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Zeta-potential measurements of OTS-covered silica samples

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Abstract We have carried out zeta-potential measurements on two different OTS (octadecyl-trichlorosilane)-covered silicas (fused silica, quartz 0001) prepared under identical conditions. Streaming current measurements on the fused silica supported OTS sample indicate a well reproducible IEP of 3.5. The major part of the study focused on the quartz 0001 supported sample with an IEP lower than that of the fused silica support and in agreement with that found in a spectroscopic study. The IEP in water (on addition of HCl) was found at around pH 3, and appeared to shift to lower values in three subsequent measurements. A final measurement after a separate series in KCl media gave the same IEP as obtained in the very first measurement, suggesting that the experiments did not significantly change the interfacial properties despite a large number of experiments. In one series of measurements care was taken to exclude any cations other than protons from the measurements, such that protons are the only counter-ions to the negative net charge.

While our IEPs with the quartz support agree well with recent estimates from sum frequency generation (SFG) investigations, none of the zeta-potential vs pH curves would mimic a pattern experimentally observed in the amplitude of the "ice-like" water band between pH 3.5 and 5 in that SFG study. Furthermore, our results do not indicate any significant chloride-ion adsorption in KCl systems, but instead the shift of the IEP with increasing KCl to higher pH values rather indicates specific effects of potassium ions. Under conditions more relevant to the spectroscopic study (i.e. in absence of potassium) no specific pattern reminiscent of the SFG results was found. When tested it was found that surface conductivity was negligible.

Keywords Hydrophobic surface · Hydroxide adsorption · OTS · Zeta-potential

1 Introduction

There is some interest in the charging behavior of hydrophobic-water and hydrophobic-electrolyte interfaces. One important question related to the observation that these interfaces show a measurable negative charge at pH values above about pH 4 as summarized by Healy and Fuerstenau (2007) is the origin of the charge. Insensitivity of measured IEPs to variations in salt concentration and composition and pH-dependence of zeta-potentials (Zimmermann et al. 2006) as well as direct titrations of oil-in-water emulsions (Beattie and Djerdjev 2004) or mass titrations of Teflon powder (Preočanin et al. 2012) from a macroscopic point of view restrict the origin of the charge to the hydroxide ion. However, most theoretical approaches to the problem do not support strong adsorption of hydroxide ions, in particular when compared to protons. Thus at pH 5, where the proton concentration is four orders of magnitude higher than the hydroxide-ion concentration, the surfaces are negatively charged and the affinity of the hydroxide-ion needs to be substantially higher than that of the proton to explain the experimental observations via hydroxide-ion adsorption. The theoretical work that contradicts this, is in agreement with surface tension increments for proton and hydroxide ions, but as discussed by Beattie et al. (2009) both theoretical work and surface tension increments refer to rather high

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concentrations of ions. This is also true for many investigations involving second harmonic generation (Petersen and Saykally 2005b) or sum frequency generation (Tian et al. 2011; Hua et al. 2011) at air-water interfaces, techniques that are sufficiently surface sensitive to yield information about the first few water layers of relevant interfaces. We note that there are also second harmonic generation studies at low concentrations (Petersen and Saykally 2005a; Petersen et al. 2004), which confirm long-debated macroscopic observations at similar concentration ranges like the Ray-Jones effect (Jones and Ray, 1935, 1937, 1941a, 1941b, 1942). From a solution chemistry point of view, the high concentrations should be discussed in terms of some appropriate model that takes into account specific ion-ion interactions, such as the Pitzer model (Pitzer and Mayorga 1973; Pitzer 1973), since at the same time as the concentrations of the solute of interest is changed, there is also a strong change in medium concentration and thus in the activity coefficient of the solute of interest. When discussing for example propensity of one ion with respect to another ion. Figure 1a shows that SHG data (Petersen and Saykally 2005b) when plotted on the molar concentration scale would suggest higher affinities of some ions to the surface with respect to others (here the proton compared to potassium, sodium). When the same data are recalculated to Pitzer based activities (Pitzer and Mayorga 1973; Pitzer 1973) of the relevant ion (i.e. I^-) in the different solutions, Fig. 1b shows that the difference in affinity between a KI and HI solution not only vanishes but is even inversed at the highest KI concentration if the average values are considered. If the error bars are considered, there are no significant differences between the different solutions. Here the differences between the three iodide systems are triggered by differences in the binary Pitzer parameters for HI, KI and NaI, i.e. the interaction parameters between positive and negative ions. Note that the data base involves no ion-pair formation, i.e. everything is handled by the interaction parameters and thus in terms of activity coefficients. The calculations are meant to serve as an example that shows that alternative interpretations might be possible. The precise outcome of the calculations obviously depends on the quality of the data base, which is not discussed here. Similar calculations for solutions containing the hydroxide ion are not shown, since it is unclear how the NaOH and KOH solutions were protected against carbon dioxide. Calculations involving saturation of those highly concentrated solutions with atmospheric carbon dioxide would result in extremely strong effects of on the resulting OH-activities. However, such calculations are highly speculative.

Figures 1a and 1b thus show that use of another *x*-axis could somewhat change the sequence of adsorption and that consequently such data at high solute concentrations need to be considered with care.

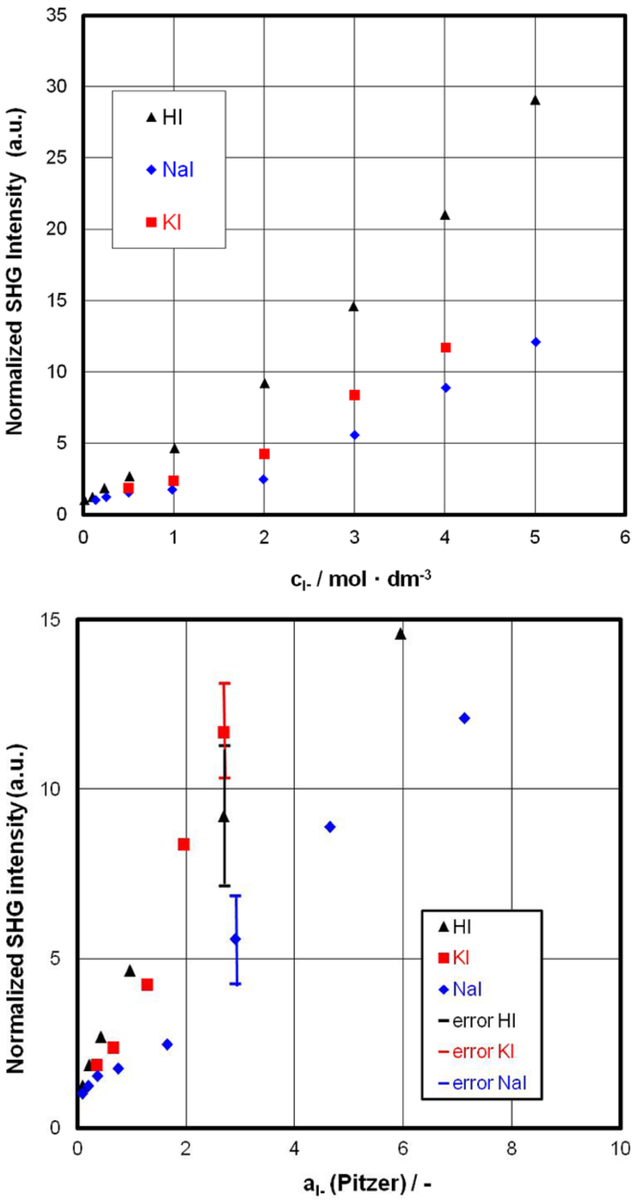
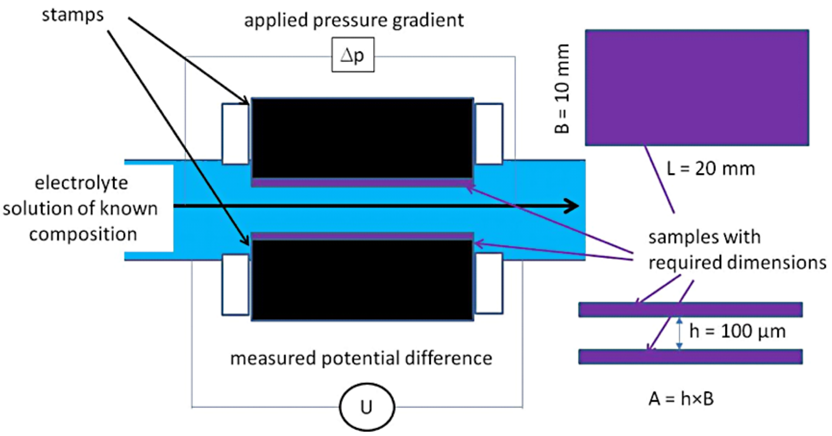


Fig. 1 Second harmonic data for different iodide containing systems (Petersen and Saykally 2005b). (*Top*) *x*-Axis as in the original publication, i.e. molar concentrations. (*Bottom*) Molar concentrations have been recalculated to iodide activity, i.e. the data are now compared on the basis of iodide-ion activities. The *error bars* in Fig. 1b have been taken from the original publication. The rescaling causes different shifts and at the highest iodide-activities, the data for HI and KI do not differ significantly

The pH-dependent charging of the hydrophobic surfaces is typically investigated at millimolar concentrations. It is not clear to what extent the different concentration ranges of the various investigations may be at the origin of the discrepancies in the conclusions about the hydroxide ion.

At low medium concentrations or in the absence of background electrolytes where acid or base is added to neat water other peculiar situations may arise. The addition of acid or



Scheme 1 Gap-cell arrangement for streaming potential and streaming current measurements. Dimensions of h, B, L and h are not to scale

base to a medium of too low concentration may influence the ionic strength, which would affect the activity coefficients of the solutes. In the absence of a background electrolyte, the omnipresent protons or hydroxide ions would act both as counter-ions to negatively or positively charged surfaces and as the ions that regulate the bulk solution pH.

In the present experimental study we have tried to mimic recent sum frequency results on OTS-electrolyte interfaces, in order to relate macroscopic data to molecular level investigations, similar to what has been done for sapphire-c (Lützenkirchen et al. 2010). In particular we were interested in the feature in SFG data on an OTS surface (Tian and Shen 2009) between pH 3 and 5, where a local maximum occurred for the amplitude of the band that represents the surface field or surface charge of that interface (the band at 3200 cm^{-1}, also referred to as the "ice"-like band, where the term "ice" does not refer to water structuring in an ice like fashion, but rather to tetrahedral co-ordination of the water molecules). It was attempted to proceed with the pH titration in a similar way as had been done in the SFG paper. Furthermore, we investigated the previously reported effect of support on the OTS layer properties (Wang and Wunder 2000), by preparing it on two different silica surfaces in otherwise identical manner. Recently, some aspects of OTS layer preparation on silica were studied in some detail (Li and Yoon 2012). In particular it was shown that the silanisation solution concentration and the silanisation step period had a major effect on the resulting contact angle of the film. Increasing the OTS concentration and the silanisation time increases the contact angle and decreases contact angle hysteresis.

In the paper we shortly review the theoretical basis of streaming potential/current measurements, then describe the experimental procedures and proceed to the results and discussion before drawing the conclusions.

2 Theory

The zeta-potential for flat surfaces is typically obtained from streaming current and streaming potential measurements. The set-up is schematically shown in Scheme 1, and more specifically the so-called gap-cell (or stamp cell). The (violet) samples are glued to the two (black) stamps and the channel width (i.e. the distance between the two violet samples) is adjusted to about 100 µm. The samples have a very precise dimension of 10 mm by 20 mm, so that they exactly fit on the stamps and can be inserted into the cell.

An applied pressure difference causes the flow of water or electrolyte solution through the rectangular channel and causes for a charged sample surface (in an electrokinetic sense) a measurable potential difference. The streaming potential, ζ_U, can be calculated from the equation.

$$\zeta_U = (dU/dp) \times \big(h/(\varepsilon_r \times \varepsilon_0)\big) \times \big(L/(A \times R)\big)$$

Alternatively the streaming current, ζ_I, can be obtained from the following equation

$$\zeta_I = (dI/dp) \times \big(h/(\varepsilon_r \times \varepsilon_0)\big) \times (L/A)$$

In the above equations the symbols have the following meaning:

U—potential, I—current, p—pressure, η—electrolyte viscosity, ε_r—dielectric constant of medium, ε_0—permittivity of vacuum, R—AC resistance in measurement cell. The geometric properties of the flow channel (h, L and A) are defined Scheme 1.

The two measurable pressure ramps (dU/dp and dI/dp) can be used to estimate the surface conductivity. According to Zimmermann (2004), the Dukhin-number ($Du = 2 \times K^{\sigma} \times h^{-1} \times K_B^{-1}$, where K^{σ} it the surface conductivity and K_B the measurable bulk electrolyte conductivity) can be calculated from the measured pressure ramps and the bulk electrolyte conductivity from the following equation.

$$Du = \frac{1}{2} \times \left\{ (dI/dp) \times (dU/dp)^{-1} \times \left(L \times (h \times B)^{-1} \times K_B \right)^{-1} - 1 \right\}$$

Essentially this equation means that when streaming current and potential measurements on one sample under comparable conditions yield different values, then surface conductivity is involved.

3 Experimental

3.1 Preparation of the OTS samples

The preparation was based on the procedure described by Wei et al. (2000). The supporting silica samples were obtained from MaTeck GmbH (Jülich, Germany). We used fused silica substrates (10 mm × 20 mm × 0.5 mm, polished on one side) or quartz 0001 substrates (10 mm × 20 mm × 0.5 mm, polished on one side). These silica samples were washed with ethanol and distilled water. They were then dried for 10 minutes at 120 °C in an oven. Subsequently the samples were boiled for 30 minutes in piranha-solution (H_2O_2 (25 %):H_2SO_4 (97 %) = 1:2) at 90 °C. After washing with distilled water they were immersed for 20 minutes in 0.5 M NaOH, then for 10 min in 0.1 M HCl and finally for 10 min in 0.5 M NaOH again. Subsequently they were washed with 0.1 M HCl and finally with distilled water and dried for 10 min at 120 °C in an oven. After transfer into a nitrogen flooded chamber they were dried for at least 30 minutes at room temperature. Within this chamber, the samples were dipped for 20 minutes into the silanisation solution (1 mM in toluene). They were then washed with toluene and taken out of the nitrogen chamber. Subsequently they were washed again with toluene, ethanol and distilled water and then dried for 20 minutes at 120 °C in an oven.

Contact angle measurements at room temperature with distilled water yielded an advancing contact angle of $73° \pm 6$ and a receding contact angle of $57° \pm 3$. A contact angle of about 16° and the measured contact angles are within the range expected from the study by Li and Yoon (2012).

3.2 Streaming potential/current measurements

All solutions were freshly prepared from MilliQ water (18.2 M cm). Salts were heated before use. Purified Argon was used to bubble MilliQ water in order to minimize intrusion of carbonate into the measurement solutions.

For the determination of the zeta potential, as a rule streaming current measurements were carried out using the SurPass Apparatus (Anton Paar). The measurements were performed at rectangular streaming channels with a length of 20 mm, a width of 10 mm and a height of about 100 µm (see Scheme 1). Before each pH titration the cell and apparatus were flushed with MilliQ water. In most cases, the desired electrolyte solution or (in case of the fused silica supported sample) MilliQ water (18.2 M cm) were filled into a beaker that was connected to the SurPass and the pH usually increased to about 9 by adding a small volume of 0.1 M KOH or NaOH. Subsequently the solution was titrated down using the system inherent acid (0.1 M HCl). During the measurements with the SurPass a constant flow of purified Argon, previously passed through two washing bottles one containing NaOH solution to capture carbon dioxide and another containing the medium under study to minimize water evaporation from the electrolyte solution in the beaker. Measurements were made at room temperature. During the measurements temperature can vary by 1 K.

The pH and conductivity electrodes were calibrated before each measurement series. For the pH calibration three commercial buffers (pH 3, 6 and 9) were used. After a given measurement series the pH was checked against a commercial buffer to verify that electrode drifts could be disregarded during the measurements. The conductivity electrodes were calibrated and checked against KCl solutions of known concentrations. The pH electrode inserted in the beaker containing the working solution has an inner electrolyte filling solution of 3 M KCl. Leakage of KCl from the pH electrode is observed by a continuous increase in conductivity. On the time scale of our experiments this marginally affects the ionic strength at the lowest electrolyte concentrations (i.e. 1 mM KCl) studied. However, when MilliQ water is used there is a clear effect on the conductivity. This side affect has been carefully avoided in some experiments by measuring the pH in a separate beaker with identical composition as the beaker containing the measurement solution.

Several measurements on the quartz 0001 supported OTS samples were carried out starting from the pH of MilliQ water (18.2 M cm), which is about pH 6 (this decrease in pH compared to the expected pH of 7 for pure water could never be avoided although the solutions were always kept under purified Argon). To this solution 0.1 M HCl was added. In some runs the pH measurement was done in a separate beaker to which identical amounts of the same HCl solution were added, while the pH in the "working" solution was only measured at the end of the experiment. In that way the only positive ion in the system was the proton. The series that involved acidifying the MilliQ water was designed to mimic the experimental procedure in the SFG study by Tian and Shen from the solution composition point of view.

For the sample that was deemed to correspond best to the SFG additional measurements involving the determination of streaming potential were done to investigate the relevance of surface conductance. In these measurements the protocol

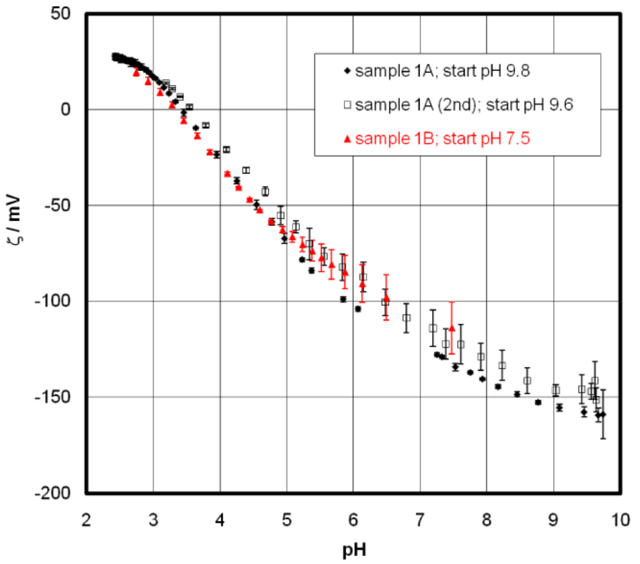


Fig. 2 Zeta-potential for the OTS-water interface. The OTS was in this case prepared on a fused silica surface. Two independent sets of samples were studied. The measurements were done in MilliQ water to which small amounts of base (NaOH) solution were added and then titrated by HCl to decrease the pH

was such that streaming current was first determined at a given pH and subsequently the streaming potential was determined for identical conditions. The data were used to determine the Dukhin number.

4 Results

The results for the fused silica supported OTS films in presence of an aqueous solution are shown in Fig. 2. It is apparent that the isoelectric point (IEP) is in the range that is expected for inert surfaces and that there is a clear pH-dependence. We also note that the IEP of the fused silica supported system is clearly at higher pH (around pH 3.5 ± 0.2, Fig. 2) than what would be expected based on the study by Tian and Shen (2009), which was lower than pH 3. The results were well reproducible among different samples and on one sample in subsequent runs. This indicates that the OTS layer is stable over time and can be reproducibly obtained.

The results for the second supporting surface (quartz 0001) are shown in Figs. 3 and 4. Data in a defined electrolyte medium are shown in Fig. 3. For the lowest KCl concentration at pH about 3 the overall ionic strength is affected by the addition of acid solution. This cannot be avoided in background electrolyes of millimolar concentrations when the isoelectric point is at such low pH values. The first three experiments were carried out by additions of HCl to neat water and the results are shown in Fig. 4 as blue symbols. Subsequently, the KCl series shown in Fig. 3 was obtained, followed by another run in HCl (i.e. red symbols in Fig. 4).

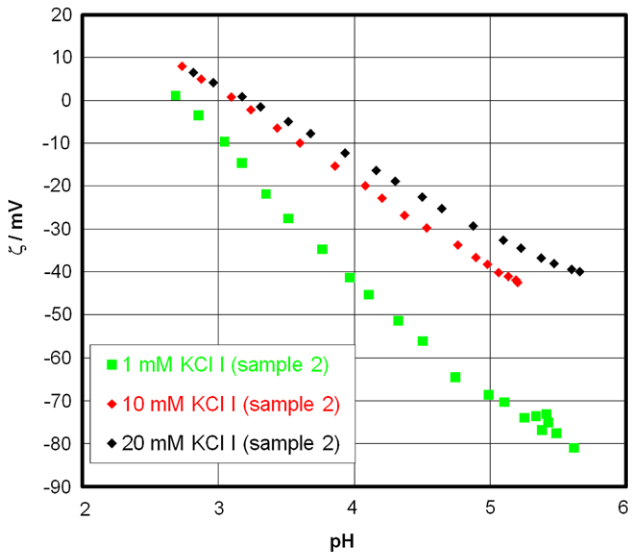


Fig. 3 Zeta-potential of OTS coated quartz 0001 surfaces as a function of pH in different KCl media

A comparison between the fused silica and 0001 quartz supported OTS films shows that the IEP of the fused silica supported system (Fig. 2) is clearly at higher pH as obvious from Figs. 3 and 4.

The 0001 quartz supported OTS sample had an IEP of about pH 3 and lower, being in better agreement with the results obtained by Tian and Shen (2009) with their sample. Their OTS was supported on a fused quartz window and prepared based on a different literature reference (Sagiv 1980). Consequently we carried out all further experiments on our 0001 quartz supported OTS films.

The results in Fig. 3 for the 0001 quartz supported sample at three different concentrations of KCl show that the IEP increases with increasing KCl concentrations. This is not expected for a hydrophobic surface, for which the IEP has been frequently reported to be insensitive to variations in salt concentration and even for different salt compositions. The absence of such shifts has actually contributed to the hypothesis (along with the pH dependence of the zeta-potentials) of strong hydroxide adsorption. The present data would not favor the idea of chloride adsorption in potassium media that would be expected from the SFG study. Rather the potassium ion is favored at the interface based on the data in Fig. 3.

Figure 4 shows data in MilliQ water, where only HCl was added and consequently protons are the only positive ions in the system. The data suggest that there is an evolution of the surface with time. The blue data were recorded before the KCl series. The red data were obtained after the KCl series. In these experiments the pH electrode was not inserted into the measurement solution so that only protons would be present as counter-ions.

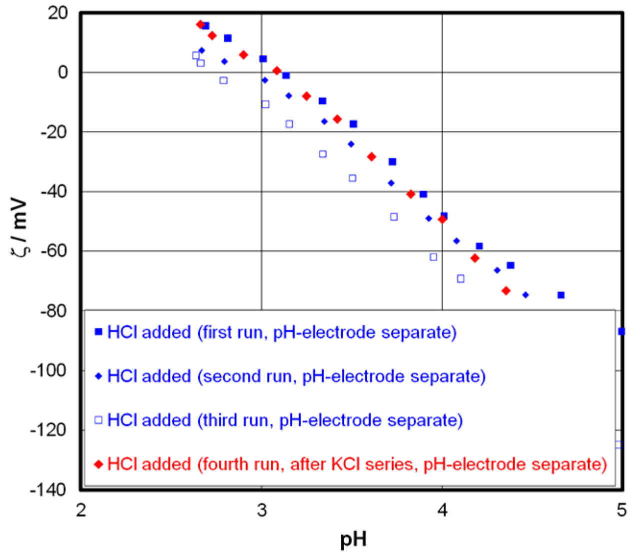


Fig. 4 Zeta-potential of OTS coated quartz 0001 surfaces as a function of pH in HCl media

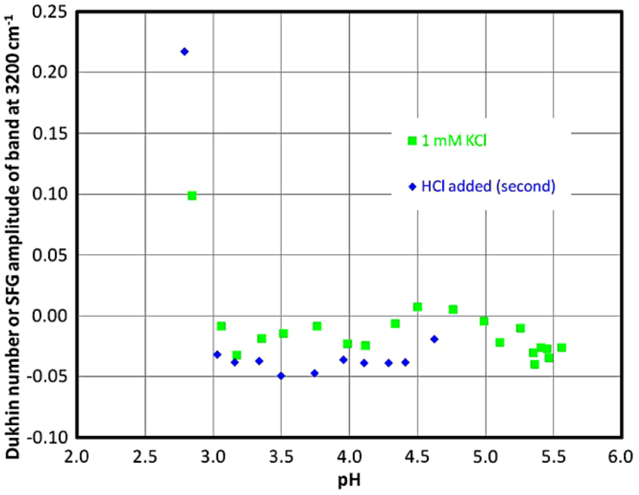


Fig. 5 Dukhin number for the OTS-quartz 0001 supported interface in the presence of 1 mM KCl and for an experiment where HCl was added to MilliQ water

We summarize the experimental results reported in Figs. 3 and 4 as follows.

- With time there is a decrease in the IEP in the first three runs. This decrease might be due to specific interaction with chloride in the absence of potassium ions, which in turn would confirm adsorption of chloride ions as reported by Tian and Shen (2009). This is also supported by clearly more negative zeta-potentials with the number of runs. Such a conclusion would imply that chloride ions could not be completely released from the samples during the washing cycles with MilliQ water that were carried out after each run (memory effect).
- After the KCl series (data in Fig. 3) the original IEP was retrieved (data in Fig. 4), which would corroborate the effect of potassium ions inferred from Fig. 3, implying that in the potassium series chloride was chased from the surface.
- Restoring the initial IEP suggests that the changes observed are not due to changes in the OTS layer due to extended exposure to aqueous solutions. This would also agree with the data for OTS on fused silica as discussed in relation to Fig. 2.
- In none of the experimental runs did we observe a feature reminiscent of the SFG data reported by Tian and Shen (2009) in the pH range 4 to 5. Instead we find the continuous change in zeta-potential as is usual observed.

In some of the experiments in which the zeta-potentials reported in Figs. 3 and 4 were obtained from streaming current measurements, after each addition of HCl we also measured the streaming potential. It was attempted to exploit the results to see if the surface conductance could show some special patterns in the pH range 4 to 5. Furthermore, the addition of HCl to MilliQ water causes the peculiar situation in which protons are the counter-ions to the negative charge assumed to be due to adsorbed hydroxide-ions within the double layer. For particle systems like Teflon powder (Preočanin et al. 2012) this is even more peculiar since in a mass titration the consumption of the hydroxide ion at the surface would cause the negative charge and the concomitant drop in pH, while the interface also would require the protons to be the counter-ions. Furthermore, the presence of the protons in the double layer and in particular within the shear plane might cause high surface conductance due to the presence of the highly mobile protons. In the KCl series there was no indication of surface conductivity, i.e. the two sets of measurements were identical within the measurement errors, and the Dukhin numbers were close to zero as shown in Fig. 5. For the series in the absence of KCl the same was obtained and again Dukhin numbers were close to zero.

The strong increase in the Dukhin number close to the isoelectric point is rather a feature caused by the very flat pressure ramps so that small deviations and measurement errors cause huge changes in the Dukhin number.

The results indicate that surface conductivity is not important in the current investigation.

5 Discussion

As obtained for many other aqueous interfaces of "inert" solids (Healy and Fuerstenau 2007; Lützenkirchen et al. 2008; Zimmermann et al. 2010) we have found a very low isoelectric point and significant pH-dependence of measured zeta-potentials for the OTS-aqueous solution interfaces studied in the present work.

Our data support the idea that the structure of the support may influence the OTS layer, which here finds its repercussion in lower IEPs at the 0001 quartz supported sample compared to the fused silica support. The precise structure of the fused silica support is not known.

There might be various explanations for the latter observation: one would be that a lower IEP might be due to a smoother interface that would be interacting more strongly with hydroxide ions (Vacha et al. 2008). There may be other reasons, though, which could be related to the structure of the OTS film and concomitant diffusion of ions into that film. Here in particular protons and potassium ions would be candidates. The bare fused silica surface used in this work has an IEP of below pH 3 as determined with the samples prior to coating, the quartz 0001 surface has an IEP lower than 2.8. At pH 2.8 the zeta-potential of the bare quartz 0001 in MilliQ water acidified by HCl is still about −15 mV. Consequently for both surfaces the coating with OTS leads to an increase of the IEP. This is an important result since for most oxides high isoelectric points are expected but for flat surfaces quite frequently low isoelectric points have been obtained as summarized for c-cuts of sapphire (Franks and Gan 2007). This has been further discussed in much detail for the sapphire-c surface, where an "inert-like" interfacial behavior caused by a particular water-structure may explain a wide number of macroscopic observations (Lützenkirchen et al. 2010). With the OTS silica systems the inert-like behavior instead causes an increase of the IEP compared to the bare support surfaces exactly as one would expect.

While it is known that contaminations easily affect the isoelectric points of oxides and in particular when small surface areas are exposed (Lützenkirchen 2007, 2010) as in the present experiments and although contaminations have been thought to be responsible for the charging of inert-surfaces (Roger and Cabane 2012), recent data on Teflon powder with high specific surface area, that were obtained without stabilizers according to the manufacturer, show that there remains a strong pH-dependence of the charging of such particles and that they compare fairly well with data obtained on flat Teflon surfaces and intermediate situations where flat Teflon surfaces were cut to smaller pieces (Preočanin et al. 2012).

We cannot exclude that our OTS samples are to some extent affected by the underlying oxide surface. Compared to previous reports on salt effects we find that the IEP of the quartz 0001 supported sample in KCl does change with KCl concentration. This suggests increased uptake of cationic solutes with increasing KCl concentration. This does not only contrast to the SFG results by Tian and Shen (2009) which rather suggest chloride adsorption, but also to observations that KCl does not significantly affect the IEP of Teflon (Preočanin et al. 2012) or inert surfaces in general (Healy and Fuerstenau 2007; Lützenkirchen et al. 2008; Zimmermann et al. 2010). The measured contact angles of our substrates in conjunction with the recent study by Li and Yoon (2012) suggest incomplete coverage. Their work also suggests that OTS adsorbs as patches, and that only under optimum conditions a smooth film will be created. Based on the results by Li and Yoon (2012) our samples would rather correspond to the patch-wise OTS coverage. Adsorption on patchwise heterogeneous oxide surfaces is highly complex in particular in the regions where two patches meet (Lützenkirchen and Behra 1997). This would imply that observations are affected by the oxide and thus cation effects may occur due to the support systems. When the cations are excluded there may be effects of chloride if it is assumed that ions may reside in the coating film and that some memory effect exists. Our data cannot be conclusive about that and additional experiments would be required to solve this issue. We therefore currently investigate specific ion effects on quartz 0001 surfaces.

6 Conclusions

Measurements on two silica supported OTS solution interfaces yield isoelectric points below pH 4. These agree with the range that is reported for many other aqueous interfaces of "inert" solids (Healy and Fuerstenau 2007; Lützenkirchen et al. 2008; Zimmermann et al. 2010). We have found a cation effect (i.e. potassium shifts the IEP to higher values) that has previously not been reported on such samples. Our current interpretation is that the surface is not completely covered by OTS as can be inferred from the contact angle measurements on those samples. This would imply that potassium effects occur on the supporting quartz 0001 surface.

We may have observed chloride adsorption on one of the samples when we rigorously exclude potassium, because in consecutive runs the charge of the sample became more negative and the isoelectric point decreased. Since these observations were made prior to contact of the samples with KCl, the most probable candidate would be the chloride ion in conjunction with a memory effect. This would agree with the SFG observations by Tian and Shen (2009).

Finally our results and a reconsideration of previous results on the air-water interface that were obtained without a constant background electrolyte imply: At low concentrations our data on the potassium free systems, at high iodide contents the SHG data by Petersen and Saykally (2005b) indicate that it is difficult to exclude medium effects when both the concentration of the solute of interest and the overall ionic strength of the system is varied. Unfortunately there are situations when this cannot be avoided, in particular when high concentrations are required to allow observations. At lower medium concentrations this may lead to situations where acid or base addition affects the overall ionic strength. For some experimental conditions it may even happen that protons or hydroxide ions are counter-ions. We have studied such systems here, but did not observe significant surface conductivity.

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