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Some data and simple models for the silanated glass-electrolyte interface

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Abstract The interface between silanated glass and aqueous KCl electrolyte solutions was studied by zeta-potential and contact angle measurements. Variation of the pH in the zeta-potential measurements yielded a sharp isoelectric point (IEP) at about pH 4, which was independent of the KCl concentration. This particular pH corresponds to zero electrokinetic potential for many hydrophobic surfaces encompassing Teflon, polyethylene and others.

The results are interpreted in terms of hydroxide adsorption at the silanated glass-aqueous interface. A previously developed model for such inert surface—electrolyte interfaces is applied to the experimental data. The model parameters are within the range of those previously obtained for comparable surfaces.

Discrepancies were observed in pH dependent contact angle measurements, which were done using both the plate and the drop method: advancing contact angles were always higher than receding contact angles. Advancing contact angles using the drop method yielded no clear tendency as a function of pH and lower values than those obtained by the plate-method. Overall the contact angle data are presented but deemed difficult to interpret in terms of pH dependence and relation to zeta-potentials. A preliminary description of the contact angle data is attempted via the Lippman-Young equation for the different contact angle data sets based on the model potentials. The model results are discussed.

Zeta-potential measurements were also performed as a function of salt content within a narrow pH range. As would be expected the presence of a 2:1 electrolyte ($BaCl_2$) results in lower absolute values when compared to the KCl case.

Keywords Hydrophobicity · Contact angle · Zeta-potential · Hydroxide ion adsorption

1 Introduction

Studies by Andrzej Waksmundzki involved preparation and characterisation of hydrophobic surfaces (Rayss et al. 1983). Thus silanization (Dawidowicz et al. 1977) as well as zeta-potential measurements on such hydrophobic surfaces (Chibowski and Waksmundzki 1978) were reported more than 30 years ago from his group.

The interface between "inert" surfaces and water or electrolyte solutions is currently attracting considerable interest (Beattie 2006; Healy and Fuerstenau 2007). Such interfaces involve for example solid surfaces like Teflon, polyethylene, or diamond in contact with aqueous electrolyte solutions, liquid-liquid interfaces such as oil-water systems, and gas-liquid systems, such as the air-water interface. Even the interfacial behaviour of the ice-water system is of interest in this context.

Dedicated to the memory of Professor Andrzej Waksmundzki (1910–1998) on the occasion of the celebration of his 100th birthday.

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While text-books have for a long time included passages that would suggest that there is no ion propensity at air-water interfaces, recent studies have indicated that accumulation of ions at these inert interfaces does occur. Stirred by reports from more than a century ago, where various scientists observed charged air bubbles or water droplets as summarized by Zilch et al. (2008) there is a current revival of interest in these issues. Recently the origin of the charge has been looked at by titrations of oil-in-water emulsions (Beattie and Djerdjev 2004) and modern techniques both experimental (Winter et al. 2009a) and theoretical (Vácha et al. 2008) have been applied to these systems to shed light on the observed phenomena. The major question remaining is what causes the charge at all these surfaces, and this might be related to the so-called "Jones-Ray-effect", which is another unresolved issue.

We resume the summary on the "Jones-Ray effect" as given by Petersen and Saykally (2005): In the 1930ies and 1940ies, a number of papers were published on the surface tension of aqueous electrolyte solutions, where especially data at dilute concentrations were controversial (Jones and Ray 1935, 1937, 1941a, 1941b, 1942). The capillary rise method gave a minimum in surface tension vs. concentration curves at millimolar concentrations for various inorganic salts. The usual tendency is an increase with concentration which implies that the ions are repelled from the surface, while decreasing surface tension would imply surface excess. The latter is in disagreement with the accepted theory that simple electrolyte ions do not accumulate at the interface, so that in the outermost surface layer of water no ions should be found. It disagrees for example with the theory of Onsager and Samaras (1934). Since then the "Jones-Ray effect" has been corroborated by some and not reproduced by others, and continues to be an open issue. Langmuir (1938a, 1938b) criticized the results of Jones and Ray and claimed it was due to an artefact that arose from the experimental technique. The charge at the capillary wall in contact with the medium was for example held responsible for the observation, because it could affect the capillary height as a function of electrolyte concentration or change properties of the wetting layer inside the capillary (Langmuir 1938a, 1938b). Despite this critique models were proposed that would allow explaining the surface tension minimum (Bikerman 1938; Dole 1937, 1938) and others actually reproduced the "Jones-Ray effect" for KCl using the ring method, for which the Langmuir artefacts would not be applicable (Dole and Swartout 1940). Schäfer et al. (1955), however, using the ring method were unable to reproduce these data. Since then other experimental approaches and models have been applied but still no agreement is achieved (see Petersen and Saykally 2005 for references). As stated above the Jones-Ray effect may be intimately related to the pH-dependent charging of inert surfaces. This is because the prevailing interpretation of these observations, namely asymmetric adsorption of water-ions (or enhanced autolysis of interfacial water) would require a Jones-Ray effect to occur as a function of hydroxide ion concentration. Unfortunately experimental data in the relevant hydroxide concentration range and also in the range of pH above the isoelectric point are not available. The fact that hydroxide ion adsorption is not reproduced in many advanced theoretical calculations (such as MD simulations, necessarily at nominally very high concentration) has resulted in a fierce dispute in the current literature (Beattie 2009; Gray-Weale 2009; Winter et al. 2009b). Here, we only quote the very recent correspondence between those two groups. Manciu and Ruckenstein (2003) were able to interpret the Ray-Jones effect involving hydroxide adsorption, and some computational approaches indeed do suggest that hydroxide adsorption does occur, in particular on hard walls (Vácha et al. 2008). The origin of the pH-dependent charging phenomena thus may be considered as not definitively settled similar to the Jones-Ray effect, which might be at the origin of hydroxide adsorption. However, many experimentalists find negative charges on these inert surfaces using different methods (e.g. Zimmermann et al. 2001; Stubenrauch and von Klitzing 2003). The observations have led Beattie (2006) or Healy and Fuerstenau (2007) to assume some kind of generic mechanism behind in terms of preferential adsorption of hydroxide ions or enhanced autolysis of water at these interfaces. In the present paper we report some data on the silanated glass aqueous electrolyte interface including results from zeta-potential and contact angle titrations. Variation of the contact angle with pH for this "inert"-electrolyte interface has to our knowledge not previously been reported. Hexadecane water systems however show pH dependence of interfacial tensions (McCafferty and Wightman 1997). Others did not find pH dependant contact angles for various inert surfaces using the drop method (Welzel et al. 2002).

2 Experimental

2.1 Solutions

All solutions were freshly prepared from MilliQ water (18.2 MΩ cm). Salts were heated before use. All chemicals used were at least analytical grade.

2.2 Substrates

Usual glass substrates were silanized as described in the following. Glass-substrates of the appropriate size were cleaned by boiling for 15 minutes in a solution of 5:1:1 volume fractions H_2O:NH_3(conc.):H_2O_2(32%) and subsequent washing H_2O and drying in a nitrogen atmosphere. The substrates were then silanated by immersion for 20 minutes in a solution consisting of 94 vol.-% acidified methanol (1.0 mM acetic acid in MeOH + 5 vol.-% water + 1 vol.-% (3-aminopropyl)-trimethoxysilane). Subsequently they were washed with EtOH und H_2O and dried under nitrogen. The glass-substrates were from Marienfeld GmbH & Co. KG Cat.No. 0111540. They are produced from pure white, entirely clear and chemically resistant borosilicate glass of first hydrolytic quality. The glass-substrates are not porous. (3-aminopropyl)trimethoxysilane was received from Aldrich (Cat 28,177-8) and 97%. The silanated samples as prepared in the present work were found to be stable over the course of the experiments. The streaming current measurements did not show any shift in the IEP, and the individual measurements at one pH and ionic strength condition were very close which is also evident from the error bars shown on the graphs. These substrates were used for subsequent coatings and those were also found to be stable in that case. Therefore we expect that a well-defined silanated surface was obtained.

2.3 Zeta-potential measurements

For the determination of the zeta potential, 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 100 µm. Before each pH titration the sample was flushed with MilliQ water, the desired electrolyte solution filled in and the pH increased to about 9 by adding a small volume of 0.1 M KOH. Subsequently the solution was titrated down to about pH 3 using the system inherent acid (0.1 M HCl).

During the measurements with the SurPass a constant flow of Ar, previously passed through two washing bottles (one containing KOH solution to capture carbon dioxide and another containing the ionic medium under study to minimise water evaporation from the electrolyte solution in the beaker), was present above the electrolyte solution.

The pH and conductivity electrodes were calibrated before each measurement series. For the pH calibration three commercial buffers were used. After a given measurement series the pH measurement set-up was checked against a commercial buffer to verify that pH 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 electrolyte solution has an inner electrolyte filling solution of 3 M KCl. Leakage of KCl from the pH electrode is inevitable and can be observed as a steady increase in conductivity when the KCl concentration is sufficiently low. On the time scale of our experiments this marginally affects the ionic strength at the lowest electrolyte concentrations studied. All measurements were made at room temperature. During the measurements temperature can vary by 1 K.

2.4 Contact angle measurements

Contact angle measurements by the plate method were carried out using a Cahn Radian 315 Thermo Fisher Scientific apparatus. The advancing and receding contact angles of the samples exposing in this case two silanated planes were measured in solutions of known proton or hydroxide concentration in 10 mM KCl solutions. The solutions were checked with respect to their surface tensions and no contamination could be detected. Contact angles were also measured by the drop method using the *dataphysics* Contact Angle System OCA10. Droplets were produced from solutions of known proton concentration and ionic strength.

2.5 Calculations

Calculations to simulate zeta-potentials were carried out in the same way as described by Lützenkirchen et al. (2008). Tentative calculations on the contact angles were also carried out. To this end the Lippman–Young equation was used. It relates the contact angle measured under an applied electric field to that at zero electric field via the equation (Digilov 2000) $\cos\{\Theta(\psi_o)\} = \cos\{\Theta(\psi_o = 0)\} + (\varepsilon_o\varepsilon_r(\Delta\psi)^2)/(2l\gamma_{sl})$ where

Θ	the contact angle
ψ_o	the surface potential (here available via model calculations as a function of pH)
ε_o	the permittivity of free space
ε_r	the relative permittivity of the interfacial layer
$\Delta\psi$	Potential difference over thickness l
l	the thickness of the interfacial layer considered
γ_{sl}	the surface tension of the electrolyte solution (here taken as constant)

The permittivity and thickness of the interfacial layer are unknown. Both could be adjusted to obtain a good fit to data. Here we assume that the dielectric constant ε_r is that of water. The thickness of the interfacial layer considered is estimated based on model inherent assumptions (Lützenkirchen et al. 2008). We apply the equation under two extreme assumptions as will be described later. Variation of ε_r was also tested. However, it is correlated to changes in the interfacial thickness. Smaller values for the relative permittivity of say 30 or 6 (dielectric saturation) will yield smaller values for $\cos\{\Theta(\psi_o)\}$. For an improved application of the highly simplifying model it would be required to have good estimates for both parameters, also as a function of pH and ionic strength.

Use of the above equation involves the assumption that the potential drop across the interfaces affects the contact angle in a similar way as in the situation of electrowetting where electric fields are applied.

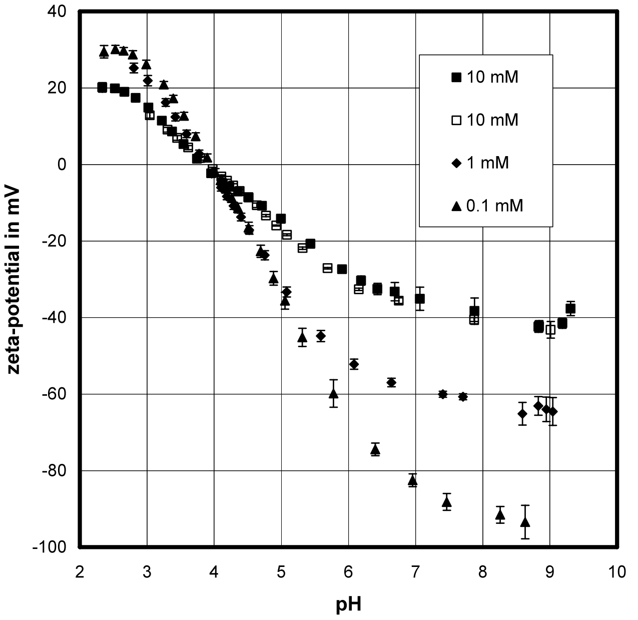


Fig. 1 Zeta-potentials of silanated glass-KCl electrolyte interfaces for three different KCl bulk concentrations

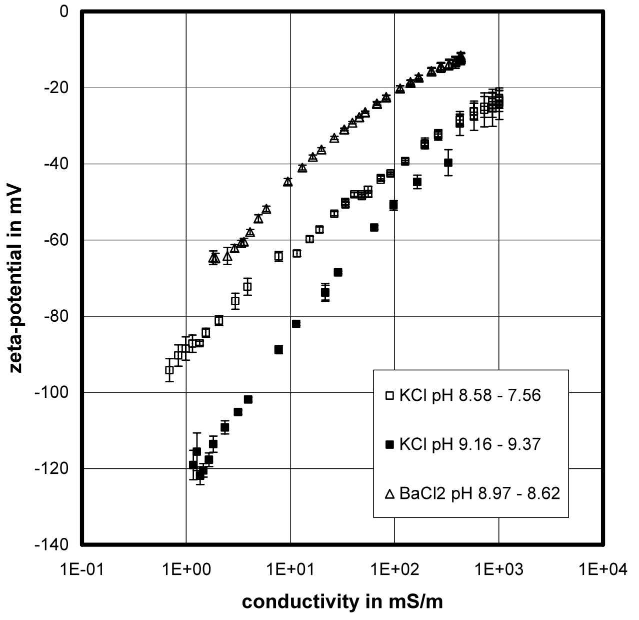


Fig. 2 Salt dependence of the zeta-potential at high pH values in terms of measured conductivity

3 Results and discussion

3.1 Effect of pH on zeta-potentials

Figure 1 shows the zeta-potential variation with pH for the silanated glass-KCl solution interface. The isoelectric point of the sample is found just below pH 4, in agreement with previously reported results for similar inert surfaces (Lützenkirchen et al. 2008). The two titrations at 10 mM KCl concentrations show that the measurements are very well reproducible. Furthermore, the standard deviations (from a total of 6 individual measurements at every pH value) are rather low. The measurements with the SurPass set-up are deemed very reliable and far more accurate than for example conventional zeta-potential data obtained by electrophoretic mobility measurements.

For the 1 mM and 0.1 mM data we note that they closely agree between pH 2.8 and 5. At pH below 3.5 this is due to the acid addition required to reach pH 3 (the ionic strength must be about 1 mM at this pH solely due to the HCl addition). The data in 0.1 mM must be affected by the acid additions around pH 4 at the latest. The co-incidence of the data up to pH 5 is somewhat unexpected. Overall the data set is in agreement with the expectations for such a surface.

3.2 Effect of salt concentration at high pH

Figure 2 shows the effect of salt concentration on the streaming current data at high pH as a function of measured solution conductivity as obtained during a salt titration by KCl solution. Figure 2 also includes data for $BaCl_2$ solutions. The KCl data suggest that at the high pH there is still increasing negative charge with increasing pH. This is not necessarily clear from Fig. 1. Finally, as should be expected the zeta-potentials in the 2:1 electrolyte are much lower in absolute value compared to the KCl solutions. The shape of the electrolyte dependence is very similar for all three curves.

3.3 Contact angles as a function of pH

In Fig. 3 we show the results of all our contact angle measurements. The advancing contact angles of the surfaces in 10 mM KCl solutions as a function of the acid concentration (given by $-\log[H^+]$) obtained by the plate method will be referred to first. The high contact angles are indicative of a hydrophobic surface, but expected for these samples. The data show a maximum of the contact angle at pH 4, which coincides with the isoelectric point found in the streaming current measurements. These data suggest that the immersing surface is most hydrophobic at the isoelectric point. However, such an interpretation would require that a film of water with properties similar to those in the zeta-potential measurements forms on the immersing surface. This would explain why beyond the isoelectric point a decrease in contact angle is observed potentially due to accumulation of charged ions which facilitate or enhance interaction with water or forming such a film. Data for the advancing contact angle obtained using the drop method show significant scatter but appear to be systematically lower than the previously discussed data. No clear trend is observed in these data. This agrees with previous results for comparable surfaces obtained with the drop method (Welzel et al. 2002)

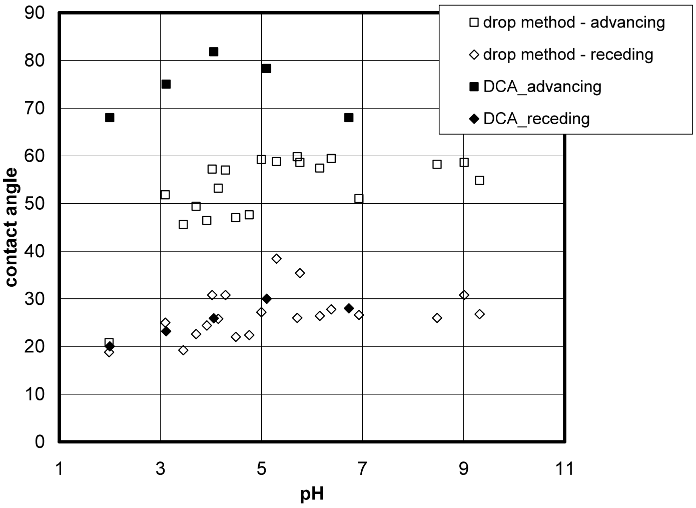


Fig. 3 Contact angles of silanated glass at various values of pH ($-\log[H^+]$) for 10 mM KCl solutions. DCA refers to the Cahn Radian apparatus, which measures the contact angle with the plate method

but disagreement exists between the drop method and the plate method and probably the preequilibration in the drop approach also plays a role (Hamadi et al. 2009). We are confident that the plate method data are reliable, since we have found similar trends with other surfaces. For example for Teflon we found that the extremum of the advancing contact angle obtained with the plate method also coincided with the measured isoelectric point (Lützenkirchen et al., in preparation). Data published by Hamadi et al. (2009) obtained with the drop method for samples pre-equilibrated with the respective solutions show exactly the same patterns as our plate method data. This makes us confident that the trends are real, but we plan to do more experimental work on the Teflon system to ascertain our data. We expect that the advancing contact angle data can also supply additional information in this context since a repulsive force was noted prior to the sample having contact with the water surface. However, we have not yet tried to evaluate those data. Noting that the air-water interface has similar properties and pH dependent behaviour as the silanated-glass water interface, there would be an explanation for why the advancing contact angles are higher than the receding ones and why their pH-dependence is much lower. The measurements with both techniques involve different processes if they are considered in detail. For example in the plate method measurements for the advancing contact angle there is interaction between the plate and the water surface, which is sensible in the force measurement already prior to contact. The interesting question is whether a water film exists on the substrate surface. Based on our macroscopic data, we are not able to answer this question which is under debate (Kaibara et al. 2003; Chakrapani et al. 2007).

Receding contact angles are much lower than the advancing contact angles and in this case we find more agreement between drop and plate methods. Even for this series we note that the scatter for the data obtained by the drop method is considerable. In the drop method this may for example be due to testing different samples, different locations on the same sample or time dependencies. In general we would expect that the receding contact angles are more representative of the "inert" surface water interface, because in this case, the surface has been or is in contact with the respective solution, while in the case of the plate method and the advancing contact angle it is in the process of getting into contact with it. Lower receding than advancing contact angles might suggest that indeed a water film remains on the surface and that the contact between this water film and the hydrophobic surface persists. The results obtained by the plate method for the hydrophobic surface would suggest weak pH dependence when compared to the advancing contact angle. Furthermore, the maximum of the contact angle appears to shift to higher pH, and away from the IEP.

For the advancing contact angles obtained by the plate method the interaction with the air-water interface might be of relevance as well. This interface has an isoelectric point between pH 3 and 4 (Healy and Fuerstenau 2007 and references therein). But an interpretation based on this issue would require knowledge about the presence or absence of a residual water film on this surface.

Later we attempt a highly simplified interpretation of all contact angle data sets to relate them to the zeta-potential values via the interface model, which we obtain from the modelling of the zeta-potential data.

3.4 Modelling of the pH dependence and ionic strength dependence of zeta-potentials

We have applied the model proposed by Lützenkirchen et al. (2008) to the data in Fig. 1 to estimate parameters. The fit results are shown in Fig. 4A as lines. The fit to the data involving the parameter values given in the figure caption is quite good. We note that the parameters are well within the

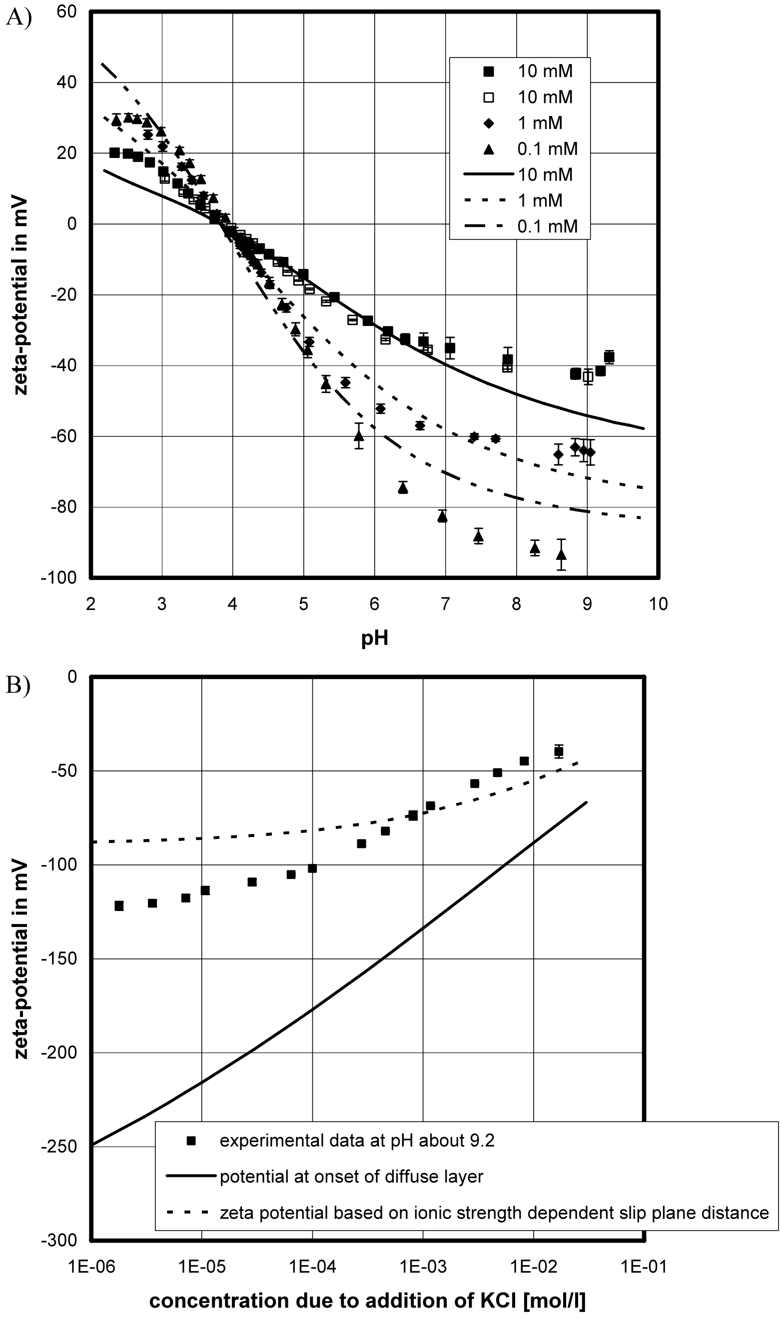
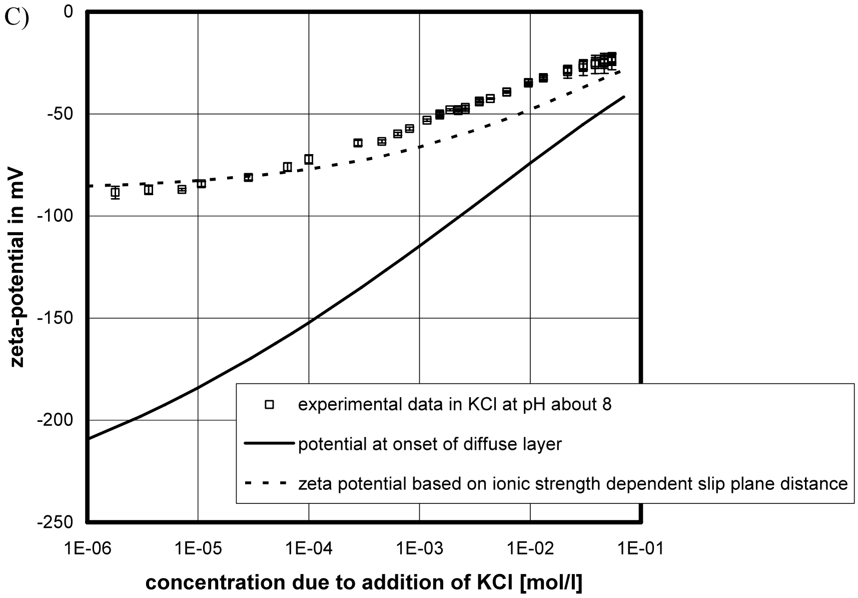


Fig. 4 Model description of the zeta-potential data. (**A**) pH-dependence: *Points* are experimental data from Fig. 1. *Lines* are model calculations using parameter values within the model by Lützenkirchen et al. (2008). (**B**) and (**C**) Ionic strength dependence: *Points* are experimental data from Fig. 2 (KCl at pH about 9.2 (**B**) and 8 (**C**), respectively). *Lines* are model calculations (see text for more details). Model parameters: $pK_{\mathrm{ass}} = 0.26$, $pK_W^{\mathrm{int}} = 6.83$, $x = 0.35$, $\sigma_{\mathrm{o}} = 0.0028\ \mathrm{C/m^2}$. Note that σ_{o} is negligible compared to the other model inherent charge densities

ranges previously established. The effect of acid-addition at the low pH on the effective ionic strength was not taken into account in our present calculations. It has been shown before (Lützenkirchen et al. 2008) that this would result in a better description of the data at low ionic strength and low pH. In particular the decrease of the zeta-potential can be accurately described. The inclusion of this effect would neither affect the model parameters significantly nor change the conclusions. The estimated parameters were used to predict the data in KCl at high pH (8 and 9.2) as shown in Figs. 4B and 4C, respectively. The calculations result in predicted zeta-potentials of correct magnitude. The exact values however cannot be predicted. In these systems, in particular at low concentrations, the salt concentrations are not known. Leakage from the combination electrode gradually increases the concentration. This can be observed in the transient increase in conductivity. Thus the starting concentration depends on how long the solution was in contact with the electrode. However, this effect cannot explain mismatch between calculation and experiment at high salt contents. This mismatch is due to the model, and was to be expected given that the pH dependence in Fig. 4A at high pH was not ex-

Fig. 4 (*Continued*)



actly modelled for all values of ionic strength. Clearly there is a need to improve the model, which is planned for the near future.

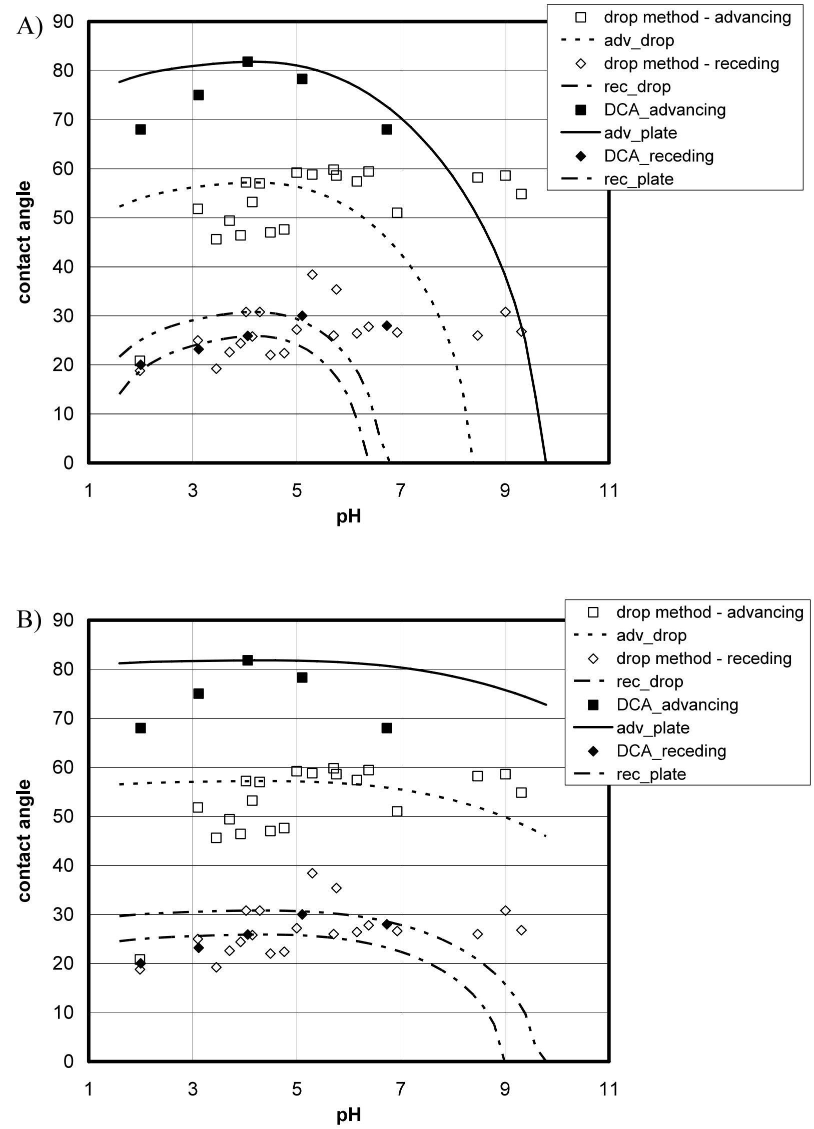
3.5 Modelling of the pH dependence of contact angles

Tentatively applying the Lippman–Young equation, and using the model inherent surface potentials we have tested two extreme cases assuming the dielectric constant of the interfacial layer to be that of water:

1. We used the model surface potentials and assumed a liquid film on the surface and potential drop within that small film of 0.4 nm thickness, which is the film thickness of the range of bilayers of water on other surfaces. Figure 5A shows the results obtained with this assumption. This might be a scenario for the advancing contact angles in case of persisting water films. Such films have been mentioned in a recent paper by McCarty and Whitesides (2008). The same work could also be taken to advocate charges in the absence of water on such surfaces. In case of a water film its properties should be known. The option to apply the surface potential pertaining to the solution into which the plate is immersed is probably not a good choice, but it may relate to the water–air surface which has similar zeta-potential as the plate.
2. We assumed as a probably more realistic potential the difference between surface potential and zeta-potential and estimated the separation between the two based on the previous paper (i.e. two water layers, about 0.4 nm in sum, which was based on MD simulations, plus the model inherent slip plane distance, i.e. about 1.1 nm). This reduces the “effective” potential difference in the Lippman–Young equation and thus decreases the pH-dependence. Figure 5B shows the results obtained with the second assumption. This might be a scenario for the receding contact angles.

The two model options appear to capture trends and we would not go further than that, given that the model is extremely simple both in terms of the zeta-potential description and even more so in terms of the contact angle description. The trends of the experimental data lie between the predictions based on options 1 and 2. Option 1 predicts a strong effect with increasing distance from the IEP. This is probably unrealistic and therefore option 2 is the more reliable one. We believe that for a more advanced model the receding contact angles are more relevant or that it needs to be established whether and what kind of water film preexists on the sample during the measurement of the advancing contact angle. In both cases the surface potential of the air water interface should also interfere. This is an interesting topic for future research and probably the variation of salt concentration can be another topic of interest. Our simple approach does allow simulation of the contact angles at other salt concentrations for the two above cases. Using option 1, which results in the most important effect as a function of pH, we observe that the effect will be not substantial (results not shown). The corresponding calculations for option 2 also suggest that the effect of ionic strength is not significant. The most interesting difference found between option 1 and 2 is that the salt dependence is inversed. The increased change of the calculated contact angle with decreasing ionic strength in option 1 is caused by the model inherent surface potentials which are significantly higher for the lower salt content. The potential differences used in option 2 are rather similar for all three salt contents and here the assumed distance makes the difference causing the biggest effect for the highest salt content. The situation may be dif-

Fig. 5 Model description of the contact angle as described in the text, (**A**) Assumption 1, (**B**) Assumption 2



ferent if the absolute contact angle at its extremum differs as a function of ionic strength. This should be investigated experimentally in the future. The major factor here is the difference in slip plane distance within the model. We stress that the calculations are based on numerous assumptions encompassing the simple model for the zeta-potentials and the assumptions involved in calculating the contact angles.

4 Summary and conclusions

We report data on the interface between a silanated substrate and aqueous electrolyte solutions. We have measured zeta-potentials as a function of pH and salt concentration and contact angles as a function of pH.

The zeta-potential data convincingly show negative values beyond the isoelectric point. The isoelectric point is not affected by the KCl concentration within the range of concentrations tested. Also the data follow the typical behaviour in terms of ionic strength dependence. Divalent cations decrease the absolute values of zeta-potential. Adopting the assumption of hydroxide ion adsorption, we can explain and model these data.

The contact angle measurements largely diverge. There is no full agreement between drop and plate method and neither between advancing and receding contact angles. We attempt to model the effect of pH on contact angles using the Lippman–Young-equation. The problem in the application of this equation is to know what boundary conditions and potential differences and separations should be used. We have tested two options, which probably represent extreme cases. The two options tested are considered upper and lower limits and the trends of the experimental data found in particular with the plate method actually lie in be-

Table 1 Equations for the model pertaining to the calculations of zeta-potentials for silanated glass surfaces. We consider 4 interfacial species and 2 dissolved species, the concentration of which is unknown. pH is imposed so that proton and hydroxide concentrations are known. Additionally, 3 potentials and 4 charge densities occur within the model. Overall 14 equations are available to solve the system for 14 unknowns

Surface potentials	$\Psi_0 > \Psi_1 > \Psi_2 = \Psi_d \geq \zeta$	
Electroneutrality	$\sigma_0 + \sigma_1 + \sigma_2 + \sigma_d = 0$	(1)
Gouy-Chapman equation	$\sigma_d = -\sqrt{8RT\varepsilon I_c}\,\sinh(-F\Psi_d/RT)$	(2)
Potential drop within diffuse layer	$\Psi_d = \frac{2RT}{F}\ln\left(\frac{\exp(-\kappa l) + \tanh(F\Psi_l/4RT)}{\exp(-\kappa l) - \tanh(F\Psi_l/4RT)}\right)$	(3)
Electrical capacitors	$C_1 = \frac{\sigma_0}{\Psi_0 - \Psi_1}$	(4)
	$C_2 = \frac{\sigma_1}{\Psi_1 - \Psi_d}$	(5)
Isoelectric point	$\zeta = 0, \Psi_d = 0, \Psi_2 = 0$	(6)
Charge at the 0-plane	$\sigma_0 = \text{const.}$	(7)
Balance of charge at plane 1	$\sigma_1 = B \times ([\equiv \mathrm{H_2OH^+}] - [\equiv \mathrm{HO^-}] - [\equiv \mathrm{HO^-} \cdots \mathrm{Na^+}])$	(8)
Balance of charge at plane 2	$\sigma_2 = B \times [\equiv \mathrm{HO^-} \cdots \mathrm{Na^+}]$	(9)
Mass law equation for interfacial water dissociation	${}^{c}K_{\text{int,hyd.}} = \frac{[\equiv \mathrm{HO^-}][\mathrm{H^+}]}{[\equiv \mathrm{H_2O}]}\exp\left(-\frac{F\Psi_1}{RT}\right)$	(10)
Reaction quotient for proton adsorption (unity)	${}^{c}K_{\text{int,pro.}} = \frac{[\equiv \mathrm{H_2OH^+}]}{[\equiv \mathrm{H_2O}][\mathrm{H^+}]}\exp\left(\frac{F\Psi_1}{RT}\right)$	(11)
Mass law equation for cation association	${}^{c}K_{\text{ass,cat}} = \frac{[\equiv \mathrm{HO^-} \cdots \mathrm{Na^+}]}{[\equiv \mathrm{HO^-}][\mathrm{Na^+}]}\exp\left(\frac{F\Psi_2}{RT}\right)$	(12)
Balance for interfacial species	$[\equiv \mathrm{H_2O}] + [\equiv \mathrm{H_2OH^+}] + [\equiv \mathrm{HO^-}] + [\equiv \mathrm{HO^-} \cdots \mathrm{Na^+}]$	(13)
Balance electrolyte ions	Na: $[\equiv \mathrm{HO^-} \cdots \mathrm{Na^+}] + [\mathrm{Na^+}]$	(14)

ε is electrical permittivity of bulk solution, I_c ionic strength, κ the Debye-Hückel parameter, l distance from the onset of the diffuse layer. R, T and F have their usual meaning. $[j]$ is concentration of species "j". σ_i are surface charge densities. Ψ_i are surface potentials. "i" denotes the plane. To calculate zeta-potentials: $l = s$ and $\Psi_{l=s} = \zeta$. Balances are calculated for the interfacial water sites, and the electrolyte ions

tween the two. However, we believe that the model is highly simplified and needs refinement. Furthermore, we think that some basic assumptions about pre-existing water films on the substrates should be evaluated.

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