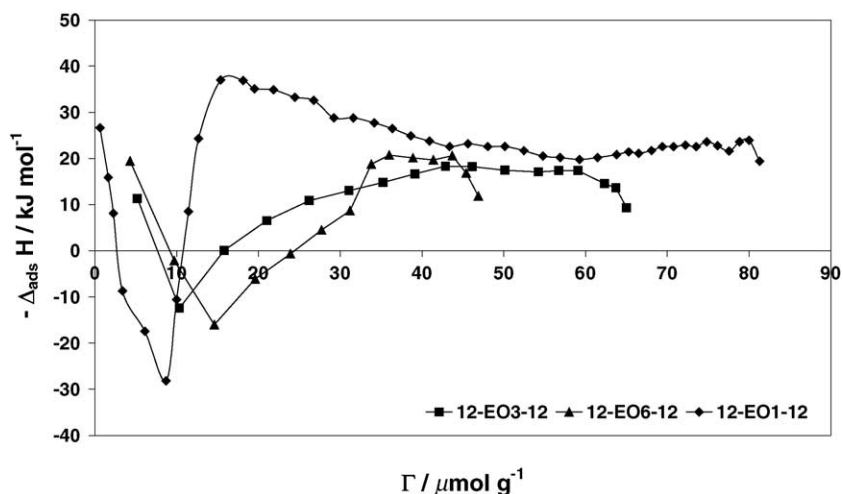


Fig. 5. Variation of the differential molar enthalpy of adsorption for 12-EO_x-12 onto SiNa at 298 K.

After the minimum has been reached, an exothermic increase in the differential molar enthalpy of adsorption is observed. In this second step of adsorption, the driving force is mainly due to hydrophobic interaction between the hydrophobic tails of the surfactant molecules adsorbed during the first stage and those being freshly adsorbed from the solution.

The appearance of the exothermic plateau means that the interfacial aggregation is the unique mechanism of adsorption at this stage. As it was assumed for the adsorption of 12-*s*-12 surfactants on the same silica surface, the aggregates grow only in size here [6].

4.2. 12-EO_x-12/SiH system (Fig. 6)

On the treated silica (SiH), negative surface sites are very scarce ($2.1 \mu\text{mol g}^{-1}$ for Na⁺ and $0.3 \mu\text{mol g}^{-1}$ for H⁺) [6]. Thus, even in this case, the negative sites created by the proton desorption are much fewer than those corresponding to

the displacement of sodium ions. For this reason the initial endothermic decrease, corresponding to the beginning of the individual surfactant adsorption, is weaker compared to the endothermic minimum for SiNa. The endothermic values for 12-EO₁-12/SiNa and 12-EO₁-12/SiH systems are 28 and 11 kJ/mol, respectively. The negative sites created by the proton desorption are labile on the one hand and, on other hand, their displacement from the silica surface should be easier. The displacement of proton and the water molecule from SiH should be also energetically more favourable. Consequently, the energetic minimum for SiNa and SiH surfaces and for 12-EO₁-12 surfactants is shifted towards the positive $\Delta_{\text{ads}}H$ values. The same phenomena are observed for 12-EO₃-12 adsorbed on the two silica surfaces (Fig. 7).

Beyond this difference, the adsorption process at higher equilibrium concentrations is governed by interfacial aggregation, which is described by the horizontal $\Delta_{\text{ads}}H$ values up to the saturation region. Obviously, the quantity adsorbed for a given surfactant is significantly different and, for this

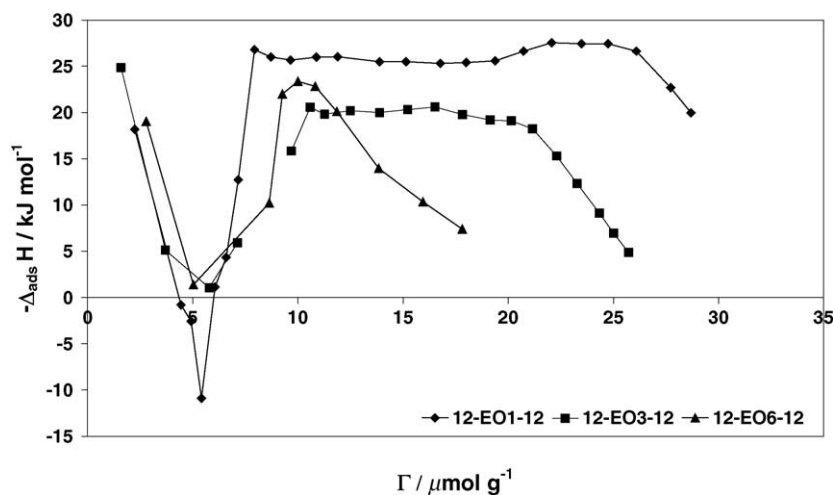


Fig. 6. Variation of the differential molar enthalpy of adsorption for 12-EO_x-12 onto SiH at 298 K.

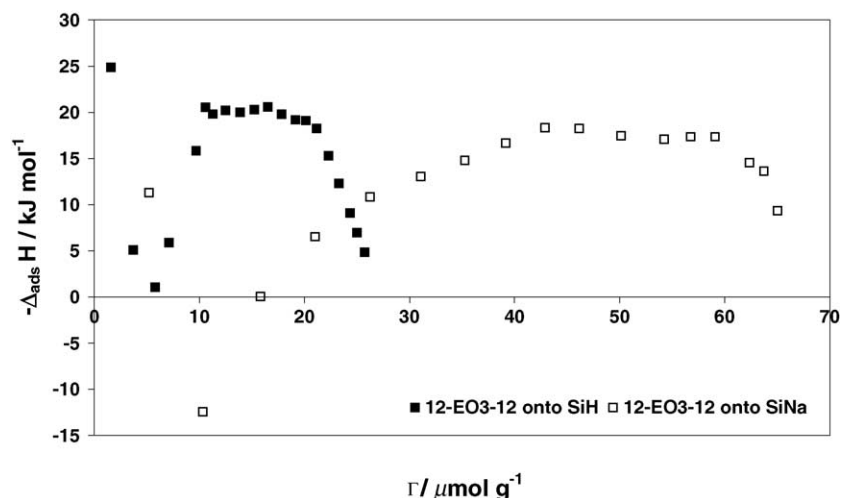


Fig. 7. Differential molar enthalpies of adsorption for the 12-EO₃-12/SiNa and 12-EO₃-12/SiH systems at 298 K.

reason, one observes a drastic decrease in the enthalpy for the same molecule and for different chemical states of the silica surface. The calorimetric results show that the variation of the enthalpy during the third step, arising from the growth of the interfacial aggregates, is more exothermic for SiH. It was stated [6] that this effect is due to the formation of pinned micelles more structured and less hydrated than the bilayer formed on SiNa.

5. Conclusion

A significant contribution to the study of the surfactant adsorption at the solid–liquid interface was due to the determination of the differential molar enthalpy of adsorption under the same physicochemical conditions as those applied during the adsorption isotherm measurements.

The profile of an enthalpy curve is complex because various adsorption mechanisms are present successively or simultaneously. The successive steps of adsorption can be

identified and differentiated owing to calorimetric investigation. On the SiNa surface, the bilayer coverage is more extended compared to that on the SiH surface, where the aggregation process gives rise to pinned micelles. Moreover, the chemical state of the silica surface is very important and determines the shape of the interfacial aggregates at the end of the adsorption process.

References

- [1] R. Zana, *Specialist Surfactants*, Chapman & Hall, London, 1997 (Chapter 4).
- [2] M. Chorro, C. Chorro, O. Dolladille, S. Partyka, R. Zana, *J. Colloid Interface Sci.* 210 (1999) 134.
- [3] M. Dreja, W. Pyckhout-Hintzen, H. Mays, B. Tiede, *Langmuir* 15 (1999) 391–399.
- [4] S.D. Wettig, X. Li, R.E. Verrall, *Langmuir* 19 (2003) 3666–3670.
- [5] J.L. Trompette, J. Zajac, E. Keh, S. Partyka, *Langmuir* 10 (1994) 812–818.
- [6] L. Grosmaire, M. Chorro, C. Chorro, S. Partyka, *J. Colloid Interface Sci.* 242 (2001) 395.