CALORIMETRIC STUDIES OF CATIONIC SURFACTANT ADSORPTION AT LOW SURFACE COVERAGES ON DIFFERENT SILICA SAMPLES

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Abstract

Calorimetric measurements of adsorption for the surfactant (benzyldimethyldodecylammonium bromide) and its polar head-group (benzyltrimethylammonium bromide) from aqueous solutions on two different silica surfaces (hydrophilic and hydrophobic one) allow a more detailed picture of the subsequent stages of the adsorption process to be drawn. It is possible to determine more precisely a boundary between the adsorption of individual molecules and the formation of surface aggregates. The local disruption of the structure of the interfacial water molecules by surfactant cations gives an endothermic contribution to the total enthalpy of displacement. This contribution depends on the length of alkyl chain as well as on the type and the origin of solid surface.

Keywords: adsorption, calorimetry, cationic surfactants, silica

Introduction

The adsorption of cationic surfactants from aqueous solutions onto silica depends strongly on the properties of the solid surface. These properties can vary extensively according to the method used for the preparation of a silica sample. Usually, two types of amorphous silica surfaces are investigated [1, 3, 6–8].

The first one, surface-hydroxylated amorphous silica obtained by precipitation of silicic acid from an aqueous solution, is hydrophilic in nature. In water at higher *pH* values, such silica particles develop a negative charge on their surface [1–8]. Thus, in the first stage of adsorption surfactant cations can adsorb as individual ions with the ionic groups directly opposite negative sites on the surface. They displace water molecules and exchange with protons, and other counterions present at the solid/water interface [2, 5]. It is highly probable that the apolar moieties of surfactant molecules assume vertical or angled orientations on a hydrophilic surface. In consequence, the phenomenon is usually ascribed only to electrostatic interactions and the role of a hydrophobic chain in

the surfactant molecule is often neglected [4, 6–8]. At higher surfactant concentrations in the bulk phase, one can distinguish a region of the formation of different surface aggregates provoked by the hydrophobic interaction between alkyl chains of different surfactant molecules.

The other type of surface behaviour is inherent in anhydrous amorphous silica particles formed at high temperatures in the gas phase. These samples are mainly hydrophobic. However, their surface may be partly hydrated as SiOH groups which will interact with water molecules and become the source of charge of low surface density [1, 3]. At low coverages the cationic head-groups of surfactant interact with the negative sites and are oriented with the apolar chains parallel to the adjacent hydrophobic patches on the silica surface. At higher coverages hydrophobic association on the surface occurs to form a close-packed monolayer [6–8].

In studying adsorption from surfactant solutions onto silicas, very little attention has been paid to the region of low surface coverages where the adsorption of individual surfactant cations takes place. This first stage determines the whole adsorption process and consequently it is necessary to elucidate its mechanism more precisely. It has a competitive character and all the effects arising from the displacement process should be taken into account. The appropriate calorimetric study, supplemented by adsorption measurements, allows a more detailed description to be obtained.

Experimental

Two types of silica samples were used. The first, RP 63-876 hydrophilic silica (Rhône-Poulenc, France), was nonporous and its specific surface area was found to be 40 m^2/g (BET., nitrogen gas adsorption at 77 K). The other sample, Cab–O–Sil hydrophobic silica (grade M5, Cabot Corporation, Germany), had a specific surface area of 207 m^2/g. Both silicas were used as received.

The surfactant, benzyldimethyldodecylammonium bromide (BDDAB), was a product of Fluka (France). It was purified by recrystallizing from ethylacetate and water. Its critical micellar concentration (cmc) and the specific surface area at the water/air interface at 298 K are equal to 5.6×10^{-3} mol/kg and 70.5 A^2/molecule, respectively.

In order to obtain information about the role of the alkyl chain during the first stage of the process, the adsorption of surfactant was compared with that of its polar head-group. The polar head-group, benzyltrimethylammonium bromide (BTMAB), was supplied by Fluka (France) and used as received.

Deionized water was used as a solvent. The solutions were not buffered to any special *pH* value.

The adsorption experiments were carried out in stoppered glass tubes. Each tube contained a known amount (about 0.5 g) of silica and the same mass (about 20 g) of aqueous solution of given molality was shaken for 12 h at a constant temperature (298 K and 308 K). The silica was then separated from the supernatant by centrifugation (13000 rpm during 20 minutes). The concentration of ions in the supernatant was determined spectroscopically (UV Varian) in the interval 240–280 nm at $\lambda_{max} = 262.8$ nm for both types of molecules.

Enthalpies of displacement for BDDAB and BTMAB were measured with a Montcal calorimeter [9]. It is a microcalorimetric batch technique which involves the introduction of adsorbate from outside of the calorimetric cell to the suspension maintained in a homogeneous state by an effective agitation. A small amount of the surfactant stock solution is injected into the calorimetric cell and the detected temperature change is a direct measure of the enthalpy change corresponding to this step of adsorption. The related change in number of moles of solute adsorbed on the surface is determined graphically or numerically from the adsorption isotherm.

Since the whole concentration range should be covered, from the beginning of the isotherm to its plateau, a stock solution must have a concentration greater than the cmc. The stock solution of molality 10 times greater then the cmc was injected into the calorimeter cell containing 16 g of solvent and 1 g of silica by steps of 0.9 mg/sec. In such a case, it is necessary to subtract from the total enthalpic effect a dilution correction term which results from the destruction of micelles and dilution of unmicellized species. The apparent differential molar enthalpy of displacement was evaluated by means of the following approximation

$$\Delta_{dpl} h = \frac{\Delta(\Delta H_{exp} - n_2^i \cdot \Delta_{dil} h)}{\Delta_a n_2}$$

where ΔH_{exp} is the experimentally measured enthalpy for the adsorption experiment; n_2^i is the number of moles of solute injected at each step; $\Delta_a n_2$ is the change in number of moles of solute adsorbed on the surface; $\Delta_{dil} h$ is the molar integral enthalpy of dilution.

The dilution curves of the surfactant at two different temperatures are presented in Fig. 1. The concentration of the stock solution injected into the calorimetric cell was the same as that for the adsorption experiment. It can be noted that the enthalpic effect of dilution in the region of low molalities (below the cmc) is almost constant so the dilution correction term also remains constant. The experimentally measured enthalpies of dilution for the polar headgroup at both temperatures were too weak to be detected. The dilution correction term could be neglected in this case.
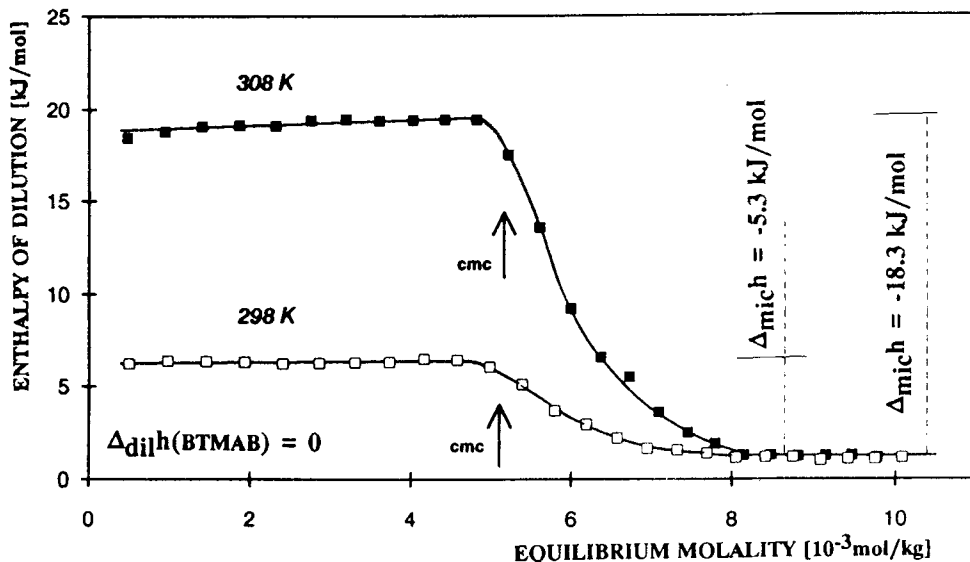
Fig. 1 Differential enthalpies of dilution for BDDAB in water at 298 K (open squares) and 308 K (black squares); $\Delta_{mic}h$ represents the molar enthalpy of micellization at a given temperature

Results and discussion

Hydrophilic silica surface

The common interpretation of the adsorption phenomenon on this type of silica surface assumes that adsorption at low surface coverages results only from coulombic interactions between surfactant ions and the negatively charged surface sites. It is doubtful that an apolar chain would lie flat on a hydrophilic surface and affect directly this initial stage. However, adsorption of individual surfactant cations, which takes the form of cation exchange with some counterions, can induce important changes in the energetic state of aqueous medium. This would give a considerable contribution to the free energy change. The effect will probably depend highly on the length of alkyl chain in the surfactant molecule and the type of counterions.

The silica sample used in the present study was obtained by precipitation from sodium silicate solution. Consequently, some of the exchangeable sites at the silica/water interface are occupied by Na^+ ions. Figures 2–4 illustrate the comparative study of the surfactant (BDDAB) and its polar head-group (BTMAB) at two different temperatures.
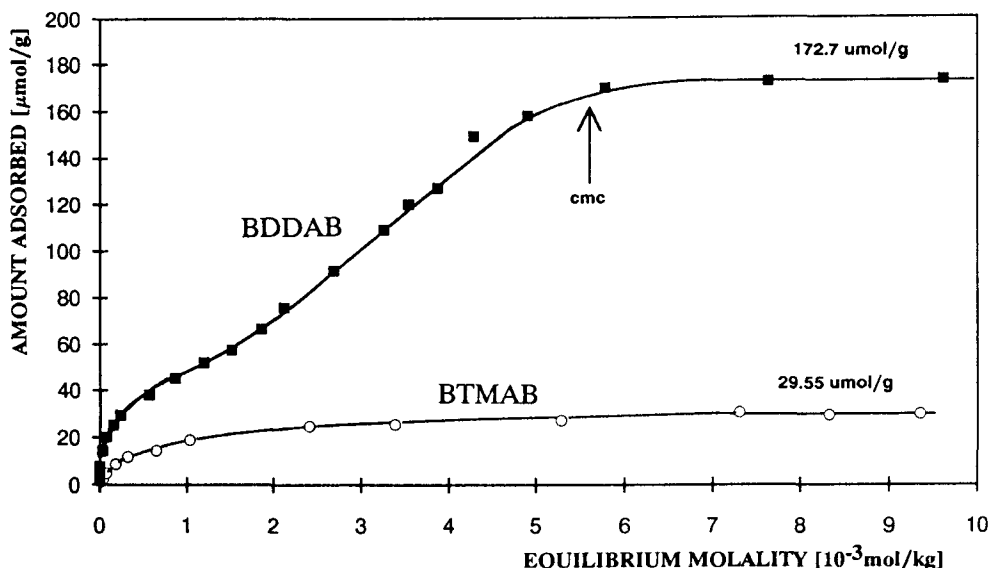
Fig. 2 Adsorption isotherms for BDDA$^+$ (black squares) and BTMA$^+$ (open circles) ions onto precipitated silica from water at 298 K (pH free)

Figure 2 shows the adsorption isotherms at 298 K. The adsorption of BDDAB is greater than that of BTMAB over the whole concentration range which illustrates an important role of the apolar moiety of surfactant ions in promoting the adsorption process. The passage between the individual and hydrophobic regions on the isotherm is very narrow and it does not take the form of a plateau. This means that already at the end of individual adsorption of surfactant ions at low surface coverages, hydrophobic interactions are sufficiently strong to provoke the formation of surface aggregates. The hydrophobic association does not occur at all in the case of polar head-group where adsorption is ascribed only to electrostatic interactions.

The differential molar enthalpies of displacement at 298 K presented in Fig. 3. The enthalpy of the polar head-group is exothermic and decreases continuously with increasing quantity of adsorption up to about 20 µmol/g. Such variation of the enthalpy of adsorption with surface coverage ratio is due to the effect of surface heterogeneity. BTMA$^+$ ions are located in the inner part of the adsorbed layer. The enthalpic effect of displacement becomes athermal above 20 µmol/g. It seems that these polar head-group cations are located in the outer part of the adsorbed layer where the enthalpic effects of cation exchange are completely neutralized by some other energy changes.

One can distinguish on the enthalpic surfactant adsorption curve an endothermic region with a maximum enthalpy of displacement. Since the process of

displacement is endothermic, it must be driven entropically; the negative value of the free energy of displacement results from the positive entropy change for the process. It can be noted that the endothermic maximum occurs at about 20 μmol/g and up to this critical value the initial part of the enthalpy curve resembles that of the polar head-group but the corresponding values are shifted down. It is obvious that there exists an endothermic contribution to the total enthalpy change which is due to the presence of a long hydrophobic chain in the surfactant ion. In the adsorption interval above 20 μmol/g, the enthalpy is dominated by hydrophobic interaction between alkyl chains.
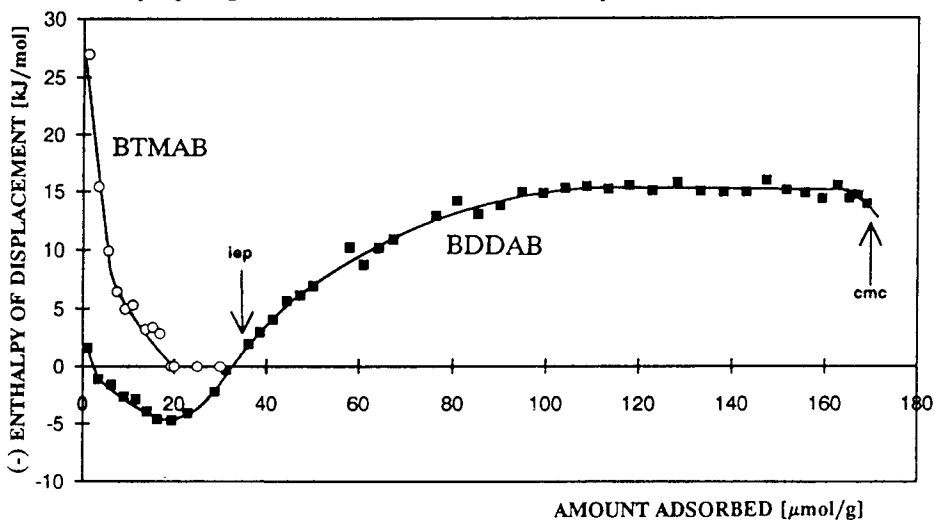

Fig. 3 Differential enthalpies of displacement for BDDAB (black squares) and BTMAB (open circles) onto precipitated silica from water at 298 K (pH free)

The theoretical analysis of the calorimetric data indicates that the changes in the energy of interaction which are favourable to adsorption must be balanced against some other energy changes unfavourable to adsorption. The endothermic effect is markedly important in the case of the surfactant molecule which contains an alkyl chain in its structure. There arises a question concerning the origin of this effect.

It is known that the presence of a surface exerts a considerable effect on the structure of water molecules near it [10, 11]. In the presence of moderate concentrations of monovalent sodium ions adsorbed specifically at the silica surface, additional structuring of water takes place due to the binding of free water molecules by cations [12]. Organic ions $BTMA^+$ and $BDDA^+$, bigger and much more hydrophobic than Na^+, will destroy this arrangement near the silica surface. The local disruption of the structure of the interfacial water molecules and the release of some of them to the bulk phase is an endothermic process accom-

panied by a significant increase in the entropy of the system. The effect is more pronounced in the case of surfactant ion, $BDDA^+$, the destructive power of which is amplified by the presence of the alkyl chain.
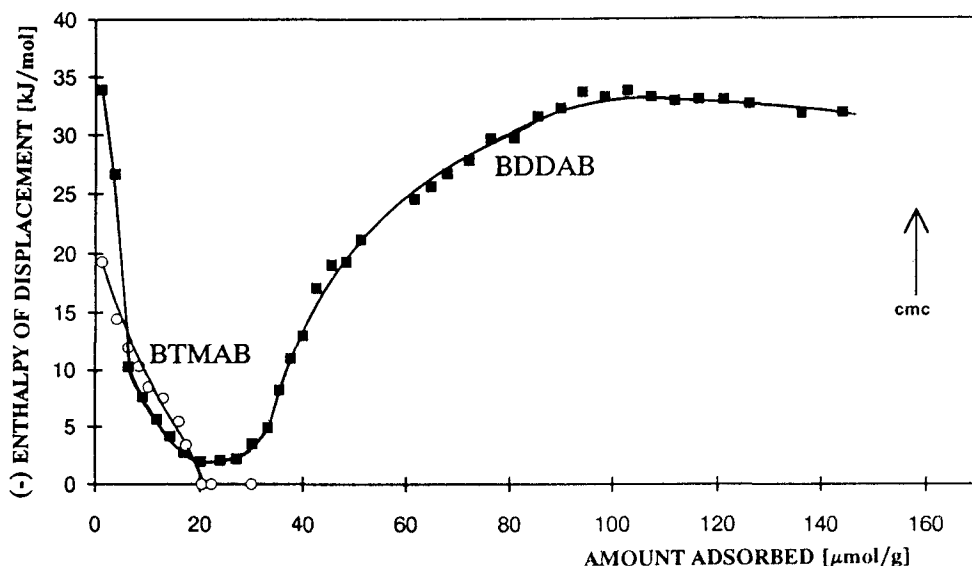

Fig. 4 Differential enthalpies of displacement for BDDAB (black squares) and BTMAB (open circles) onto precipitated silica from water at 308 K

In order to find other arguments which can confirm this idea, adsorption and calorimetric measurements were carried out at a higher temperature. The arrangement of the interfacial water decreases at higher temperatures and so does the endothermic contribution. The enthalpies of displacement at 308 K are presented in Fig. 4. All the curves keep their general shapes and the minimum on the surfactant curve is still at 20 μmol/g. The mechanism of the process does not change drastically and the boundary between the individual adsorption and the formation of surface aggregates occurs at the same amount of adsorption. Since the enthalpic curve for the surfactant lies completely above the zero-energy level, the displacement is exothermic. It is obvious that the solid-solute interaction hardly changes in the investigated temperature range; the endothermic contribution becomes apparently smaller.

Hydrophobic silica surface

It is evident that the arrangement of the interfacial water will depend strongly on the type of silica surface. On a hydrophobic surface of Cab–O–Sil the number of charged sites is small and there are, perhaps, no sodium counter-

ions which would enhance a long-range effect of the surface on the arrangement
of water molecules. In consequence, alkyl chains of surfactant molecules can
penetrate into the aqueous medium in the vicinity of the solid surface and inter-
act directly with a hydrophobic part of this surface. Thus, the adsorption will
be chain-length sensitive already in this region. The surfactant adsorption on
both types of silica have been compared and the results are presented in Figs 5
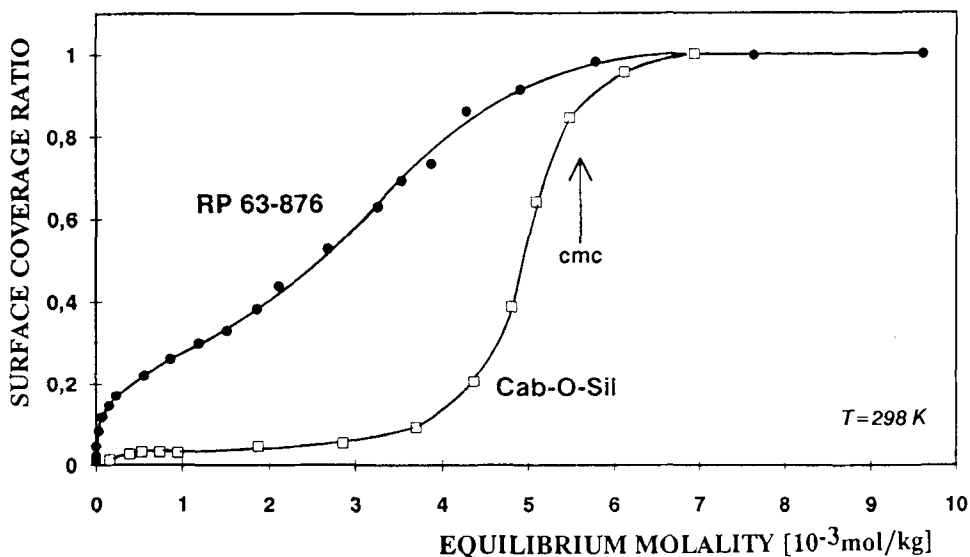and 6.

Fig. 5 Adsorption isotherms for BDDAB on a hydrophilic (black circles) and a hydrophobic
(open squares) silica surface from water at 298 K (*pH* free)

Figure 5 shows the adsorption isotherms. The general shapes are very simi-
lar but there is a well-marked first plateau on the Cab–O–Sil curve. It is evident
that the number of negative sites on the hydrophobic surface is much smaller
and a region of a sharp change in the amount of adsorption lies at higher equi-
librium molalities. The first plateau corresponds to such a situation where the
increase in the bulk concentration is not able to increase the quantity of adsorp-
tion. When the chemical potential of the surfactant in the bulk phase becomes
sufficiently strong to provoke the hydrophobic association on the surface (equi-
librium molality approaches the cmc), the adsorption increases rapidly. Surfac-
tant molecules, adsorbed on hydrophobic sites in this region, are vertically
orientated with their ionic heads toward the solution phase.

The results of calorimetric measurements confirm the idea that the hydro-
phobic silica surface does not induce any strong arrangement of water mole-
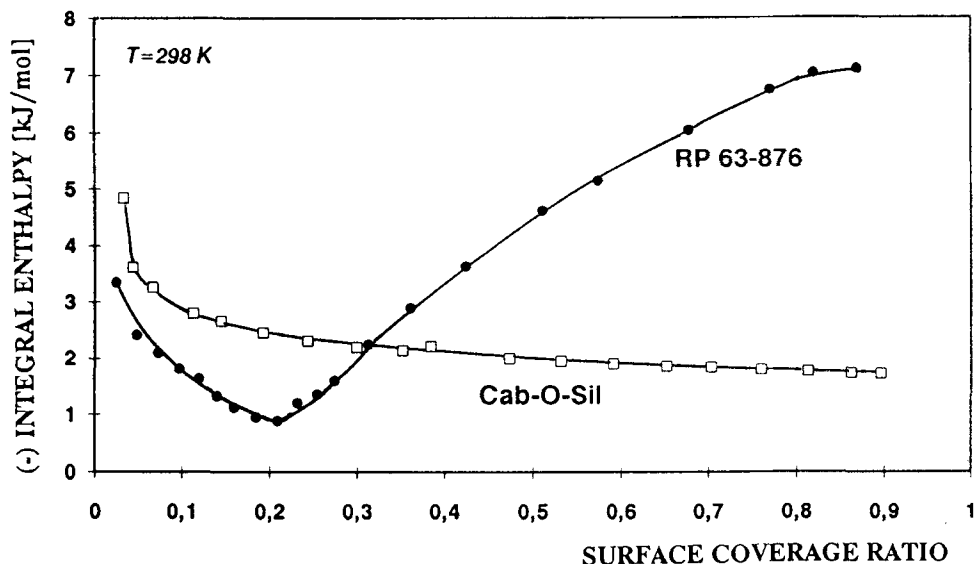cules near it. Figure 6 presents the integral enthalpies of displacement for the

Fig. 6 Integral enthalpies of displacement for BDDAB on a hydrophilic (black circles) and a hydrophobic (open squares) silica surface from water at 298 K (*pH* free)

surfactant on both types of silica at 298 K. In the case of Cab–O–Sil the effect of displacement is exothermic over the whole adsorption range. In the beginning, the integral enthalpy decreases due to the surface heterogeneity of negatively charged sites, and then changes linearly with increasing surface coverage ratio. The latter corresponds to the hydrophobic interactions on the surface which are energetically homogeneous.

Conclusion

Comparative calorimetric measurements for the individual adsorption of long-hydrophobic-chain surfactant molecules on different solid samples seem to be a promising way for studying the effect of structuring of water molecules in the vicinity of these surfaces. Such measurements make possible some insight into the wettability of these solid samples.

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Zusammenfassung — Kalorimetrische Messungen der Adsorption der oberflächenaktiven Substanz (Benzyldimethyldodecylammoniumbromid) und ihrer polaren Kopfgruppe (Benzyltrimethylammoniumbromid) aus wäßriger Lösung an zwei verschiedenen Siliziumdioxidoberflächen (einer hydrophilen und einer hydrophoben) erlauben ein detailierteres Bild der nachfolgenden Schritte des zu beschreibenden Adsorptionsprozesses. Es besteht die Möglichkeit, eine schärfere Grenze zwischen der Adsorption einzelner Moleküle und der Bildung von Oberflächenaggregaten zu bestimmen. Die lokale Störung der Grenzflächen-Wassermoleküle durch die Kationen oberflächenaktiver Substanzen liefert einen endothermen Beitrag zur Gesamtenthalpie des Austausches. Dieser Beitrag ist abhängig von der Länge der Alkylkette als auch von Typ und Ursprung der festen Oberfläche.