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ORIGINAL CONTRIBUTION

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The influence of an acid treatment on the surface charge density of silica gel

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Abstract The influence of an acid treatment on the pore structure as well as on the surface charge density of porous silica was investigated. It is shown that this treatment causes only small changes of the pore structure. Positive values of the surface charge density at pH > 4 are interpreted in terms of surface impurities consisting of Na^+ ions resulting from the synthesis of the gel from sodium silicate solution. This effect is strongly influenced by the acid treatment. The surface charge density parameters were evaluated on the basis of the triple-layer model for the electrical double layer. Here two different mechanisms of counterion attachment in the inner Helmholtz plane are discussed.

Key words Surface charge density – silica gel – potentiometric titration – triple-layer model

Introduction

The properties of colloidal suspensions of solids in aqueous electrolyte solutions depend strongly on the surface charge density which is connected with the electrical double layer (edl). This includes the colloid stability [1, 2], electrokinetic phenomena [3], the particle diffusion [4, 5] as well as the rheological behaviour [6]. For oxides the surface charge density turns out to be a parameter which governs the kinetics of phase transition (dissolution of the oxide or precipitation of the solid from a supersaturated solution) [7, 8] as well as the coagulation of solid particles [1]. From this behaviour results the possibility to synthesize porous solids with a tailor-made pore structure by means of the concentration of potential determining ions [9, 10] (H^+ and OH^- in the case of oxides).

The most common methods for the characterization of the properties of the edl are electrokinetic investigations as well as the potentiometric pH titration [11] and the mass titration [12]. For basic investigations concerning the relationship between the surface charge density, the pH and the concentration of the background electrolyte by means of potentiometric titration specially cleaned solids were used in some cases [13, 14]. Unger et al. [15] have published the results of extensive investigations on the influence of a pretreatment with acids on the properties (with priority of chromatographic properties) of commercial silica. Within this investigations only a small effect on the behaviour of aqueous suspensions was found with the exception of a treatment with 10 wt% H_2SO_4.

For silica a point of zero charge (pzc) at pH ≈ 2 is usually found [16]. By contrast the surface charge density–pH plots on porous glasses published by Janusz et al. [17] yield values for the pzc between pH 4 and pH 7. A quantitative analysis of the experimental data was performed under application of the method of Davis et al. [18] in this paper. This results in an interpretation of positive values of the surface charge density, σ, at pH > 3 because of a protonation of silanol groups.

On the other hand, the preparation of colloidal oxides "... usually leads to particles incorporating the solution from which they were precipitated. This content is hard to remove..." [19]. Obviously these impurities lead to a displacement of the pzc. Possibly they are the reasons for the above-mentioned phenomena. Zalac and Kallay [19] have developed a method for the determination of the extent of such surface impurities from the displacement of the pzc determined by mass titration. The role of such impurities is pointed out also by Kosmulski [20] in connection with a comparison between results of electrokinetic measurements and σ determined by potentiometric titration. Furthermore, an increase of pH during hydrothermal aging of silica gels was explained by Titulaer et al. [21] on account of Na^+ adsorbed on the surface.

In the present work the pH dependence of σ of silica gel prepared from sodium silicate solution was investigated. The measurements were carried out using an untreated xerogel as well as after a treatment with HCl. Under application of two models for the surface charge formation, a coupled counterion binding in the inner Helmholtz plane (iHp) as well as an uncoupled counterion adsorption in the iHp, both in connection with the dissociation of acidic surface silanol groups, surface charge density parameters were evaluated within the framework of the triple layer model including the extent of surface impurities.

Materials and methods

Silica gel preparation

The silica gel called SP7 in this paper was prepared from sodium silicate solution and HCl. Thereby the experimental conditions were chosen in a manner to get a gel with a pore size greater than the inverse Debye–Hückel-parameter, κ^{-1}, on the one hand and with a sufficient specific surface area on the other hand. Because of the relative small gel time at pH $\approx$ 7 related with problems of an exact pH measurement in such a system as well as of sample homogeneity, a two-step procedure was applied. Sodium silicate solution (Merck) diluted with the double volume of deionized water and equilibrated for 1 month was mixed with 4% HCl (prepared from 37% HCl, Laborchemie Apolda, and deionized H_2O) under intensive stirring (5 min) at 25 °C. The volume of HCl was chosen to adjust to a pH $\approx$ 4. Under these conditions a hydrogel is formed during 2 h. This hydrogel was suspended in the double volume of H_2O. A pH of 7 was now adjusted with some drops of a NaOH solution and the suspension was stirred for 2 h again. After drying this product at 110 °C the resulting xerogel was washed with deionized H_2O until no Cl^- was detectable in the solution (precipitation with $AgNO_3$) and dried again.

A part of this product was now treated with 1 wt% HCl at 25 °C (twice for 1 h), washed (Cl^- detection) and dried again. This gel is called SP7/HCl.

Nitrogen adsorption and desorption

Nitrogen sorption isotherms were measured at 77 K by the AUTOSORB-1 (Quantachrome). For the analysis of the data the software included in this equipment was used. The specific surface area was calculated under application of the BET equation [22] and the pore size distribution from the desorption branch with the BJH method [23]. Before the measurement the samples were evacuated at 350 °C for 2 h.

Determination of the surface charge density

The determination of the surface charge density was performed by means of potentiometric pH titration (HCl and NaOH volumetric standard 0.1N from Aldrich) in comparison to a blank and with NaCl as background electrolyte. A detailed description of the experimental details can be found elsewhere [24]. Shortly, the sample was dispersed in the electrolyte solution of a desired NaCl (pa, Fluka) concentration prepared from deionized water (SERALPUR PRO 90 CN, Seral, conductivity <0.1 μS/cm). After adding an equal amount of NaOH standard to the sample (pH $\approx$ 8.5) and to the blank (pH $\approx$ 10.5) both solutions were titrated with HCl. All experiments were carried out under an Ar stream. To minimize possible diffusion effects within the pores the samples were ground in an agate mill. Only a sieve fraction smaller than 0.25 mm was used for the titration experiments and an equilibrium time of 8 min between each dosage and the pH reading was chosen. The background electrolyte concentrations in this investigation lay between 0.3 mol/l and 0.03 mol/l. The reason for these rather high values results from the objective to have a greater pore radius, R_P, than κ^{-1}. Under such conditions surface curvature influences on σ may be neglected [25]. All presented σ – pH plots are averaged values of four single measurements.

Leaching in H_2O

The two considered silica gels were immersed in deionized H_2O at room temperature for 24 h and then separated with a centrifuge. The Na^+ concentration in the clear solution was determined with a flame photometer PFP 7 (Jenway).

Surface charge density formation model

We consider a surface with acidic silanol groups in contact with an aqueous electrolyte solution in the pH range between 4 and 8. The formation of positive $\equiv \mathrm{SiOH}_2^+$ groups may be neglected in this pH area [25, 26]. Then the dissociation of silanol groups according to

$$\equiv \mathrm{SiOH} \rightleftharpoons \mathrm{SiO}^- + \mathrm{H}^+ \tag{I}$$

is the charge formation reaction. The emergence of an edl is connected with the formation of this surface charge. Because of the relation between the pore size and the inverse Debye–Hückel parameter, κ^{-1}, the edl is described with the triple-layer model [27] for a flat geometry. Thus the charge developed according to the reaction (I) is located in the area $x = 0$. Here, x is the distance from the surface. After introducing a dimensionless electrical potential, U, which is defined with Faraday's constant, F_A, the temperature, T, the gas constant, R_G, and the electrical potential, ψ, as

$$U = F_\mathrm{A} \cdot \psi / (R_\mathrm{G} \cdot T) \,, \tag{1}$$

an apparent acidity quotient, Q_A, [18] may be formulated for the reaction (I):

$$Q_\mathrm{A} = \frac{\{\equiv \mathrm{SiO}^-\}}{\{\equiv \mathrm{SiOH}\}} \cdot [H^+] = K_\mathrm{A}^\mathrm{int} \cdot \exp(U_0) \,. \tag{2}$$

Here, $K_\mathrm{A}^\mathrm{int}$ is the intrinsic acid constant, { } mean surface concentrations, [ ] mean volume concentrations in the bulk electrolyte far away from the surface ($U = 0$) and "0" stands for $x = 0$. With the total concentration of silanol groups, N_S, the surface charge density at $x = 0$, σ_0, is given by:

$$\sigma_0 = (\{\equiv \mathrm{SiOH}\} - N_\mathrm{S}) \cdot F_\mathrm{A} \,. \tag{3}$$

A part of the counterions (Na^+ in the considered case) are located in the iHp at $x = a$. A surface charge, σ_a, is attributed to these counterions within the iHp:

$$\sigma_\mathrm{a} = \{\mathrm{Na}^+\}_{\mathrm{X}=\mathrm{a}} \cdot F_\mathrm{A} \,. \tag{4}$$

Here two mechanisms are possible which are discussed in detail later. The remainder of the surface charge resulting from the reaction (I) is counterbalanced by the diffuse part of the edl beyond the outer Helmholtz plane, oHp, located at $x = d > a$. This compensating charge within the diffuse part of the edl divided by the surface area is called σ_d and may be calculated from the charge balance of the edl [11]:

$$\sigma_0 + \sigma_\mathrm{a} + \sigma_\mathrm{d} = 0 \,. \tag{5}$$

For the dimensionless potential at the oHp, U_d, results from the Gouy–Chapman theory

$$U_\mathrm{d} = 2 \cdot \sinh^{-1} \left\{ - \frac{F_\mathrm{A} \cdot \sigma_\mathrm{d}}{2 \cdot R_\mathrm{G} \cdot T \cdot \varepsilon_\mathrm{r} \cdot \varepsilon_0 \cdot \kappa} \right\} \tag{6}$$

with the dielectric constant, ε_r, and the permittivity of vacuum, ε_0. Within the Stern layer a linear drop of the potential, U, with a blip in the iHp exists. With the capacity of the inner layer, C_in, ($0 < x < a$) and that of the outer layer, C_out, ($a < x < d$) the potentials ψ_0 and ψ_a ($x = a$) may be calculated [28]:

$$\psi_\mathrm{a} = \psi_0 - \frac{\sigma_0}{C_\mathrm{in}} = \psi_0 + \frac{\sigma_\mathrm{a} + \sigma_\mathrm{d}}{C_\mathrm{in}} \,. \tag{7}$$

$$\psi_\mathrm{d} = \psi_\mathrm{a} - \frac{\sigma_\mathrm{a} + \sigma_0}{C_\mathrm{out}} \,. \tag{8}$$

The application of the bulk value for ε_r within the diffuse layer seems to be justified in the triple-layer model. For the inner layers ε_r is included in C_in and C_out as a parameter. σ_0 according to Eq. (3) agrees with the surface charge density determined by potentiometric titration [24] in the case of clean surfaces only. But this is not the case if the surface is contaminated with ions interchangeable with H^+ or OH^-. We assume, in agreement with [21], that these impurities in the case of silica prepared from sodium silicate solutions are Na^+ ions. Therefore an ion exchange

$$\mathrm{Na}^+_{\mathrm{Imp,surf}} + \mathrm{H}^+_{\mathrm{bulk}} \rightleftharpoons \mathrm{H}^+_{\mathrm{Surf}} + \mathrm{Na}^+_{\mathrm{bulk}} \tag{II}$$

must be taken into consideration. Then the surface concentration of interchangeable impurities, N_I, causes an apparent surface charge density, σ_I,

$$\sigma_\mathrm{I} = (N_\mathrm{I} - N_\mathrm{S} + \{\equiv \mathrm{SiOH}\}) \cdot F_\mathrm{A} = \sigma_0 + N_\mathrm{I} \cdot F_\mathrm{A} \tag{9}$$

which is determined by potentiometric pH titration.

Coupled counterion binding

A coupled binding of the counterions Na^+ on dissociated silanol groups, $\equiv \mathrm{SiO}^-$, is considered now. This process is described by the reversal reaction

$$\equiv \mathrm{SiONa} \rightleftharpoons \equiv \mathrm{SiO}^- + \mathrm{Na}^+ \tag{III}$$

since then the equilibrium for this reaction may be described by an equation similar to Eq. (2). The equilibrium constant is now called $K_\mathrm{D}^\mathrm{int}$ and depends on the potential, U_a, in the following manner.

$$K_\mathrm{D}^\mathrm{int} = \frac{\{\equiv \mathrm{SiO}^-\}}{\{\equiv \mathrm{SiONa}\}} \cdot [\mathrm{Na}^+] \cdot \exp(-U_\mathrm{a}) \,. \tag{10}$$

Thus the reactions (I) and (III) represent a coupled chemical equilibrium. $\{\mathrm{Na}^+\}_{\mathrm{x}=\mathrm{a}}$ in Eq. (4) is for this case identical with $\{\equiv \mathrm{SiONa}\}$ in Eq. (10). This corresponds to the "triple-layer model" described by Hayes et al. [27] and is similar to a lot of models published with different names, with a different formulation of the equilibrium constant for the reaction (III) or different locations of the charge center of the bounded counterions [18, 29–33].

At first glance it seems to be impossible to combine Eq. (1–10) in such a manner that an analytic expression between σ_I and the pH results. Therefore, two covering ratios of the surface are introduced, the ratio between the amount of surface charges counterbalanced by the diffuse part of the edl and the total amount of surface sites, α, on the one had and the share of dissociated silanol groups, β, on the other hand.

$$\alpha = \{\equiv \mathrm{SiO}^-\}/N_\mathrm{S} \tag{11}$$

$$\beta = (\{\equiv \mathrm{SiO}^-\} + \{\equiv \mathrm{SiONa}\})/N_\mathrm{S} \tag{12}$$

Thus we have the following relationships between α and β and the surface charge densities characterized in Eq. (5):

$$\sigma_0 = -\beta \cdot N_\mathrm{S} \cdot F_\mathrm{A}$$

$$\sigma_\mathrm{a} = (\beta - \alpha) \cdot N_\mathrm{S} \cdot F_\mathrm{A}$$

$$\sigma_\mathrm{d} = \alpha \cdot N_\mathrm{S} \cdot F_\mathrm{A} \tag{13}$$

For a given set of parameters $\{N_\mathrm{I}, N_\mathrm{S}, C_\mathrm{in}, C_\mathrm{out}, K_\mathrm{D}^\mathrm{int}, K_\mathrm{A}^\mathrm{int}\}$ as well as for a known concentration of Na^+ in the solution and with the relation

$$N_\mathrm{S} = \{\equiv \mathrm{SiOH}\} + \{\equiv \mathrm{SiO}^-\} + \{\equiv \mathrm{SiONa}\} \tag{14}$$

it is possible to derive such a relationship in the form:

$$[H^+] = f(\alpha)$$

$$\sigma_\mathrm{I} = f(\alpha)\,. \tag{15}$$

This includes the following steps. U_d is calculated from Eq. (13) and Eq. (6) for a given α. After introducing the abbreviation $E(\alpha)$,

$$E(\alpha) = \exp\left\{\frac{\alpha \cdot N_\mathrm{S} \cdot F_\mathrm{A}^2}{C_\mathrm{out} \cdot R_\mathrm{G} \cdot T} - U_\mathrm{d}\right\}, \tag{16}$$

the combination of Eq. (1, 2, 6, 7, 10, 12, 14, 16) yields after several tedious transformations

$$\beta = \alpha \cdot \left(1 + \frac{[\mathrm{Na}^+] \cdot E(\alpha)}{K_\mathrm{D}^\mathrm{int}}\right). \tag{17}$$

Thus we can calculate $\{\equiv \mathrm{SiOH}\}$ with Eq. (12, 14) in and then $\sigma_\mathrm{I} = f(\alpha)$ from Eq. (9). On the other hand, all variables (with Eq. (11)) are now given for the evaluation of $[\mathrm{H}^+]$ from Eq. (2). Now it is possible to describe the σ_I–pH relation in an indirect manner.

Uncoupled counterion adsorption

Now a counterion adsorption in the iHp according to a Langmuir-type equation is considered. That means that this adsorption takes place at adsorption sites which are not necessarily identical with the surface silanol groups, and that this adsorption is coupled to the dissociation of the silanol groups by the electrical potential only, not by a coupled chemical equilibrium. This results in an adsorption site density, N_AS, which may be different from N_S [34]. For the characterization of the ratio between these two site densities the abbreviation, Q, is introduced.

$$Q = N_\mathrm{AS}/N_\mathrm{S}\,. \tag{18}$$

Because of the mathematical equivalence of a Langmuir-type adsorption with the dissociation of surface groups [25] this adsorption is described again by the reversal process

$$\mathrm{ASNa}^+ \rightleftharpoons \mathrm{AS} + \mathrm{Na}^+ \tag{IV}$$

since then a similar relation as for the reaction (III) may be used for the intrinsic equilibrium constant for the reaction (IV), which is called again $K_\mathrm{D}^\mathrm{int}$.

$$K_\mathrm{D}^\mathrm{int} = \frac{\{\mathrm{AS}\}}{\{\mathrm{ASNa}^+\}} \cdot [\mathrm{Na}^+] \cdot \exp(-U_\mathrm{a}) \tag{19}$$

$\{\mathrm{Na}^+\}_{x=a}$ in Eq. (4) is now identical with $\{\mathrm{ASNa}^+\}$ in Eq. (19). For the calculation of the σ_I-pH relation the most of the equations mentioned above for the first model may be used again with the following four exceptions:

i) Eq. (10) must be replaced by Eq. (19).

ii) The total site density of silanol groups, N_S, is now given by

$$N_\mathrm{S} = \{\mathrm{SiOH}\} + \{\mathrm{SiO}^-\} \tag{20}$$

instead of Eq. (14).

iii) If α and β should have the same meaning as mentioned above, then Eq. (11) and Eq. (12) must be modified in the following form:

$$\alpha = (\{\equiv \mathrm{SiO}^-\} - \{\mathrm{ASNa}^+\})/N_\mathrm{S} \tag{21}$$

$$\beta = \{\equiv \mathrm{SiO}^-\}/N_\mathrm{S}\,. \tag{22}$$

Now α can be negative. This corresponds to the superequivalent counterion adsorption described by Stern [35].

iv) The relation between β and α is now:

$$\beta = \alpha + \frac{Q \cdot [\mathrm{Na}^+]/K_\mathrm{D}^\mathrm{int}}{E(\alpha) + [\mathrm{Na}^+]/K_\mathrm{D}^\mathrm{int}}\,. \tag{23}$$

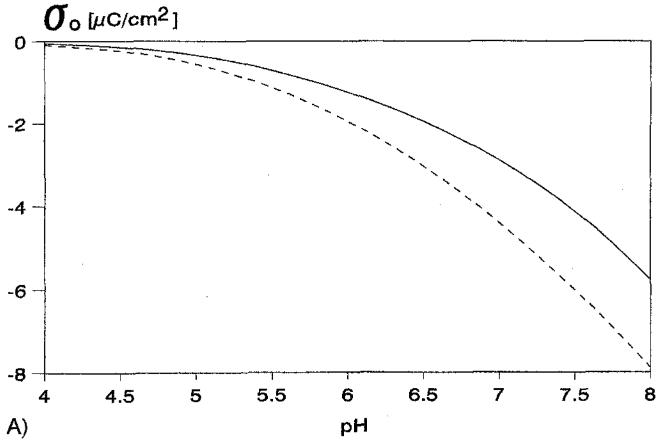
Thus we have (after the extension of the parameter set with Q) a relationship $\sigma_\mathrm{I} = f(\alpha)$ (Eqs. (22, 20, 9) and pH $= f(\alpha)$ (Eqs. 22, 20, 2), which allows us to calculate σ_I–pH plots.

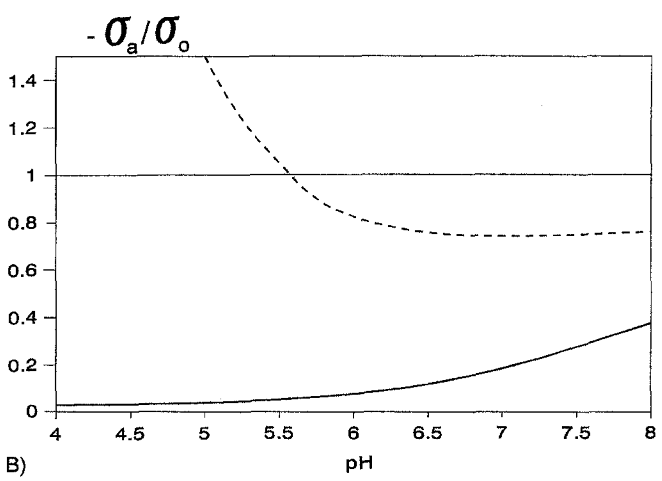
Comparison of the two models

For the comparison of the two models the case $N_l = 0$ is considered. Figure 1A and Fig. 1B show the fundamental difference in σ_0 between the two described models. Here the same set of parameters was used for both models and in the case of the uncoupled adsorption $Q = 1$ (i.e., $N_{AS} = N_S$). A noticeable difference may be seen if we look at $-\sigma_a/\sigma_0$, the part of the surface charge which is counterbalanced by counterions in the iHp. For the counterion binding model a continuous increase of $-\sigma_a/\sigma_0$ with pH is found. For decreasing pH $-\sigma_a/\sigma_0$ approaches a limit which depends on the ratio $[Na^+]/K_D^{int}$. In the case of the uncoupled adsorption of counterions a minimum in $-\sigma_a/\sigma_0$ in dependence on pH is found. With decreasing pH a steep rise occurs and $-\sigma_a/\sigma_0$ grows to values greater than 1. This phenomenon coincides with the change of the sign of the potential within the Stern layer as described in [35].

For the model of uncoupled adsorption the higher $-\sigma_a/\sigma_0$ is accompanied by a higher value of the amount of surface charge density, $|\sigma_0|$, in the whole pH range considered in Fig. 1A and Fig. 1B in comparison with the coupled binding model (for the same set of parameters). Furthermore it can be noticed that at pH = 8 only 15% of the silanol groups are dissociated ($pK_A^{int} = 7$).

Fig. 1A Results of model calculation for the coupled counterion binding model (—) and the uncoupled counterion adsorption (- - -); Surface charge density-pH plot; $pK_A^{int} = 7$; $[Na^+] = 0.1$ mol/l; $N_S = N_{AS} = 3/nm^2$; $C_{in} = 140\ \mu F/cm^2$; $C_{out} = 100\ \mu F/cm^2$; $pK_D^{int} = -0.6$. **B** Results of model calculation: The ratio of counterion charge within the iHp counterbalancing the surface charge, $-\sigma_a/\sigma_0$, in dependence on pH; lines and constants have the same meaning as in Fig. 1A; Note the super-equivalent charge in the iHp at low pH for the counterion adsorption model





Results and discussion

In Fig. 2 as well as in Table 1 the results of the nitrogen measurements for both porous silicas investigated are shown. It can be seen that the treatment with hydrochloric acid causes only small differences in the pore structure of the samples. This is verified by a very similar form of the isotherms. The difference in specific surface area is approximately 3% and the difference in specific pore volume is about 10%. For both samples the calculation of the pore size distribution under application of the BJH method yields two maxima, the first at $R_P = 8$ nm for SP7/HCl or $R_P = 9$ nm for SP7, respectively, and the second with a lower intensity at $R_P \approx 14$ nm for both samples. As a result of a comparison of these radii of the maximum of the pore size distribution with the inverse Debye–Hückel parameter of the lowest electrolyte concentration in the

Fig. 2 Nitrogen adsorption and desorption isotherms (77 K) for the samples SP7 (—) and SP7/HCl (- - -)

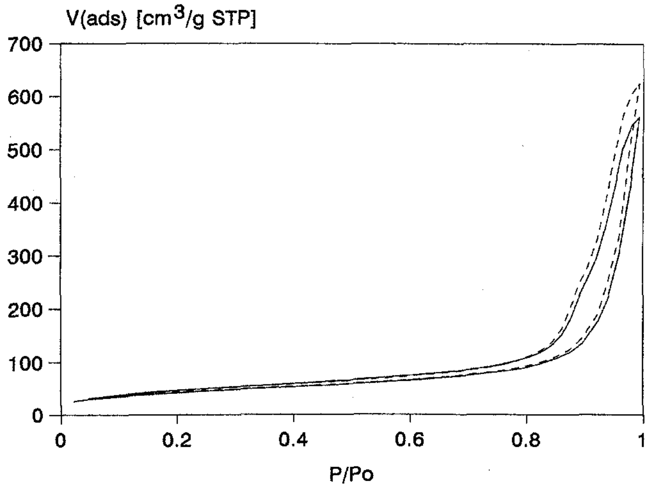


Table 1 Results of the N_2 pore structure investigations (S: specific surface area, V_P: specific pore volume, $R_{P,i\,max}$: maxima of the pore size distribution)

Sample	$S[\mathrm{m}^2/\mathrm{g}]$	$V_P[\mathrm{cm}^3/\mathrm{g}]$	$R_{P,1\,max}[\mathrm{nm}]$	$R_{P,2\,max}[\mathrm{nm}]$
SP7	145.9	0.85	9.0	14.4
SP7/HCl	150.9	0.94	8.0	14.6

experiments ($\kappa^{-1} \approx 1.8$ nm) the application of a model for a flat electrical double layer seems to be justified.

The results of the determination of the dependence of the surface charge density on pH determined by potentiometric titration are depicted in Fig. 3 (points). It is evident that the plots approach a limit if the pH decreases to 4. This limiting value is independent of the electrolyte concentration, but different for the two samples. In both cases $\sigma_I > 0$ is found. For both samples a dependence of the position of the apparent pzc on the electrolyte concentration appears. However, in the case of the sample SP7/HCl an exact determination of this apparent pzc is difficult because of the low gradient of the plots at $\sigma_I \approx 0$. For the sample SP7 the apparent pzc increases with decreasing electrolyte concentration.

To evaluate the parameters characterizing the σ_I–pH dependence according to the two models described above the following concept was applied.

i) The capacity of the inner layer was considered as a constant with $C_{in} = 140\ \mu\mathrm{F/cm}^2$ according to [33, 36].

ii) For a given set of parameters $\{N_S, (N_{AS}), K_D^{int}, K_A^{int}, C_{out}\}$ as well as for a given α the value of $[\mathrm{H}^+]$ was calculated according to the way outlined above.

iii) Now α was varied until the calculated $[\mathrm{H}^+]$ agrees with the experimental one. For this α then σ_I^{calc} was calculated. This procedure was repeated for all experimental points including three concentrations for both samples. Then $\Sigma(\Delta\sigma)^2$ characterizes the difference between the calculated points and the experimental data.

$$\sum(\Delta\sigma)^2 = \sum_{\text{all points}} (\sigma_I^{calc} - \sigma_I^{exp})^2 \,. \qquad (24)$$

Because of the acid treatment of one sample a different surface structure should be expected. Therefore the parameters N_S, N_I and K_A^{int} depend on the sample. On the other hand it was assumed that the influence of the acid treatment on the interaction with counterions is small (K_D^{int}, C_{out} and N_{AS} are assumed to be independent of the treatment).

iv) Now the steps ii) and iii) were repeated with a systematic variation of the set of parameters until $\Sigma(\Delta\sigma)^2$ reaches a minimum.

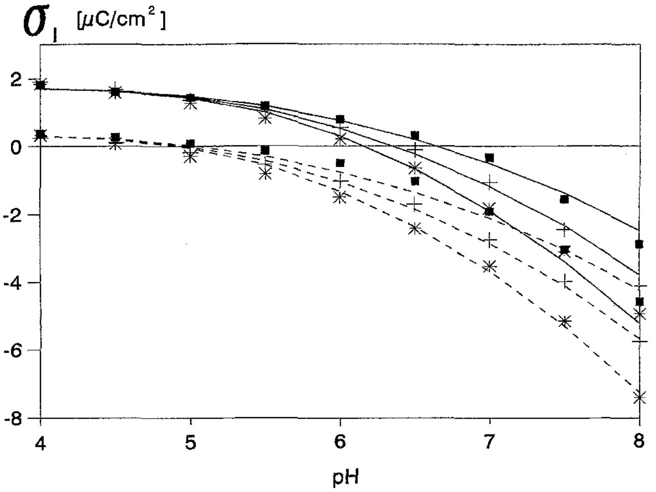


Fig. 3 Experimental data of surface charge density (points) in comparison with the result of the parameter evaluation for the counterion binding model (lines); ■: 0.03 mol/l NaCl; +: 0.1 mol/l NaCl; *: 0.3 mol/l NaCl; ——: SP7; – – –: SP7/|HCl

For a comparison of the agreement of the calculated curves with the experimental data for different models $\Sigma(\Delta\sigma)^2$ is not suitable because of different numbers of parameters N_P. After introducing the residual deviation, $s(\sigma)$,

$$s(\sigma) = \sqrt{\frac{\sum(\Delta\sigma)^2}{N_D - N_P}} \qquad (25)$$

(N_D: number of experimental points) such a comparison is possible.

Table 2 shows the numerical results of the parameter evaluation. Both models yield a good agreement with the experimental data. This is shown for the coupled counterion binding model in Fig. 3. For the uncoupled counterion adsorption nearly identical curves result (not shown) with the parameters given in Table 2.

Comparing the two described models it can be seen that the counterion adsorption model yields higher values for $\mathrm{p}K_A^{int}$ and lower values of N_S. This tendency reflects the principal differences in the σ_o–pH dependence shown in Fig. 1. For both models we have values for C_{out} higher than that determined by electrokinetic investigations [33]. This may be an indication for the fact that the slipping plane is located beyond the oHp. The disagreement between ψ_d and the ζ-potential was also found by Zhang et al. [36]. The difference in C_{out} between the two models seems to be relatively large. C_{out} does not determine the difference between ψ_d and ψ_a, but rather $1/C_{out}$ does. From this fact we can conclude rather a small difference between ψ_d and ψ_a for both cases instead of a great

Table 2 Results of surface charge density parameter evaluation

Parameter	Sample	Counterion binding	Counterion adsorption
pK_A^{int}	SP7	6.97	7.38
$N_S\,[nm^{-2}]$	SP7	2.17	1.89
$N_I\,[nm^{-2}]$	SP7	0.11	0.10
pK_A^{int}	SP7/HCl	6.92	7.35
$N_S\,[nm^{-2}]$	SP7/HCl	2.71	2.36
$N_I\,[nm^{-2}]$	SP7/HCl	0.02	0.02
pK_D^{int}	both	− 0.79	− 0.05
$N_{AS}\,[nm^{-2}]$	both	–	1.00
$C_{out}\,[\mu F/cm^2]$	both	258	90
$s(\sigma)\,[\mu C/cm^2]$	both	0.17	0.17

Table 3 Comparison of the part of the surface charge density caused by surface impurities (Na^+) determined by different methods (values are given as $\sigma[\mu C/cm^2]$)

Sample	Counterion binding	Counterion adsorption	Leaching
SP7	0.11	0.10	0.09
SP7/HCl	0.02	0.02	0.02

difference in the thickness of the outer layer predicted by the two models.

The comparison between the two samples shows that the influence of an acid treatment on pK_A^{int} is relatively small. On the other hand the value of the surface site density, N_S, is approximately 25% higher for the acid treated sample according to both models. This speaks for a change of the surface structure during the acid treatment. Both models yield a nearly identical result (but different for the two samples) for the surface concentration of impurities. These values agree with those from the leaching experiment in water (Table 3). That means that an acid treatment (with the concentration and time applied here) leads to a reduction of the surface impurities of about 80%.

Summary

1) The influence of an acid treatment on the pore structure determined by N_2 sorption measurements at 77 K and on the pH dependence of the surface charge density in aqueous NaCl solution determined by potentiometric titration of porous silica was investigated. It appears there are only small effects of this treatment on the pore size distribution, on the specific pore volume and on the specific surface area. But this acid treatment influences the surface charge density–pH behaviour. For porous silica prepared from sodium silicate solution and HCl positive values of σ at pH >4 were found as well as an apparent pzc which depends on the electrolyte concentration. The acid treatment moves this apparent pzc to a lower pH. An interpretation of these results in terms of surface impurities consisting of Na^+ ions from the sodium silicate solution is possible. Obviously, it would be also possible to analyse the experimental data after a correction including the common intersection point (cip) [28]. But the method described in the present paper gives the cip a chemical meaning.

2) Surface charge density constants for silica were evaluated on the basis of the triple-layer model for a flat geometry. In addition to the dissociation of acidic surface silanol groups as the charge formation reaction two mechanisms for the attachment of counterions in the iHp are discussed, a site binding on $\equiv SiO^-$ on the one hand and an uncoupled Langmuir-type adsorption on the other hand. Both models describe the experimental σ_I–pH dependence in a similar good manner. However, a qualitative comparison with results of electrokinetic measurements on SiO_2 [33] shows no significant change of the isoelectric point with electrolyte concentration. That means that a superequivalent counterion adsorption is not probable. This fact encouraged us to give preference to the counterion binding model.

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