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Adsorption of Cationic Surfactants on Silica. Surface Charge Effects

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The surface charge of Aerosil OX50 in an aqueous dispersion has been studied in the presence of cationic surfactants (alkylpyridinium chlorides and trimethylammonium bromide) as a function of pH and salt concentration. The measurements were complemented with surfactant isotherms. To investigate the effect of the aliphatic surfactant tail, the surface charge–pH curves have also been measured in the presence of tetramethylammonium bromide (TMAB). At low salt concentration the surfactant isotherms show a two-step behavior. In the first step the surface charge follows the surfactant adsorption, indicating that head-on adsorption occurs. In the second step the surface charge increases only slightly. Comparison of the results for the surfactants and TMAB shows that the surface charge adaptation is strongly affected by the hydrocarbon tail and that the kind of head group is of secondary importance. Up to the first pseudoplateau, the molecules adsorb with their head groups and tails on the surface. For the second part of the isotherm, surfactant self assembly occurs. At high salt concentration the initial surface charge is relatively large and the surface charge adjustment is small. Due to the relatively large surface charge the surface is less hydrophobic and hydrophobic interactions with the surface become less probable. Instead hydrophobic tail–tail interactions become important also in the lower part of the isotherm. Surfactant self assembly occurs both before and after the surface charge is compensated by the surfactant charge.

Introduction

Silica is a classical sorbent to study adsorption of cationic surfactants on negative surfaces. The large impact of surfactant adsorption phenomena on silica for many technical applications has led to a large number of experimental and theoretical studies. The main experimental features of adsorption of cationic surfactant on silica have been demonstrated in refs 1–10. The adsorption appeared to be dependent on surface charge density, pH, surfactant structure, and electrolyte concentration. On the basis of these results it was established that the driving forces for adsorption of cationic surfactants on silica are the Coulombic attractions between surfactant ions and charged surface groups and the hydrophobic interactions between hydrocarbon moieties. But specific interactions between the surfactant ions and the surface, leading to a better screening of the surface charge density (or briefly the surface charge), can also have a pronounced effect on adsorption processes especially at surfactant concentrations below the critical micelle concentration

(cmc). In most of the preceding references little attention has been given to this aspect. Recent work on silica^{11,12} and rutile¹³ surfaces has shown not only that adsorption of surfactants varies strongly with pH but also that the ionization of the surface groups increases upon adsorption of the ionic surfactant. This change in surface charge leads to a change of pH in solution. The fact that often only the initial pH is specified is the reason why it is so difficult to make a quantitative comparison between adsorption isotherms obtained in different studies. Actually, the most widely used method to determine adsorption isotherms is to measure the surfactant depletion from a solution brought in contact with adsorbent. The pH change that occurs depends on the surface area to solution volume ratio and on the surfactant concentration. If no pH control is made, the pH values may vary along the isotherm and from isotherm to isotherm.

In general, the surface charge of silica is well studied. Silica has its isoelectric point (iep) at about pH 2 and a salt concentration dependent surface charge.^{14–18} The charge–pH curves have a characteristic shape that is different from that of other well studied metal oxide surfaces.^{19–21} Direct potential measurements using the ISFET technique²² and modeling studies²¹ indicate that the surface potential of silica as a function of pH is highly

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Table 1. Critical Micelle Concentrations of DPC, CPC, and CTAB

surfactant	KCl, mol/dm ³	temp, °C	cmc, mmol/dm ³
DPC	0.001	25	16.5
	0.01	25	13.6
	0.1	25	5.3
CPC	0	25	0.9
	0.01	25	0.4
	0.1	25	0.16
CTAB	0.001	25	0.82
	0.01	25	0.49
	0.1	25	0.23

non-Nernstian. This behavior also distinguishes silica from the other metal oxides. Though the surface properties of silica in electrolyte solutions are rather well studied, the mechanism of charge formation in surfactant solutions is not well understood and consistent data are absent in the literature. Therefore in the present study the effect of surfactant adsorption on the surface charge of silica is investigated in detail. It will be shown that this type of information is also very useful for the study of the structure of the adsorbed layer.

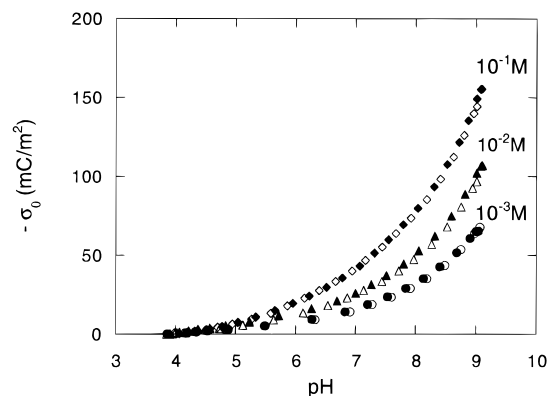
Adsorption and surface charge isotherms in the presence of various KCl concentrations have been measured for two surfactants with different tail lengths: dodecylpyridinium chloride and cetylpyridinium chloride (hexadecylpyridinium chloride) briefly referred to as DPC and CPC. These surfactants have been selected because their concentration can be easily determined using UV spectroscopy. As a further check of both head-group effect and the effect of a hydrophobic moiety in a surfactant molecule, charge–pH curves in KBr solutions in the absence or presence of cetyltrimethylammonium bromide (CTAB) and in tetramethylammonium bromide (TMAB) solution were investigated.

Materials and Techniques

Chemicals. Water was purified using an Elgastat UHP unit. KCl and KBr were received from Merck and were proanalysis quality. Tetramethylammonium bromide (TMAB) was obtained from Fluka and was used without further purification. DPC was synthesized from the appropriate chloroalkane and pyridine, using the method of Colichman.²³ CPC and CTAB were obtained from BDH and were used without further purification. To check the purity of the surfactants, the surface tension (γ)–log concentration curves in the absence of salt were determined at 20 °C by the Wilhelmy plate method. For none of the surfactants were minima in the γ –log c curves obtained, which indicated the absence of strongly adsorbing impurities. The observed critical micelle concentrations (cmc's) were in good agreement with literature values.²⁴ For an easy comparison, relevant cmc values of these surfactants, taken from ref 24, are summarized in Table 1.

Adsorbent. A pyrogenic unporous silica Aerosil 0 × 50 (Degussa) with a BET surface area of 50 m²/g and mean particle size of 40 nm was used. The silica is obtained from SiCl₄ at high temperature and is known to have a rather low concentration of surface hydroxyl groups (about 4 OH nm⁻²).²⁵

Surface Charge–pH Isotherms. Surface charge–pH curves of Aerosil OX50 in KCl or KBr solutions both in the absence and presence of surfactants or TMAB were determined at 25 °C using an automatic titration setup, described in ref 26. For the measurements 50 mL of solution and 0.4 g of Aerosil were mixed and sonified during 5 min. Before the titration was started the

**Figure 1.** Charge–pH curves for Aerosil OX 50 at three KCl (open symbols) and KBr (dark symbols) concentrations.

Aerosil suspension was purged with nitrogen for at least 0.5 h at a pH of about 3.5. The Aerosil suspension was titrated between pH 3.5 and pH 9 using 0.1 M KOH and 0.1 M HCl. To be able to calculate the surface charge values, blank titrations, i.e. electrolyte titrations in the absence of Aerosil, were performed. Blank results were checked by comparing them with theoretical calculations. Upon good agreement the theoretical blanks corresponding exactly with the suspension titrations can be calculated. Thus obtained theoretical blanks were subtracted from titration data in the presence of Aerosil to calculate the relative surface charge density. At pH < 4 the surface charge of silica asymptotically approaches zero.^{19–21} See also the discussion of Figure 1. Therefore, the relative surface charge curves were transformed into absolute surface charges by assuming that the surface charge at pH 3.5 was negligible in all cases.

Adsorption Isotherms. Adsorption isotherms were measured at room temperature (22 ± 2 °C) using the depletion method. To prepare the silica suspension, an appropriate amount of Aerosil was weighed into a 10-mL polycarbonate tube and 4 mL of KCl solution was added. The suspension was then sonified for 5 min, and the pH was adjusted using 0.01 M or 0.1 M KOH and 0.01 M HCl. Subsequently surfactant solutions of the required pH were added to give a total volume of 8 mL. After the mixture was shaken by hand the pH was measured and readjusted to its original value. After end-over-end rotation for 2 h the pH was measured again and, if necessary, readjusted. This process was repeated until no further changes in pH were observed. Equilibrium was then achieved, and aerosil was separated from the solution at 20,000 rpm in a Beckman J2-21 centrifuge. The UV absorption of the pyridinium ion in the supernatant was measured at 260 nm. The molar extinction coefficient for both DPC and CPC was found to be 4100 dm³/(mol cm).

By recording the additional amount of KOH or HCl required to keep the pH constant after surfactant addition, the surface charge adjustment of the silica has been calculated, and by combining this information with the initial surface charge, the equilibrium surface charge isotherms have been obtained.

Experimental Results

Surface Charge–pH Isotherms. The effect of pH on the surface charge of Aerosil, in the absence of surfactant, measured at three KCl and three KBr concentrations is shown in Figure 1. No significant differences between the two electrolytes were observed. Results are in good agreement with existing literature values.^{14–18} The surface charge density of silica increases with pH, being more pronounced at pH > 6. As expected,²¹ the isotherms superimpose below pH 4.0, where they nearly asymptotically approach zero surface charge. As a consequence of this asymptotic behavior, it is not possible to establish an intersection point between the isotherms measured at different salt concentrations and to determine the point of zero charge from this intersection point. The asymptotic approach of the pzc illustrates that the charging of SiO₂ is different from that of other metal oxides.²¹

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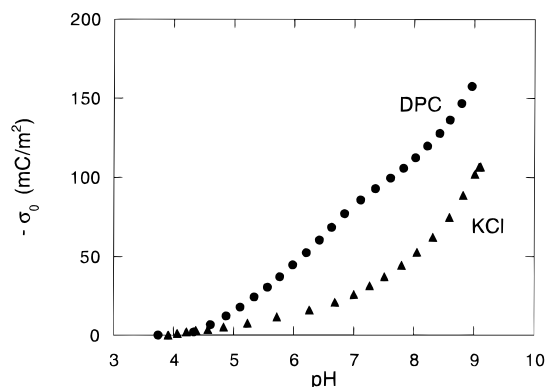


Figure 2. Charge–pH curves of Aerosil OX 50 in 0.01 M KCl in the absence and presence of 0.02 M DPC.

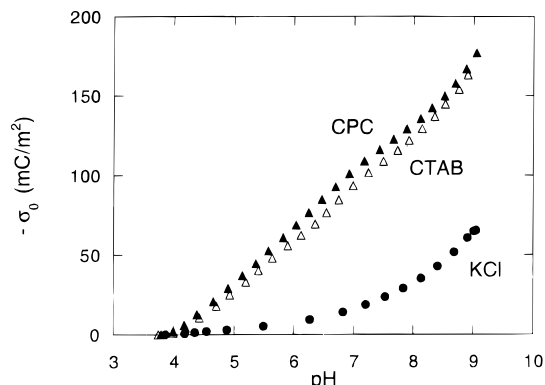


Figure 3. Charge–pH curves of Aerosil OX 50 in 0.001 M KCl in the absence and presence of 0.002 M CPC and CTAB.

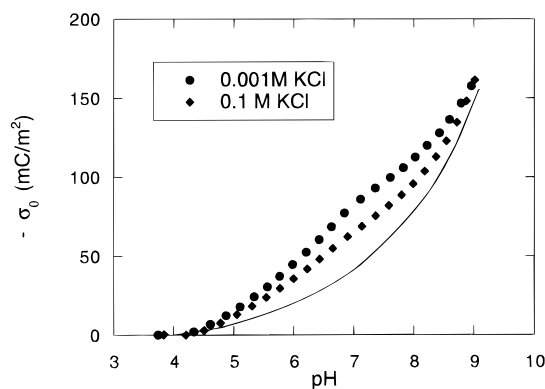


Figure 4. Charge–pH curves of Aerosil OX 50 at two KCl concentrations in the presence of 0.02 M DPC. The curve without symbols shows the charge of Aerosil as a function of pH at 0.1 M KCl in the absence of DPC.

Surface charge–pH curves of Aerosil in the presence of excess surfactant and some background electrolyte are shown in Figures 2–5. The initial DPC, CPC, and CTAB concentrations were 0.02, 0.002, and 0.002 M, respectively. This ensures that at all pH values the equilibrium concentration of DPC was above the cmc, so the maximum adsorption is reached. In CPC and CTAB solutions the equilibrium concentration was above the cmc at high salt concentration, whereas at low salt concentration at pH 9 the equilibrium surfactant concentration was slightly below the cmc. The effect of the surfactant on the surface charge is most clearly seen in Figure 2 for DPC and Figure 3 for CPC and CTAB. The background electrolyte concentration in Figure 2 is 0.01 M KCl, and that in Figure 3 equals 0.001 M. For DPC a tenfold concentration is chosen because of the high cmc value. Due to surfactant addition the overall ionic strength is about twice the

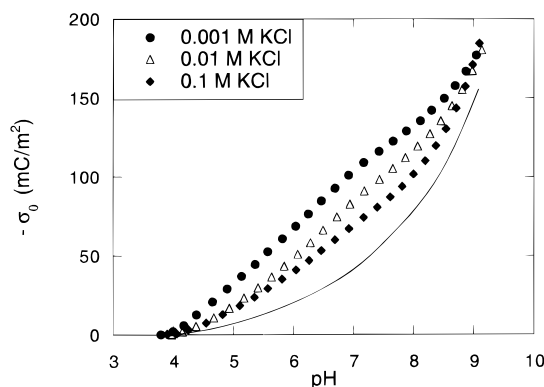


Figure 5. Charge–pH curves of Aerosil OX 50 at three KCl concentrations in the presence of 0.002 M CPC. For a comparison the charge–pH curve (without symbols) of Aerosil OX 50 at 0.1 M KCl in the absence of CPC is also presented.

background electrolyte concentration. The deviations between the curves in the absence and presence of surfactant start at about pH 4, indicating a strong specific adsorption of surfactant molecules, leading to a very efficient screening of the surface charge. The strong specific interaction between the surfactant ions and the surface induces proton desorption, and consequently a surface charge increases at a given pH. The final surface charge in the presence of DPC is somewhat smaller than that for CPC or CTAB, although the ionic strength is higher. The negative surface charge in CPC solution is slightly higher than that in CTAB solution, indicating a little more effective screening of surface charge by the cetylpyridinium ion than by the cetyltrimethylammonium ion. These observations indicate that the screening of the surface charge is dominated by the surfactant rather than by the added salt and that the nature of the surfactant also plays a role.

Surface charge–pH curves of Aerosil in the presence of DPC and CPC at different KCl concentrations are shown in Figures 4 and 5, respectively. The drawn curves indicate the surface charge at 0.1 M KCl in the absence of surfactant. The surface charge in the presence of surfactant slightly decreases with salt concentration, but even at the highest salt concentration the surfactant increases the surface charge. For both DPC and CPC the increase in surface charge starts at about pH 4.5. The salt effect becomes most pronounced in the neutral pH region and disappears at around pH 9. Apparently, specific interactions between surfactant ions and the surface diminish when the total amount of charged surface sites increases due to an increase in both the salt concentration and pH values. This indicates that hydrophobic interactions between aliphatic tails and the surface play an important role during the surfactant adsorption.

Surface Charge and Surfactant Isotherms. To study the effect of surfactant adsorption on the surface charge in more detail, DPC and CPC adsorption isotherms and surface charge isotherms at a given salt concentration can be compared. The surface charge isotherms express the proton desorption at constant pH. The adsorption and surface charge isotherms for DPC and CPC measured at low salt concentration at pH 7 and 9 are shown in Figures 6 and 7, respectively. To facilitate the comparison, the surface charge is expressed as $\Gamma_0 \equiv \sigma_0/F$, where F is the Faraday constant. In this way surface “charge” and the adsorbed amount of surfactant, Γ_s , are both expressed in micromoles per meter squared. At low salt concentration and both pH values, DPC isotherms clearly show two steps, indicating a good correlation with literature data.^{4,5,8,9} For

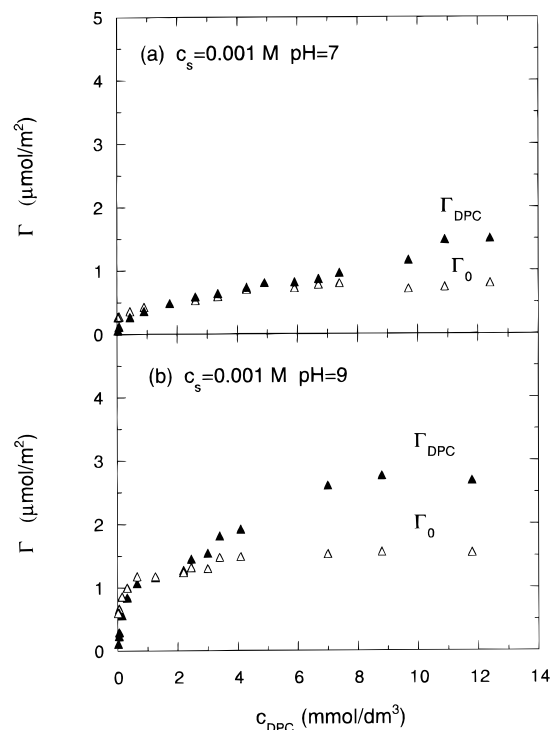


Figure 6. Adsorption of DPC and surface charge (σ_0/F) of Aerosil OX 50 at 0.001 M KCl as a function of the DPC concentration at pH 7 (a) and pH 9 (b).

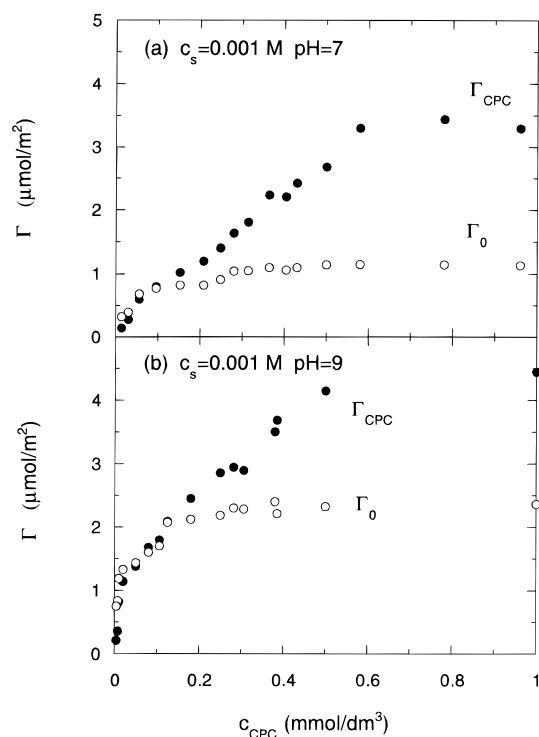


Figure 7. Adsorption of CPC and surface charge of Aerosil OX 50 at 0.001 M KCl as a function of the CPC concentration at pH 7 (a) and pH 9 (b).

CPC the two steps in the isotherms are less pronounced due to the stronger hydrophobic interactions between hydrocarbon tails. Due to the same effect the final adsorption level for CPC is larger than that for DPC. A detailed discussion of the surfactant adsorption isotherms will be given in a subsequent paper; for the moment we will concentrate on the comparison of Γ_s ($s = \text{DPC or CPC}$) and Γ_0 .

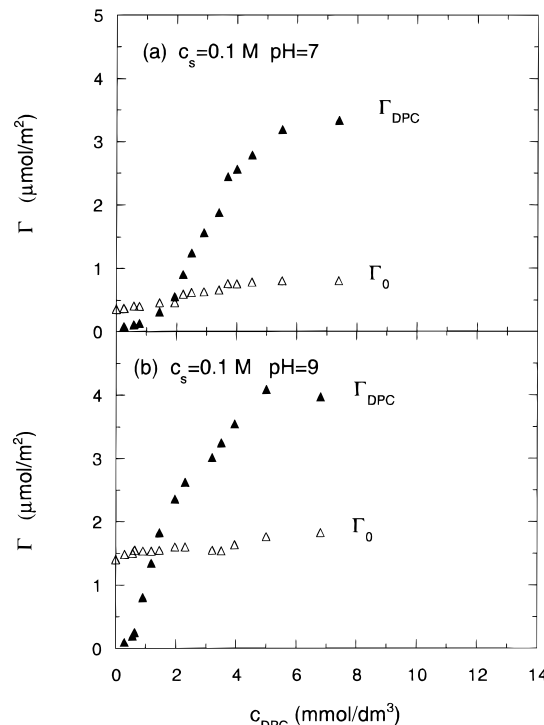


Figure 8. Adsorption of DPC and surface charge of Aerosil OX 50 at 0.1 M KCl as a function of the DPC concentration at pH 7 (a) and pH 9 (b).

The maximum change in surface charge occurs at low surfactant and low salt concentrations, where the adsorption and surface charge isotherms almost coincide. It means that with almost every adsorbing surfactant ion a proton is desorbed. This indicates that in this region practically all adsorbed surfactant ions have their head groups close to the surface. After compensation of the surface charge by surfactant (the crossover part of the isotherms) the surface charge becomes almost independent of the surfactant concentration, whereas the adsorption of surfactant continues to increase. This indicates that adsorption of surfactant in a second layer starts, i.e. with its head group directed to the solution. In this case the effect of surfactant adsorption on the surface charge will be small. For surfactant concentrations around the cmc the value of surface charge corresponds with the surface charge observed by the titration experiments.

The adsorption and surface charge isotherms for DPC and CPC measured at high salt concentration for two pH values are presented in Figures 8 and 9. At high salt concentration S-shaped surfactant isotherms are obtained, indicating how difficult it is for a surfactant ion to start adsorption with its head group close to the surface in the presence of a large concentration of K^+ . The high concentration of salt ions screens the surface charge effectively and leads to relatively large initial σ_0 values. Therefore, the changes in surface charge due to the surfactant adsorption are much less than those at low salt concentration. At both pH 7 and 9 a weak but steady increase of σ_0 results. Once the surfactant adsorption starts, it increases very strongly over a narrow concentration region, causing a sharp intersection point with the surface charge isotherms.

Effect of Surfactant Tail. A further insight into the mechanism of silica surface charge adjustment can be obtained by studying the effect of the aliphatic tail on the surface charge. As far as we know this effect has not been studied before for oxide surfaces. To assess the effect of a long hydrocarbon tail of the surfactant on the screening of the surface charge, the effect of CTAB on the surface

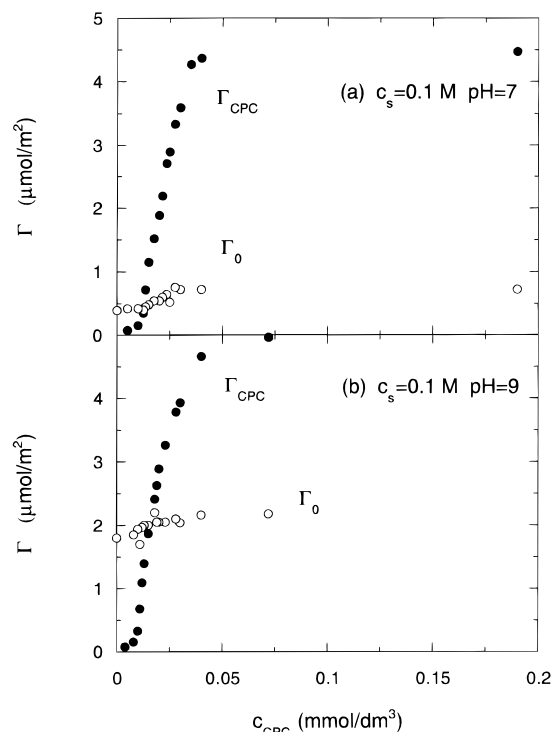


Figure 9. Adsorption of CPC and surface charge of Aerosil OX 50 at 0.1 M KCl as a function of the CPC concentration at pH 7 (a) and pH 9 (b).

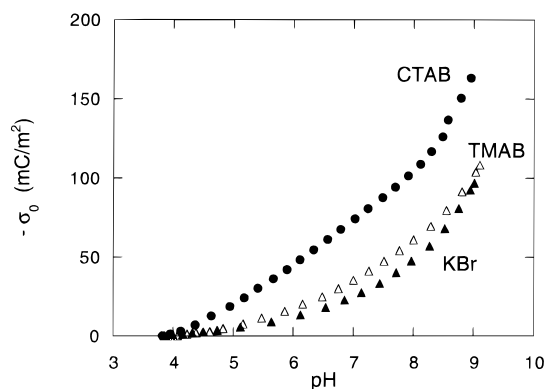


Figure 10. Charge-pH curves of Aerosil OX 50 in 0.01 M KBr, 0.01 M TMAB, and 0.01 M CTAB in the presence of 0.002 M of CTAB.

charge can be compared to that of TMAB. The surface charge-pH curve of Aerosil in the presence of 0.01 M TMAB is shown in Figure 10 together with that in the presence of CTAB and 0.01 M KBr and that for 0.01 M KBr itself. Two trends are obvious. (1) The screening of silica charge by TMAB is only slightly better than that by KBr. (2) As compared with the symmetrical quaternary ammonium ion, the asymmetrical CTA^+ surfactant ion screens the surface charge much more effectively. This indicates that the hydrophobic attraction between the adsorbed surfactant ion and the surface constitutes a very important contribution to the specific adsorption energy of the surfactant ion. As follows from Figures 6 and 7 and the surface charge adjustment at the first step of adsorption, the hydrophobic attraction is more pronounced at low salt and low surfactant concentrations. The importance of hydrophobic interactions with the surface at low coverage is also emphasized by the fact that with the pyridinium surfactants the surface charge of silica increases with increasing surfactant tail length, as follows from the surface charge isotherms shown in Figures 6 and 7. The longer the aliphatic part of the surfactant ion

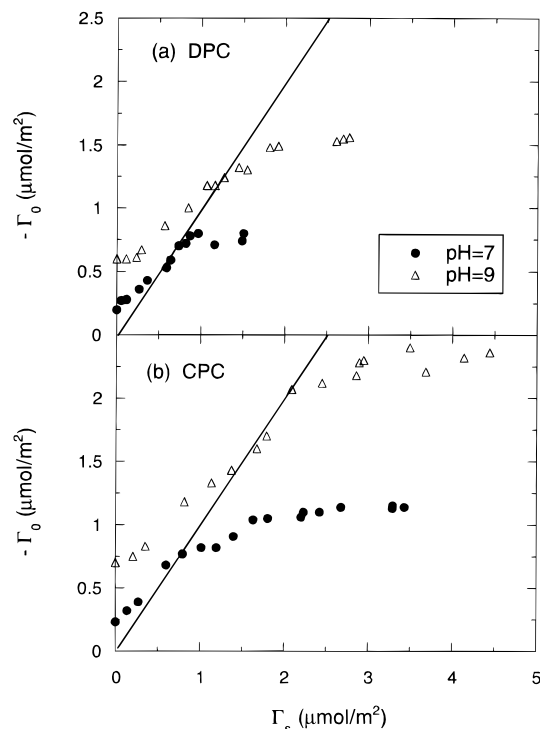


Figure 11. Surface charge of Aerosil OX 50 as a function of the adsorbed amount of DPC (a) and CPC (b) measured at 0.001 M KCl and pH 7 and pH 9.

is, the stronger is the hydrophobic surfactant-surface attraction and the higher is the plateau level of the surface charge. For high salt concentration the surface charge adjustment is rather small and the effect of chain length vanishes; see Figures 8 and 9. This indicates that at relatively high surface charges the possibilities for hydrophobic surfactant-surface attractions are diminished.

Discussion

Both the potentiometric results and the surface charge isotherms demonstrate that at low salt concentrations the surface charge of silica increases significantly upon surfactant adsorption. To emphasize this effect, in Figure 11 the surface charge, expressed as Γ_0 in micromoles per meter squared, is plotted as a function of the adsorbed amount of surfactant, Γ_s , for DPC (a) and CPC (b) at 0.001 M KCl. The line of unit gradient is also included. For low surfactant adsorption Γ_s is smaller than Γ_0 , yet the surface charge immediately starts to increase upon surfactant adsorption. Surfactant ions not only replace the inorganic counterions but also create additional surface ionization. Near the charge compensation point (intersection with the control line) the slope of the curve is close to unity, indicating that the increase in the amount of negative sites at the surface almost coincides with the increase in surfactant adsorption. In this range the surfactant ions have replaced nearly all potassium ions from the surface. This range corresponds to the region of the slow increase of the adsorption isotherms.

Comparison of the titration results for DPC (Figure 2), CPC (Figure 3), and CTAB (Figures 3 and 10) with those for TMAB (Figure 10) shows that surface charge adjustment is more strongly influenced by the presence of a surfactant tail than by the nature of the surfactant head group. This indicates that hydrophobic attraction between aliphatic tails and the hydrophobic parts of the surface is important for silica. This is mainly due to the presence of the siloxane parts on the surface. The hydrophobic character of these groups has been mentioned in ref 25.

It can be concluded that a number of factors lead to the improved screening of the surface charge by the surfactant ions: (i) a specific attraction between the surfactant head group and the charged group of the surface; (ii) a specific interaction between the aliphatic tails and the hydrophobic parts of the surface; and (iii) lateral attractions between surfactant ions adsorbed head-on. All these mechanisms lead to strong binding of surfactant molecules with the surface and promote the creation of new negatively charged sites at the surface.

Strong surface charge adjustment upon surfactant adsorption has also been found for metal oxides like rutile.^{13,27,28} For these surfaces the surface hydroxyl concentration is in general much higher than that for silica. As a consequence for these oxides, factor ii is much less important than for silica. The lack of hydrophobic interactions with the surface is, however, compensated by the lateral hydrophobic attractions: the high concentration of the surface hydroxyls allows for the creation of additional surface charges in the immediate vicinity of sites already occupied with surfactant ions, so that the surfactant tails can strongly interact.

With respect to the structure of the adsorbed layer at low salt concentration the following conclusion can be drawn. In the first part of the isotherm, surfactant molecules are present on the surface with both their head groups and tails in contact with the surface. As a result of this orientation a (local) crowding effect can arise at intermediate surface coverages, leading to a "hesitation" in adsorption and the appearance of a first plateau in the isotherms. After compensation of the surface charge by surfactant ions superequivalent adsorption of surfactant starts around the initially adsorbed molecules, and small admicelles are formed.

At high salt concentration the initial surface charges are much higher than at low salt concentration and the surface charge adjustment is much smaller. The surfactant ions have to replace the ordinary counterions, and the adsorption starts at much higher surfactant concentrations than at low salt concentrations. This is clearly reflected in Figure 12, where the surface charge is plotted as a function of both DPC (a) and CPC (b) adsorption at high salt concentration. In all cases the slope is much less than unity, indicating that ion exchange is dominant. However, under these conditions the head group repulsions are relatively small, and once the adsorption starts, it increases fairly steeply. The existing relatively high surface charge density reduces the surface hydrophobicity, but it increases the possibility for lateral hydrophobic tail-tail interactions. As a consequence the hesitation region is absent. Surfactant molecules form small hemimicelles (head groups toward the surface) before the charge compensation point. After passing the charge compensation point the Coulombic attraction between charged surface sites and surfactant head groups is gone and only the lateral hydrophobic attraction and the head group-head group repulsion remain. This leads to growth of the surface aggregates, in such a way that the newly adsorbed molecules are oriented predominantly with their head groups toward the solution (admicelle formation).

The fact that in the presence of surfactant and at low electrolyte concentration the salt ions hardly contribute to the surface charge compensation means that the amount of surfactant adsorbed head-on can be determined from the surface charge. As a consequence, the amount of surfactant adsorbed in the second layer with the head

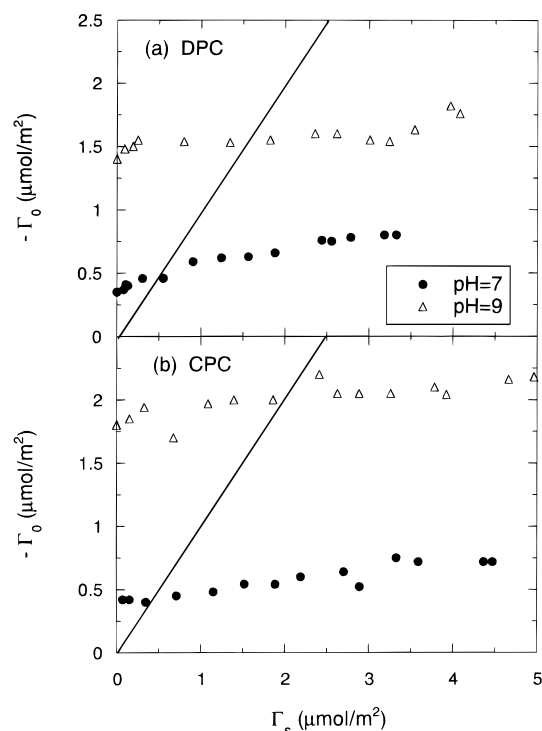


Figure 12. Surface charge of Aerosil OX 50 as a function of the adsorbed amount of DPC (a) and CPC (b) measured at 0.1 M KCl and two pH values.

Table 2. Adsorbed Amount of Surfactant with the Head Groups toward the Surface (Γ_1) and toward the Solution (Γ_2) near the Cmc

surfactant	pH	c_{salt} , mol/dm ³	Γ_1 , $\mu\text{mol/m}^2$	Γ_2 , $\mu\text{mol/m}^2$	Γ_{tot} , $\mu\text{mol/m}^2$
DPC	7.0	0.001	0.8	0.8	1.6
		0.1	0.8	2.6	3.4
	9.0	0.001	1.5	1.3	2.8
		0.1	1.7	2.3	4.0
CPC	7.0	0.001	1.1	2.4	3.5
		0.1	0.8	3.7	4.5
	9.0	0.001	2.3	2.1	4.4
		0.1	2.2	2.8	5.0

groups toward the solution can also be estimated. The amount of head groups in contact with the surface (Γ_1) and the amount of surfactant ions adsorbed head-out from the surface (Γ_2) near the cmc are presented in Table 2.

At low salt concentration adsorption in both the first and second layer increases with chain length of the surfactant molecule. It indicates that for the surfactant adsorption on silica hydrophobic interactions are very important in both the inner and outer parts of the adsorption layer. Using the Γ_1 values for DPC and CPC at pH 9, the molecular area per surfactant ion can be estimated. Calculations show these molecular areas for DPC and CPC to be 1.07 and 0.73 nm², respectively. The molecular area for DPC at the air–0.001 M electrolyte solution interface was assessed at 0.53 nm².²⁹ The comparison shows that the adsorption density in the first layer for silica is much lower than that at the liquid–air interface, despite the advantage of better screening of intermolecular repulsion. This again indicates a relatively flat conformation of surfactant molecules on silica at low salt concentrations with the head groups and aliphatic tails close to the surface.

Whereas salt concentration has only a small effect on adsorption in the first layer, adsorption in the second layer

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increases significantly with salt concentration, especially for DPC. It indicates that adsorption of surfactant ions with their head groups toward the solution in the second layer is also dictated by the electrostatic repulsion of the head groups.

Conclusions

Surface charge measurements show that at low salt concentration the surface charge of silica increases significantly upon surfactant adsorption, especially during the first adsorption step. The charge adjustment is strongly influenced by the presence of the hydrocarbon tail of the surfactant molecules. It means that surfactant molecules may realize their hydrophobic affinity through the interactions between aliphatic tails and hydrophobic regions of the silica surface. In other words, at low salt concentration surfactant molecules adsorb during the first

step in the isotherms with their head groups and tails close to the surface. In the second part of the isotherms small adsorbed surfactant aggregates are formed.

At high salt concentration the initial surface charge is much higher, making it more difficult to increase the surface charge. Due to the high initial surface charge the surface hydrophobicity is reduced. Hydrophobic tail–tail interactions become more important and both before and after the charge compensation point surfactant aggregates will be present at the surface.

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