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ORIGINAL CONTRIBUTION

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# Surface charge density on spherical silica particles in aqueous alkali chloride solutions

## Part 2. Evaluation of the surface charge density constants

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**Abstract** Experimental data concerning the dependence of the surface charge density of AEROSIL 300 in aqueous alkali chloride solutions on pH are analyzed under application of two different models for a spherical electrical double layer. Data for the alkali ions $Li^+$, $Na^+$, $K^+$, $Rb^+$ and $Cs^+$ are included at five electrolyte concentrations. In the first model a counterion binding in combination with a pure diffuse spherical double layer is considered; here, a good agreement between the recalculated plots and the experimental data is found for low electrolyte concentrations ($c < 0.05$ mol/l) only. The second model with a charge free Stern layer and without counterion binding seems to be applicable for higher electrolyte concentrations also. Furthermore the surface charge density constants from the second model agree better with those published and determined with other models or experimental methods.

**Key words** Surface charge density – silica – spherical particles – counterion binding – Stern layer

## Introduction

The influence of different counterion species on the surface charge density, $\sigma_0$, of colloidal dispersions as well as on properties related to $\sigma_0$ are of interest for basic research and applied science. This concerns, for example, the colloid stability [1, 2]. Furthermore, the adsorption of ions in the interface depends on $\sigma_0$. This phenomenon is applied in ion chromatography and is of importance in connection with nuclear waste respositories (see e.g. [3]).

Alkali ions are often considered as indifferent ions for oxides [4–6], since they do not affect the position of the point of zero charge (p.z.c.). On the other hand the influence of different alkali ion species on the amount of the surface charge density is verified by some experimental results and is described by an alkali sequence. This alkali sequence depends, however, on the oxide under consideration (see e.g. [7]). Furthermore the sequence may change with the electrolyte concentration [2] or with pH [8].

For the interpretation of the differences between $\sigma_0$-pH plots in the presence of different alkali ions two fundamental mechanisms are discussed in the literature: i) the different radii of solvated ions [9] or ii) a specific ion binding or adsorption [7, 10–13].

Systematic investigations of the dependence of $\sigma_0$ on pH in the presence of different alkali ions were published by Tadros and Lyklema [9] and by Kosmulski and Matijevich [7, 14]. In both cases porous silica was investigated in a limited concentration range. The interpretation of the data was done qualitatively or quantitatively on the basis of a model for a flat electrical double layer.

The aim of the present article is a quantitative analysis of the extensive experimental results presented in part 1 [15]. Doing so, both ideas mentioned above, i) ion binding and ii) radius of solvated ions which should influ-

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ence the Stern layer thickness, are connected with a spherical double layer model. The constants describing the relation between $\sigma_0$, pH and the electrolyte concentration are evaluated. Because of the limited pH range investigated (see part 1) the calculations are restricted to the dissociation of acidic surface silanol groups as surface charge formation reaction.

## Experiments

The surface charge density on AEROSIL 300 was determined in dependence on pH in the presence of five different alkali chlorides, $Li^+$, $Na^+$, $K^+$, $Rb^+$ and $Cs^+$, at five different concentrations (0.005 mol/l to 0.3 mol/l) by potentiometric pH titration in comparison with a blank. The experimental details are described indepth in [15].

## Specific counterion binding

Spherical particles with a radius, $R_p$, are considered. Since the experimental data are limited to pH > 4 the protonation of silanol groups may be neglected. Then the dissociation of silanol groups according to

$$\equiv SiOH \leftrightharpoons \equiv SiO^- + H^+ \qquad (I)$$

is the charge formation reaction. This surface charge is connected with the emergence of an electrical potential, $\psi$, which has a value $\psi_0$ in the plane of the surface charge and which decreases to zero with increasing distance from the surface. Furthermore, this surface potential causes a local concentration of the ions within the electrical double layer different from that in the bulk liquid. The local ion concentration can be described by the Boltzmann distribution. Thus, we have two possibilities to characterize the equilibrium of the reaction (I):

i) An intrinsic acid constant, $K_S^{int}$, includes the local concentration of protons immediately at the plane of surface charge, $[H^+]_{surf}$. But it is difficult to determine this local concentration experimentally.

ii) An apparent coefficient, $K_S^{app}$, includes the proton concentration in the bulk ($\psi = 0$) and depends on the surface potential $\psi_0$. The relationship between $K_S^{int}$ and $K_S^{app}$ is given by Eq. (1).

$$K_S^{app} = \frac{\{\equiv SiO^-\}}{\{SiOH\}}\cdot[H^+] = K_S^{int}\cdot\exp(U_0)\,. \qquad (1)$$

Here, $\{\ \}$ means surface concentration (mol/m$^2$) and $[\ ]$ volume concentration in the bulk liquid far away from the interface. For the relation between the surface potential, $\Psi_0$, and the dimensionless surface potential, $U_0$, we have

$$U_0 = \frac{\Psi_0\cdot F_A}{R_G\cdot T} \qquad (2)$$

with the Faraday constant, $F_A$, the gas constant, $R_G$, and the temperature, $T$.

Furthermore, a specific binding of counterions ($M^+$) is considered:

$$\equiv SiO^- + M^+ \leftrightharpoons \equiv SiOM\,. \qquad (II)$$

Besides it is assumed that the charge formed according to (I) and the charge of the bounded ions $M^+$ are located both in the surface $r = R_p$. Here, $r$ is the distance from the centre of the particle. This approximation is justified for amorphous silica due to an incompletely condensed surface structure [16]. Obviously, the equilibrium of the reaction (II) is described in the literature by different equilibrium constants. Healy and White [17] have introduced the constant, $K_{-+}$,

$$K_{-+} = \frac{\{\equiv SiOM\}}{\{\equiv SiO^-\}\cdot[M^+]_{surf}} \qquad (3)$$

which is the intrinsic equilibrium constant of the reaction (II). Yates et al. [18] used the reciprocal value and Davis et al. [12] gave preference to characterize the counterion binding by an equilibrium constant, $K_{M^+}$, which is valid for a coupled equilibrium of (I) and (II):

$$K_{M^+}^{int} = K_S^{int}\cdot K_{-+}\,. \qquad (4)$$

In the present article the approach of Yates et al. [18] is applied. Since this equilibrium constant describes the reversal reaction of (II), that means a dissociation of the $\equiv SiOM$ group, called $K_D^{app}$. Thus the same dependence on $U_0$ is valid for $K_D^{app}$ and for $K_S^{app}$:

$$K_D^{app} = \frac{\{\equiv SiO^-\}}{\{SiOM\}}\cdot[M^+] = K_D^{int}\cdot\exp(U_0)\,. \qquad (5)$$

With the total concentration of surface groups, $N_S$, in mind,

$$N_S = \{\equiv SiOH\} + \{\equiv SiO^-\} + \{\equiv SiOM\} \qquad (6)$$

it is useful to define two covering ratios, i) on the one hand the fraction of charged surface sites, $\alpha$,

$$\alpha = \{\equiv SiO^-\}/N_S \qquad (7)$$

and ii) the fraction of dissociated silanol groups, $\beta$,

$$\beta = \frac{\{\equiv SiO^-\} + \{\equiv SiOM\}}{N_S}\,. \qquad (8)$$

Furthermore, three charge densities must be distinguished.

i) The surface charge density, $\sigma_0$, which is detected by the potentiometric titration (see detailed discussion in part 1). Since $\sigma_0$ is determined by pH measurement it includes two types of surface groups, $\{\equiv\mathrm{SiO}\}$ and $\{\equiv\mathrm{SiOM}\}$.

$$\sigma_0 = -N_S \cdot \beta \cdot F_A \,. \tag{9}$$

ii) The share of $\{\equiv\mathrm{SiOM}\}$ on $\sigma_0$ contributes not to the real surface charge density within the considered model, but to the measured one. For the characterization of this part the "charge per unit area of bonded counterions", $\sigma_a$, is defined.

$$\sigma_a = \{\beta - \alpha\} \cdot N_S \cdot F_A \,. \tag{10}$$

Furthermore the counterbalancing charge density in diffuse part of double layer, $\sigma_d$, must be considered. The latter can be calculated under consideration of the electroneutrality condition [19].

$$\sigma_0 + \sigma_a + \sigma_d = 0 \,. \tag{11}$$

In the further considerations it is assumed that the diffuse part of the double layer begins at $r = R_p$. Then the relation between the dimensionless surface potential, $U_0$, and the charge density in diffuse part of double layer, $\sigma_d$, as derived elsewhere [20] is applicable (note that $\sigma_0$ in [20] must be replaced by $-\sigma_d$):

$$\begin{aligned} U_0 &= -2 \cdot \ln\left(X - \sqrt{X^2 - 1}\right) \\ X &= -R_R + \sqrt{(R_R + 1)^2 + Q} \\ Q &= l^2/4 \\ R_R &= 2/(\kappa \cdot R_p) \\ l &= \frac{-\sigma_d \cdot F_A}{\varepsilon_r \cdot \varepsilon_0 \cdot R_G \cdot T \cdot \kappa} \end{aligned} \tag{12}$$

Here, $\kappa$ is the Debye–Hückel parameter, $\varepsilon_r$ the dielectric constant and $\varepsilon_0$ the permittivity of vacuum. Obviously it seems to be impossible to get an analytic relation between $\sigma_0$ and $[\mathrm{H}^+]$ by the combination of the Eqs. (1, 2, 5–12). However, if a set of parameters $\{K_S^{\mathrm{int}}, K_D^{\mathrm{int}}, N_S, R_p\}$ is given and $[\mathrm{M}^+]$ is known from the experimental conditions, $U_0$ can be calculated from a given value of $\sigma_d$ (or $\alpha$ or $\{\equiv\mathrm{SiO}^-\}$) with Eq. (12). Thus we have $\{\equiv\mathrm{SiOM}\}$ from Eq. (5) and than $\beta$ and $\sigma_0$ from (8) and (9), respectively. Furthermore, now all variables are known to calculate $\{\equiv\mathrm{SiOH}\}$ from Eq. (6) and $[\mathrm{H}^+]$ from Eq. (1). This means that an analytic relation exists between $\sigma_0$ and $[\mathrm{H}^+]$ in form of two equations.

$$\begin{aligned} \sigma_0 &= -\sigma_d \cdot \left[1 + \frac{[\mathrm{M}^+]}{K_D^{\mathrm{int}}} \cdot \exp(-U_0)\right] \\ [\mathrm{H}^+] &= \left[\frac{N_S \cdot F_A}{\sigma_d} - 1\right] \cdot K_S^{\mathrm{int}} \cdot \exp(U_0) - \frac{[\mathrm{M}^+] \cdot K_S^{\mathrm{int}}}{K_D^{\mathrm{int}}} \,. \end{aligned} \tag{13}$$

Using this approach the constants describing the surface charge density of AEROSIL 300 in aqueous solutions of different alkali chlorides were determined in the following manner:

i) The nominal radius, $R_p = 4$ nm, [21] was used as a constant.

ii) For all data under consideration ($\sigma_0$, $[\mathrm{H}^+]$, $[\mathrm{M}^+]$) and one parameter set $\{K_S^{\mathrm{int}}, K_D^{\mathrm{int}}, N_S\}$ $\sigma_d$ was varied until the calculated values of $[\mathrm{H}^+]$ agree with the experimental ones.

iii) Then $\sigma_0^{\mathrm{calcul}}$ was calculated from this $\sigma_d$ as well as

$$\sum(\Delta\sigma)^2 = \sum(\sigma_0^{\mathrm{calcul}} - \sigma_0^{\mathrm{exp}})^2 \,. \tag{14}$$

iv) Now the points ii) and iii) were repeated with different parameter sets until $\sum(\Delta\sigma)^2$ reaches a minimum.

In this way calculations were performed using all 25 data sets described in [15] or only a part of them. To reduce the time for the calculation a maximum value of $K_D^{\mathrm{int}} = 10^6$ mol/l was setted. Higher values of $K_D^{\mathrm{int}}$ correspond to a negligible ion binding. The residual deviation, $s(\sigma_0)$, was calculated. $s(\sigma_0)$ gives the possibility of a comparison between the results of the estimation of the constants under inclusion of different numbers of data points

$$s(\sigma_0) = \sqrt{\frac{\sum(\Delta\sigma)^2}{Z_w - Z_p + 1}} \tag{15}$$

($Z_w$: number of points, $Z_p$: number of parameters).

In a first run five data sets for one alkali ion at five concentrations were analyzed simultaneously ($Z_p = 3$). The results are shown in Table 1. It can be seen that the values of $s(\sigma_0)$ are similar to each other for all five cations. Furthermore, for all five ions the setted minimum value of $pK_D^{\mathrm{int}} = -6$, i.e. a negligible counterion binding, was found. Differences in the $\sigma_0$ – pH plots between the different electrolyte ions are expressed in the constants $N_S$ and $pK_S^{\mathrm{int}}$. This result was surprising and questionable. In a second run data sets of all five considered alkali ions were included simultaneously. Now we have $Z_p = 7$ with a parameter set $\{K_S^{\mathrm{int}}, N_S, K_D^{\mathrm{int}}(\mathrm{M}^+)\}$. As shown in Table 2 for $\mathrm{Li}^+$ the minimum value $pK_D^{\mathrm{int}} = -6$ was found again. The alkali sequence is now reflected in an increasing of $pK_D^{\mathrm{int}}$ from $\mathrm{Li}^+$ to $\mathrm{Cs}^+$. The evaluated values of $N_S$ and

**Table 1** Results of the parameter estimation for the counterion binding model under application of data for one ion five concentrations

| Electrolyte | $s(\sigma_0)$ [$\mu$C/cm$^2$] | $N_S$ [1/nm$^2$] | $pK_S^{\mathrm{int}}$ | $pK_D^{\mathrm{int}}$ |
|---|---|---|---|---|
| LiCl | 0.30 | 0.74 | 6.44 | $\leq -6$ |
| NaCl | 0.31 | 0.73 | 6.35 | $\leq -6$ |
| KCl | 0.29 | 0.80 | 6.27 | $\leq -6$ |
| RbCl | 0.33 | 0.91 | 6.23 | $\leq -6$ |
| CsCl | 0.33 | 0.91 | 6.06 | $\leq -6$ |

**Table 2** Results of the parameter estimation for the counterion binding model under application of data for five ions at three concentrations (0.005 M + 0.01 M + 0.05 M) and five concentrations (+ 0.1 M + 0.3 M) in comparison with other published data

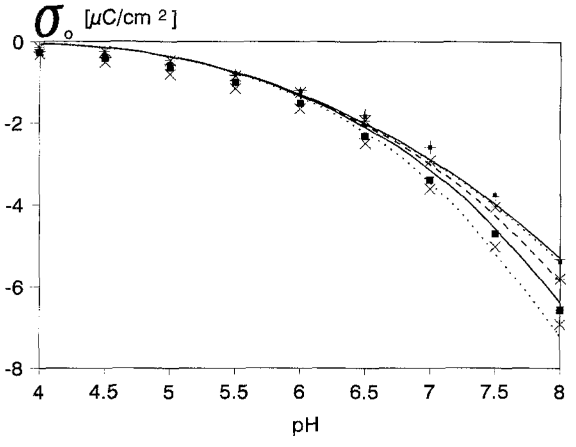
| | Three conc. | Five conc. | Publ. [20] | Publ. [12] |
|---|---|---|---|---|
| $s(\sigma_0)$ [$\mu$C/cm$^2$] | 0.27 | 0.44 | – | – |
| $N_S$ [1/nm$^2$] | 0.62 | 0.74 | 0.79 | 5¹) |
| $pK_S^{int}$ | 6.24 | 6.32 | 6.30 | 7.2 |
| $pK_p^{int}$ (LiCl) | $\leq -6$ | $\leq -6$ | – | – |
| $pK_D^{int}$ (NaCl) | – 1.32 | – 5.96 | – | – |
| $pK_D^{int}$ (KCl) | – 0.48 | – 1.02 | – | 0.5 |
| $pK_D^{int}$ (RbCl) | – 0.13 | – 0.49 | – | – |
| $pK_D^{int}$ (CsCl) | 0.23 | – 0.10 | – | – |

¹) determined by an independent method

$pK_S^{int}$ agree approximately with those reported elsewhere [20] for NaCl as background electrolyte and calculated under application of a model without counterion binding. Somewhat greater deviations occur in comparison with the parameters published by Davis et al. [12]. In this connection it must be noted that $N_S$ is not a parameter in [12], it was determined by an independent method. Furthermore, the value of $pK_D^{int}$ given in [12] for $K^+$ (and recalculated using Eq. (4)) is about 30 to 40 times higher than that evaluated in the present investigations. That means that our results suggest a much weaker counterion binding than postulated in [12].

Figure 1 shows a comparison between the experimental points and the recalculated data using the optimal parameter set. For the sake of clarity the data for one concentration are shown only, but those of three concentrations (0.005 M, 0.01 M and 0.05 M) are used for the calculation simultaneously. A qualitative agreement in the trend (but rather poor) may be seen. The agreement between the experimental and the recalculated data becomes worse if data for higher electrolyte concentrations are used in the calculation. This is reflected also in an increase of $s(\sigma_0)$ (see Table 2).

**Fig. 1** The result of the parameter estimation for the counterion binding model. Here only the data for 0.01 M solutions are depicted for the sake of clarity. 15 data sets were included in the calculation (five alkali ions at concentrations of 0.05 M, 0.01 M and 0.005 M). Points: experimental values; curves: recalculated relations using the parameters given in Table 2) ■; —— LiCl, +; ···· NaCl, ∗; - - - - KCl, ▮; —— RbCl, ×; ···· CsCl



## Stern layer model

Now, spherical particles with a radius, $R_p$, surrounded with a charge free Stern layer of the thickness, $d$, are considered. The diffuse double layer begins at $r = R_p + d$. A specific counterion binding is not included in this considerations. The surface charge formation is caused by the reaction (I) solely and the contribution of the reaction (II) is considered to be negligibly small. For such a model the Eqs. (1, 2, 7) are applicable immediately. In the Eqs. (6, 8, 9), $\{\equiv \text{SiOM}\} = 0$ and $\sigma_a = 0$ must be taken into account. Furthermore, $\alpha = \beta$ is valid. If now $\sigma_d$ is considered as the net charge of the diffuse part of the double layer divided by the area described by $r = R_p + d$, the electroneutrality condition reads instead of Eq. (11):

$$\sigma_d = -\sigma_0 \cdot \frac{R_p^2}{(R_p + d)^2} \,. \tag{16}$$

Furthermore, Eq. (12) is applicable for the calculation of the dimensionless potential, $U_d$, at $r = R_p + d$ in the following modified form:

$$U_d = -2 \cdot \ln(X - \sqrt{X^2 - 1}) \,. \tag{17}$$

To calculate $U_0$ a solution of Poissons differential equation for a charge free spherical shell,

$$\frac{1}{r^2} \cdot \frac{d}{dr}\left[ r^2 \cdot \left( \frac{d\psi}{dr} \right) \right] = 0 \tag{18}$$

is required. After inserting of Eq. (2), this solution is

$$U = C_1/r + C_2 \,. \tag{19}$$

For the further considerations it is now necessary to determine the integration constant, $C_1$. With

$$U_{(r=R_p)} = U_0$$
$$U_{(r=R_p+d)} = U_d \,, \tag{20}$$

it follows immediately that

$$C_1 = (U_0 - U_d) \cdot \frac{R_p \cdot (R_p + d)}{d} \,. \tag{21}$$

Taking into account that the surface charge density (in this model under consideration $\sigma_0$) is proportional to the gradient of the potential, $U$, at $r = R_p$ we have:

$$U_0 = U_d + \sigma_0 \cdot \frac{R_p \cdot d}{R_p + d} \cdot \frac{F_A}{\varepsilon_r \cdot \varepsilon_0 \cdot R_G \cdot T} . \tag{22}$$

A value of $\varepsilon_r = 78.5$ was used for the calculations. The difference of $\varepsilon_r$ between the Stern layer and the bulk liquid is a subject for further investigations. Thus for a given set of parameters $\{K_S^{\mathrm{int}}, d, N_S, R_p\}$ such as the known value of $\kappa$, for each $\sigma_0$ it is possible to calculate $\sigma_d$ from Eq. (16), $U_d$ from Eq. (17), $U_0$ from Eq. (22), $\{\equiv \mathrm{SiOH}\}$ from Eq. (6) with $\{\equiv \mathrm{SiOM}\} = 0$ and finally $[\mathrm{H}^+]$ from Eq. (1). That is, an immediate analytic relation between the measured quantities $\sigma_0$ and pH exists in the form $\mathrm{pH} = \mathrm{pH}(\sigma_0)$. But, for the analysis of the experimental results the method described above (calculation of $[\mathrm{H}^+] = f(\sigma_d)$, $\sigma_0 = f(\sigma_d)$) was applied. This includes the possibility for the calculation of $s(\sigma_0)$ and for the comparison of this value with that of the counterion binding model. Furthermore, the calculations were performed for the three lower concentrations on the one hand and including all 5 concentrations on the other hand for all 5 alkali ions simultaneously. The results are summarized in Table 3.

Though the values of the parameters calculated with different numbers of data sets are not entirely identical, some general conclusions are obviously. The parameter $N_S$ is much higher in the case of the Stern layer model than in the case of the counterion binding model. Now $N_S$ is comparable with reported values [12, 22] determined with other experimental techniques. This is connected with an increase of $pK_S^{\mathrm{int}}$. This value may now be compared with a published $pK_S^{\mathrm{int}} = 6.81$ [23, 24]. The alkali sequence is reflected in different values of the Stern Layer thickness. The calculated Stern layer thickness agree in magnitude as well as in the alkali sequence with published data [25, 26] for the radii of solvated ions.

Comparing $s(\sigma_0)$ for the two considered models and the calculation for the three lower electrolyte concentrations the same value appears (compare Table 2 and Table 3). For the analysis with all considered experimental results $s(\sigma_0)$ increases somewhat, but not in such a manner as in the case of the counterion binding model. Figure 2 depicts for example the comparison between the experimental and the recalculated $\sigma_0$–pH dependence. Here for the sake of clarity only three curves for RbCl are shown, but the calculation was performed including all 25 experimental data sets.

**Table 3** Results of the parameter estimation for the Stern Layer model under application of data for five ions at three concentrations (0.005 M + 0.01 M + 0.05 M) and five concentrations (+0.1 M + 0.3 M) in comparison with other published data

| | Three conc. | Five conc. | $d$ [25] | $d$ [26] |
|---|---|---|---|---|
| $s(\sigma_0)$ [$\mu$C/cm$^2$] | 0.27 | 0.34 | – | – |
| $N_S$ [1/nm$^2$] | 7.75 | 4.07 | – | – |
| $pK_S^{\mathrm{int}}$ | 7.15 | 6.90 | – | – |
| $d$ (LiCl) [nm] | 0.92 | 0.63 | 0.38 | 0.6 |
| $d$ (NaCl) [nm] | 0.65 | 0.54 | 0.36 | 0.4 |
| $d$ (KCl) [nm] | 0.40 | 0.37 | 0.33 | 0.3 |
| $d$ (RbCl) [nm] | 0.26 | 0.24 | – | – |
| $d$ (CsCl) [nm] | 0.17 | 0.17 | 0.33 | 0.25 |

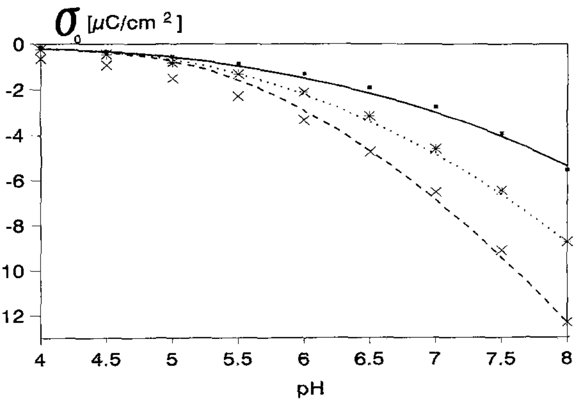
Having arrived at a set of parameters that fit the potentiometric data, the potentials $U_0$ and $U_d$ were calculated (see Figs. 3A and 3B). It can be seen that only small differences exist in $U_0$ between the different alkali ions investigated. An alkali sequence $U_0(\mathrm{Li}^+) > U_0(\mathrm{Na}^+) > U_0(\mathrm{K}^+) > U_0(\mathrm{Rb}^+) > U_0(\mathrm{Cs}^+)$ was found. If $U_d$ is considered, then the differences in Stern layer potentials are higher and the alkali sequence is reversed because of the Stern layer thickness, $d$.

For an examination of whether only one set of parameters is able to describe the experimental data or not, further calculations were performed with a reduced parameter set. That means that $N_S$ was taken as a constant. From Table 4 it can be seen that, if $N_S$ is comparable with published values and not too low, $s(\sigma_0)$ changes only slightly with $N_S$. An increase of $N_S$ is connected with an increase of $pK_S^{\mathrm{int}}$. But, the alkali sequence in $d$ is not influenced.

## Summary

i) The experimental data concerning the dependence of the surface charge density, $\sigma_0$, of AEROSIL 300 on pH

**Fig. 2** The result of the parameter estimation for the Stern layer model. Here only the data for RbCl at three concentrations are depicted for the sake of clarity. All 25 data sets were included in the calculation. (Points: experimental values; curves: recalculated relations using the parameters given in Table 3) ■; —— 0.005 M, +; ···· 0.05 M, *; ---- 0.3 M



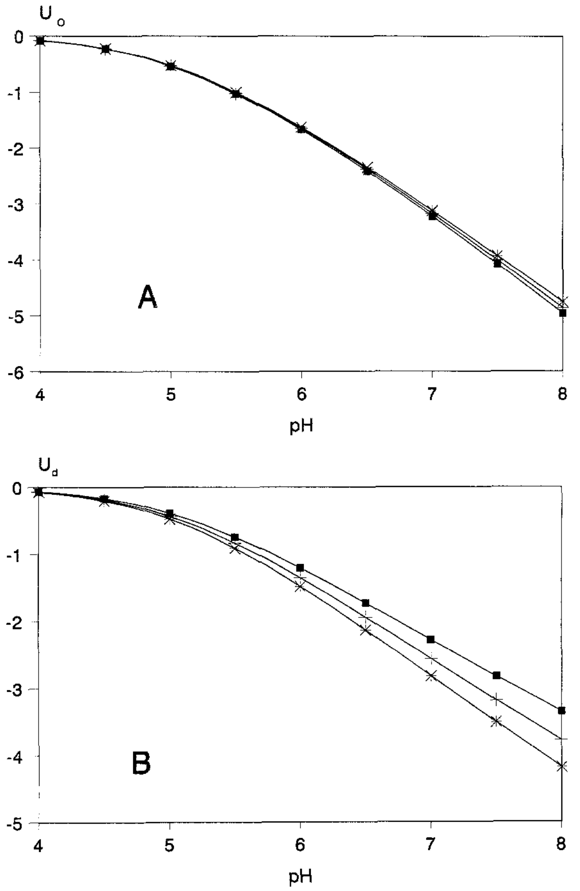


**Fig. 3A** Surface potential, $U_0$, in dependence of pH for 0.01 M alkali chloride solutions. $U_0$ was calculated under application of the parameter set given in Table 3 (Stern layer model with 5 ions and 5 concentrations) ■: LiCl, +: KCl, ∗: CsCl. **B.** Stern layer potential, $U_d$, in dependence on pH for 0.01 M alkali chloride solutions. The parameter set and the symbols are the same as in Fig. 3A.

**Table 4** Results of the parameter estimation for the Stern Layer model under application of data for five ions at five concentrations with a reduced parameter set ($N_S$ = const.)

| $N_S$ [1/nm$^2$] | 1.00 | 4.07 | 5.00 | 7.00 |
|---|---|---|---|---|
| $s(\sigma_0)$ [$\mu$C/cm$^2$] | 0.41 | 0.34 | 0.35 | 0.36 |
| $pK_S^{int}$ | 6.08 | 6.90 | 7.00 | 7.16 |
| *d* (LiCl) [nm] | 0.62 | 0.63 | 0.63 | 0.63 |
| *d* (NaCl) [nm] | 0.52 | 0.54 | 0.55 | 0.55 |
| *d* (KCl) [nm] | 0.32 | 0.37 | 0.37 | 0.37 |
| *d* (RbCl) [nm] | 0.17 | 0.24 | 0.24 | 0.24 |
| *d* (CsCl) [nm] | 0.17 | 0.17 | 0.17 | 0.17 |

in aqueous solutions of five alkali chlorides at five different concentrations were analyzed with two models for spherical particles with acidic surface groups, a counterion binding model in connection with a pure diffuse electrical double layer on the one hand and a Stern layer model on the other hand. Such investigations including equations for a spherical geometry are scarce. Comparable approaches were published by De Wit et al. [27] and by Spitzer [28]. In [27] a counterion binding model in connection with spherical particles with acidic surface groups was discussed for the interpretation of experimental data for humic substances. The results of model calculations are presented, but a determination of parameters is published for a model without counterion binding only. Spitzer [28] did investigate an ion binding in the inner Helmhotz plane for spherical particles with a constant surface charge density and a Stern layer thickness which depends on the electrolyte concentration. The results are discussed qualitatively in comparison with electrokinetic data. In both articles the influence of the type of counterion is not investigated.

ii) The counterion binding model applied to the data of one ion (different concentrations) yield always equilibrium constants, $pK_D^{int}$, corresponding to a negligible ion binding. Differences in $pK_D^{int}$ are found if $\sigma_0$–pH data of different ions are included simultaneously. For lower electrolyte concentrations ($c \leq 0.05$ M) this model is able to describe the experimental values qualitatively. But, if higher concentrations are considered, noticeable deviations occur.

iii) A better agreement between the experimental points and the recalculated $\sigma_0$–pH plots is found under application of the Stern layer model and under incorporation of the data of higher electrolyte concentrations. Especially, this model yields values for $N_S$ and $pK_S^{int}$ which agree with published data (partially determined with other methods). The alkali sequence is described here by differences in the Stern layer thickness, the latter agrees in magnitude and order with the radii of hydrated ions.

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## References

1. Iler RK (1955) The Colloid Chemistry of Silica and Silicates, Cornell University Press, Ithaca, New York
2. Milonjic SK (1992) Colloid Surf 63:113–119
3. Kosmulski M (1989) J Radioanal Nucl Chem 129:149–154
4. Ahmed SM (1966) Can J Chem 44:1663–1670
5. Berube YG, De Bruyn PL (1968) J Colloid Interface Sci 27:305–318
6. Lyklema J (1987) In: Tadros ThF (ed) Solid/Liquid Dispersions, Academic Press, London, pp 45–90

7. Kosmulski M (1993) Pol J Chem 67:1831–1839
8. Dumont F, Warlus J, Watillon A (1990) J Colloid Interface Sci 138:543–554
9. Tadros ThF, Lyklema J (1968) J Electroanal Chem 17:267–275
10. Ahmed SM (1969) J Phys Chem 73:3546–3555
11. Berube YG, De Bruyn PL (1968) J Colloid Interface Sci 28:92–105
12. Davis JA, James RO, Leckie JO (1978) J Colloid Interface Sci 63:480–499
13. Kallay N, Colic M, Fuerstenau DW, Jong HM, Matijevic E (1994) Colloid Polym Sci 272:554–561
14. Kosmulski M, Matijevic E (1992) Colloid Polym Sci 270:1046–1048
15. Sonnefeld J, Göbel A, Vogelsberger W, (1995) Colloid Polym Sci 273:926–931
16. Hiemstra T, Van Riemsdijk WH (1991) Colloids Surf 59:7–25
17. Healy TW, White LR (1978) Adv Colloid Interface Sci 9:303–345
18. Yates DE, Levines S, Healy TW (1974) J Chem Soc Faraday Trans I 70:1807–1818
19. Lyklema J (1991) Pure Appl Chem 63:895–906
20. Sonnefeld J (1993) J Colloid Interface Sci 155:191–199
21. Schriftenreihe Pigmente 50 (1984) Degussa AG, Frankfurt (Main)
22. Schriftenreihe Pigmente 11 (1982) Degussa AG, Frankfurt (Main)
23. Iler RK (1979) The Chemistry of Silica, Wiley, New York
24. Schindler PW, Kamber HR (1968) Helv Chim Acta 51:1781–1786
25. Oh SG, Shaw DO (1993) J Phys Chem 97:284–286
26. Kim HG, Lee JH, Lee HB, John MS (1993) J Colloid Interface Sci 157:82–87
27. De Wit JCM, van Riemsdijk WH, Nederlof MM, Kinnibugh DG, Koopal LK (1990) Anal Chim Acta 232:189–297
28. Spitzer JJ (1992) Colloid Polym Sci 270:1147–1158