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Adsorption of Short-Chain Tetraalkylammonium Bromide on Silica

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The adsorption of tetraalkylammonium (TAA) ions on silica shifts the isoelectric point to higher pH values. The IEP shift increases with increasing alkyl chain length. Also, tetraethylammonium (TEA) and tetrapropylammonium (TPA) ions can be adsorbed in larger amounts than tetramethylammonium (TMA) ions. The chemisorption of TAA ions can be explained by assuming an attraction between hydrophobically hydrated regions around surface siloxane bridges and around the TAA ions. The adsorption data of TMA ions are compatible with the stimulated adsorption model.

Introduction

Solutions containing both silicate ions and tetraalkylammonium (TAA) ions are of interest in chemical technology because they are used in zeolite syntheses;¹⁻⁶ in such solutions precursors of zeolite crystals are expected to be formed. This refers among others to TAA ions with rather short alkyl chains (up to butyl). In these solutions pronounced quantities of oligomeric silicate ions (cyclic trimer, cubic octamer) have indeed been found.⁷⁻⁹ From a theoretical point of view the interaction between the TAA and the silicate ions, which is responsible for such a precursor formation, is interesting.

This interaction is expected in first instance to be an attraction between the TAA and the silicate ions due to their opposite electrical charges. However, the viscosity of tetraalkylammonium silicate solutions indicates that in addition a repulsive force is present.¹⁰ This conclusion is supported by the observation that, in solutions containing a sufficient amount of TAA and silicate ions, plus other ions (e.g., sodium and bromide), separation into two coexisting aqueous phases (coacervation) is found. On phase separation, silicate and TAA ions are accumulated predominantly in different phases.¹¹

The question then arises of how this repulsion between TAA and silicate ions can be combined with the fact that chemisorption of TAA ions on silica has been observed.¹² In order to clear this point, we investigated the adsorption of TAA ions on silica from tetraalkylammonium bromide solutions, similar to the ones investigated with regard to viscosity and coacervation in previous studies.^{10,11}

Experimental Section

Materials. The following materials were used: silica, Aerosil 200 ex Degussa (surface area 200 m²/g); tetramethylammonium

bromide, ex Merck, >99%; tetraethylammonium bromide, ex Janssen Chimica, >99%; tetrapropylammonium bromide, ex Merck, >99%; KBr, ex Merck, 99.5%; KOH, ex Merck, Titrisol 1 M; HNO₃, ex Merck, Titrisol 0.1 M; HCl, ex Merck, Titrisol 0.1 and 1 M; sodium tetraphenylborate, ex Janssen Chimica, 98%.

The silica used in our experiments (Aerosil 200) is usually classified as pyrogenic silica. Compared to precipitated silica, the surface of pyrogenic silica has a more hydrophobic character (see Iler,^{13a} where further references can be found).

Methods. ζ potentials were measured as a function of pH, by coupling a Malvern Zetasizer III to a titration vessel thermostated at 298.15 K. In this vessel, the pH was measured by means of a Radiometer Copenhagen PHM 84 research pH meter, using a glass electrode and a calomel electrode connected by a van Laar salt bridge.¹⁴ The pH was adjusted, starting from an alkaline value, with 0.1 M HCl or 0.1 M HNO₃ using a Radiometer Copenhagen Abu 80 autoburet: the pH was changed at constant time intervals (90 min) with constant pH differences (0.5 unit).

ζ potentials were calculated from the electrophoretic velocities using Von Smoluchowski's equation¹⁵ (κa being in the order 50–150, where κ is the reciprocal Debye length and a is the particle radius). Samples for the ζ potential measurement were taken just before the next acid addition; every sample was measured twice. ζ potentials were measured in 300-mL suspensions with 0.1% w/w silica, in 0.001 and 0.01 M electrolyte solutions.

Changes in the surface charge, σ_0 , were determined by acid-base titration, i.e., by registering the H⁺ or OH⁻ consumption necessary to effect a certain pH change. The measurements were performed using the titration unit of a Matec ESA 8000 system. In the titration vessel, about 250 mL of dispersion medium or 1.5% w/w silica dispersion was titrated with 1 M HCl or KOH. By subtracting the H⁺/OH⁻ consumption of the dispersion medium from the H⁺/OH⁻ consumption in the suspension, the amount of adsorbed H⁺/OH⁻, and thus the change in surface charge, could be obtained.

Both ζ potential and surface charge measurements were performed on samples obtained in a nitrogen atmosphere, in order to minimize the influence of CO₂. The electrolytes used were KBr, (TMA)Br, (TEA)Br and (TPA)Br. In addition, KNO₃ was used in ζ potential measurements.

Adsorption of TAA ions on silica was determined in 100 or 150 mL of (TAA)Br solutions added to 5 g of silica. The concentrations of the solutions were 0.001, 0.003, 0.01, 0.03, and 0.1 M (TMA)Br, (TEA)Br, or (TPA)Br. The pH was adjusted at pH 3 and 5 with HCl or NaOH. Adsorption measurements were performed after 24 h of shaking at 25 °C. During this period, the pH shifted at most 0.3 unit; the pH was adjusted and the suspension centrifuged. TAA concentrations were determined

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Figure 1. ζ potential of silica in solutions of potassium nitrate.

Figure 2. ζ potential of silica in solutions of potassium bromide.

Figure 3. ζ potentials of silica in solutions of (TMA)Br.

by a potentiometric titration with sodium tetraphenylborate, using an Orion 940/960 autochemistry system and a TAA-sensitive electrode.¹⁶

Results and Discussion

Figures 1–5 show the ζ potentials of silica as a function of pH in the presence of various electrolytes. In KNO_3 solutions (Figure 1) the ζ potential is near 0 at low pH values, decreases below 0, and further increases in absolute value with increasing pH. The absolute values of the ζ potentials are lower in 0.01 than in 0.001 M solutions, as expected from theory for an inert electrolyte. The isoelectric point (IEP) is near pH 3.2. There is a small difference between this value and the data reported by Iler,^{13b} according to which the point of zero charge (PZC)

Figure 4. ζ potential of silica in solutions of (TEA)Br.

Figure 5. ζ potential of silica in solutions of (TPA)Br.

varies for silica between 2 and 3. This difference with our results may be due to the pyrogenic character of the silica employed here.^{13a}

The ζ potentials of silica in KBr solutions (Figure 2) differ slightly from those found in KNO_3 solutions; this applies especially to the 0.001 M solution. The difference indicates a slight tendency of bromide ions to chemisorption, which is outdone at higher concentrations by simultaneous physisorption of potassium ions behind the electrokinetic slipping plane. Differences in ζ potential versus pH curves for silica in solutions are much more pronounced, however, between KNO_3 and TAA solutions (Figures 3–5): the ζ potentials shift in positive direction with respect to the values found in KNO_3 solutions. Consequently, the IEP shifts toward higher pH values; therefore, at low pH values the TAA ions effect a charge reversal of the silica. This agrees with the chemisorption on silica of other quaternary ammonium ions reported by Rubio and Goldfarb.¹²

Figure 6 shows the IEP values for different (TAA)Br as a function of the length of the alkyl chains in the TAA ions. Generally, the IEP shift increases with increasing alkyl chain length. This indicates that the interactions between the TAA ions and the silica, involved in the adsorption, are of hydrophobic nature. A bilayer formation as described by Somasundaran et al.¹⁷ for long-chain alkylammonium ions is unlikely, as the absence of it was reported by Claesson, Horn, and Pashley¹⁸ in the concentration range used here.

The ζ potentials reported here are in agreement with the stability values of silica suspensions reported by Rubio

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Figure 6. IEP shifts for some TAA ions.

Figure 7. Adsorption of TAA ions on silica at pH 3.

Figure 8. Adsorption of TAA ions on silica at pH 5.

and Goldfarb,¹² if it is assumed that, according to Wiese and Healy,¹⁹ at ζ values < 0.014 V rapid coagulation occurs.

Influence of pH on TAA Adsorption. Figures 7 and 8 show the adsorbed amounts of TAA ions at two different pH values. Adsorption values at pH 5 are only slightly higher than at pH 3, the difference being of the order of 2×10^{-8} mol/m² over the whole concentration region investigated. Figure 9 shows the relative surface charge on silica as a function of pH, with a 10^{-3} or 10^{-2} M KBr solution as the dispersion medium. The changes in surface charge, as measured by titration, could not be transformed into absolute values, because of the point of zero charge (PZC) being outside the range of our measurements. However, absolute values for the surface charge are not required for the interpretation (see also below). The relative surface charge σ_0 , as indicated in Figure 9, is related

Figure 9. Relative surface charge on silica in solutions of potassium bromide.

to the surface charge at pH 3, not the PZC. Going from pH 3 to pH 5, the absolute value of the surface charge increases considerably.

The above observations indicate that between pH 3 and pH 5 the adsorption of TAA ions on silica is hardly influenced by the surface charge. This confirms that the adsorption does not predominantly occur at charged surface groups, and that the nonelectrostatic forces are very important in the interaction between TAA ions and silica. This excludes interpretation of the data by the "site-binding" model²⁰ and the model of Rutland and Pashley.²¹ As adsorption does not take place at charged surface silanol groups, TAA is likely to adsorb on the other type of surface group present: the siloxane bridge.

The driving force for adsorption of TAA ions on silica can be understood as being primarily related to the hydrophobic character of the TAA ions, rather than to the attraction by charged silanol groups (though the latter contributes also to the adsorption energy, as will be discussed below). The hydrophobic hydration of TAA ions, as determined by Heuvelsland,²² increases with the alkyl chain length, and so does the IEP shift (see Figure 6). Previous investigations concerning viscosities and phase separation in solutions containing TAA and silicate ions indicate a repulsive interaction between hydrophilically induced hydration regions around silicate ions and hydrophobically induced hydration regions around TAA ions. Since surface silanol groups on silica are strongly hydrophilically hydrated,^{13c} a repulsion between TAA ions and silanol groups is also expected. It is likely that the hydration regions present around surface siloxane bridges are more compatible with hydrophobic hydration. The driving force for adsorption of TAA ions then is the overlap between hydrophobically induced hydration regions around TAA ions and siloxane bridges.

The assumption of a predominant hydrophobic character of the driving force for TAA adsorption is consistent with the different values for the maximum degree of silica surface coverage by the different TAA ions. TMA adsorption reaches a plateau value, at both pH values investigated, at about 18×10^{-8} mol/m². This value corresponds to an area of about 10^{-17} m² per adsorbed ion, equivalent to an average mutual distance between adsorbed ions of about 3.5 nm, at maximum coverage. If the adsorbed amount mentioned corresponds to complete

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Figure 10. First derivative of the surface charge as a function of the cation type at pH 3.

Figure 11. First derivative of the surface charge as a function of the cation type at pH 5.

occupation of the sites concerned, the distance of 3.5 nm mentioned is the average distance between sites on the silica surface which are hydrophobic enough to attract TMA ions; such a distance does not appear to be unacceptable.

The adsorption of TEA and TPA ions does not reach a plateau within the range of our measurements, but this is expected to occur at higher concentration and higher adsorbed quantities. The observation that larger amounts of TEA and TPA can be accommodated on the silica surface can be explained by assuming hydrophobic interactions between adsorbed TAA ions on adjacent sites. The TMA ion has a relatively small hydrophobically hydrated region compared to TEA and TPA. This region may be too small to create an overlap between the hydrophobically hydrated regions of two or more TMA ions adsorbed on adjacent sites: the adsorption takes place at isolated sites. For the TEA and TPA ions an overlap between the hydrophobically hydrated regions would be more likely to occur, because of the greater size of these regions. At low surface coverage, sites will still be isolated. At higher surface coverage, however, the interaction between adsorbed ions at adjacent sites will induce adsorption on energetically less favorable sites.

Changes in the Surface Charge of the Silica. From measurements of changes of surface charges on the silica due to adsorption or desorption of H^+ or OH^- ions, on changing the pH, the quantity of $d\sigma_0/d(pH)$ can be calculated. This is shown at pH 3 and 5, in Figures 10 and 11 respectively, as a function of the chain length of the cation at two different concentrations.

It is interesting that, in an absolute sense, $d\sigma_0/d(pH)$ is larger for the hydrophobic cations than for potassium ions, especially at large concentrations and with the larger

Figure 12. Schematic view of the stimulated adsorption model.

cations. This is consistent with the following explanation: at low concentrations, the cations are predominantly adsorbed at siloxane bridges which are not very heavily shielded by surrounding silanol groups (e.g., on a site like A in Figure 12). This influences the local potential at nearby silanol groups, e.g., at B in Figure 12, by expelling the protons on them to a larger extent than would occur in the presence of inert ions like potassium. The presence of negative charges at site B makes conditions at sites like C favorable enough for adsorption of TAA ions on these sites as well. The influence of site occupation on the adsorption energy at adjacent sites can be interpreted within the framework of the "stimulated adsorption model".²³⁻²⁵

Quantitative Application of the Stimulated Adsorption Model to TMA Adsorption. The stimulated adsorption model²³⁻²⁵ describes the adsorption of cations and anions on a solid/electrolyte interface, e.g., the adsorption of Ca^{2+} and OH^- on $CaSiO_3$, or NR_4^+ and OH^- on silica. The model is based on the observation that, with increasing concentration, the adsorbed amount of such ions increases more than could be expected for an inert substrate, or for an interface characterized by an average potential. The model assumes adsorption to be influenced by the local rather than the average electrical potential, which is calculated from the change in the adsorbed amount upon changing electrolyte concentrations.

The chemical potential of an adsorbed ion is assumed to be described by

$$\mu_{\text{adsorbed}} = \mu^{\circ}_{\text{adsorbed}} + RT \ln \frac{\theta}{1-\theta} + zF\psi$$

where $\mu^{\circ}_{\text{adsorbed}}$ is a function of pressure and temperature only, θ is the fraction of sites occupied at a certain concentration, z is the valency of the adsorbed ions, F is the Faraday constant, and ψ is the local potential at an adsorption site.

For the surfaces investigated in previous studies regarding this model²³⁻²⁵ ($CaSiO_3$ in alkaline solutions with constant $[NaOH]$ and varying $[CaCl_2]$), $d\psi/d(\ln c)$ was found to be negative. For an inert substrate, $d\psi/d(\ln c)$ should be zero, while for the surfaces concerned, $d\psi/d(\ln c)$ was found to be positive. This was interpreted in the following way: not all adsorption sites are characterized by an equal sum of $\mu^{\circ}_{\text{adsorbed}} + zF\psi$. At low electrolyte concentrations, only those sites will be occupied for which the sum $\mu^{\circ}_{\text{adsorbed}} + zF\psi$ is strongly negative. However, when such a site becomes occupied by a cation, the local potential near an adsorption site will shift in the positive direction. This stimulates the adsorption of anions on nearby anion adsorption sites, which in turn will change

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Table I. Stimulated Adsorption Model Calculations for (TMA)Br on Silica

[(TMA)Br] (10 ⁻³ M)	adsorbed amount ^a (10 ⁻⁸ mol/m ²)	$e_0/kT \, d\psi/d \log (\gamma m)$	
		$w/f = 0.1$	$w/f = 0.5$
pH 3			
0.997	0.22	-11.95	-13.37
2.862	1.61	0.08	-1.60
9.687	3.38	-5.51	-1.60
29.09	11.75	-1.31	-4.98
96.11	18.83	-11.58	<i>b</i>
pH 5			
0.823	1.63	1.17	-0.46
2.713	2.48	-0.09	-2.06
9.318	6.93	-0.28	-2.91
28.88	13.24	-0.25	-3.67
96.31	17.13	-1.11	-5.82

^a Value corrected for the amount present in the diffuse part of the double layer. ^b Large value for average adsorption energy required for explaining the experimentally measured adsorbed amount. In this case, the integrals could not be calculated for the broad range of adsorption energies between $-5w$ and $+5w$.

the local potential at yet unfavorable cation adsorption sites, making adsorption on them possible.

In the derivation of the equations concerned, it is assumed that sites differ in adsorption energy and that the adsorption energy of sites to be occupied may change when more and more sites become occupied, but that this change in adsorption energy is due to the changes in local potential only. Thus, since the data suggest that with the adsorption of TEA and TPA ions the adsorption energy changes not only by changes in local potential, but also by differences in hydrophobic interaction energy when adjacent sites become occupied, the model can only be assumed to be applicable to the TMA adsorption.

Table I surveys the results of the calculations of changes in average local potential at adsorption sites for the case of TMA. To perform the calculation, a distribution in the driving force $\mu^{\circ}_{\text{adsorbed}} + zF\psi$ had to be assumed. This distribution is assumed Gaussian, characterized by an average value (f) and a standard deviation (w). The results are shown for a narrow distribution ($w/f = 0.1$) and for a

broad distribution ($w/f = 0.5$). As can be seen from Table I, the width of the distribution does not affect qualitative trends, in particular the sign of $d\psi_{\text{local}}/d \log(\gamma m)$. It has also been reported²⁵ that the type of distribution assumed (Gaussian or otherwise) does not greatly influence the results. In the case of the lowest concentration investigated, the accuracy of the results is limited because of experimental uncertainties; nevertheless, the general trends for the local potential change with increasing concentration are (a) that the change is <0 and (b) that the absolute value of $d\psi_{\text{local}}/d \log(\gamma m)$ increases with increasing concentration. This is to be expected, since the average distance between occupied A-type and C-type sites (see Figure 12) decreases with increasing surface coverage, and therefore the effect of a dissociation of a surface silanol group at B will be felt to a greater extent.

Conclusions

Adsorption of TAA ions causes a shift in the IEP, which is linearly dependent on the chain length. This indicates that hydrophobic interactions play a major role in the adsorption mechanism. Also, the adsorption proved to be nearly independent of the pH. Therefore, it is very unlikely that TAA adsorption takes place on charged surface groups. The results of the adsorption can be explained by assuming that the adsorption sites consist of small siloxane-like hydrophobically hydrated places on the silica surface.

The adsorption data for TMA are consistent with stimulated adsorption by cations and anions, even in this case where we are dealing with the adsorption of nonlattice ions. For TEA and TPA this theory is not applicable because adsorption on an adjacent site influences not only the local electrical potential but also the hydrophobic interaction energy. The high adsorption for (TEA)Br and (TPA)Br at high concentrations can be explained assuming a more preferable hydrophobic interaction energy because of the overlap of hydrophobically hydrated regions. This assumption agrees with the fact that the distances between the sites were found to be on the order of twice the radius of the hydration radius.