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ORIGINAL CONTRIBUTION

J. Sonnefeld
A. Göbel
W. Vogelsberger

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

Part 1. Experimental results

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Dr. J. Sonnefeld (✉) · A. Göbel
W. Vogelsberger
Friedrich-Schiller-Universität Jena
Institut für Physikalische Chemie
Lessingstraße 10
07743 Jena, Germany

Abstract The results of a systematic investigation on the influence of different alkali ion species on the surface charge density, σ_0, of spherical silica particles (AEROSIL 300) in the pH range between 4 and 8 and with electrolyte concentrations from 0.005 M to 0.3 M are presented. The accuracy of the data may be described by a residual deviation, $s(\sigma_0^m)$, including at least four single measurements: $s(\sigma_0^m) < 0.2\ \mu C/cm^2$. The alkali sequence found for the spherical particles is in agreement with data for porous silica published by other authors.

Key words Surface charge density – silica – spherical particles – potentiometric titration

Introduction

The influence of the so-called background electrolyte on the surface charge density, σ_0, of solids with ionizable surface groups and on phenomena, related to σ_0, are of scientific and practical interest. Recently, a series of papers was published in connection with the nuclear waste repository concerning the adsorption of Cs^+ on marl [1], zeolites [2], Fe_2O_3 [3] as well as porous glasses and silica gel [4].

The influence of the alkali cation on the surface charge density is often interpreted in terms of specific ion adsorption or site binding on the one hand, or on the basis of the size of the solvated ions on the other hand. In this connection different alkali sequences were found for different oxides (see e.g. [5, 6]), a result which cannot be explained by the size of the ions solely. Even for the same oxide the alkali sequence depends on the preparation condition or for the same sample on the analysis method (e.g. [7]).

According to Iler [8] silica sols can better be stabilized against aggregation in the presence of LiOH as in the case of NaOH because of the Na^+ adsorption in the Stern layer. On the other hand, Wijnen et al. [9] did not find differences in the aggregation kinetics of silica particles prepared from different alkali silicate solutions (Li^+, Na^+, K^+, Rb^+). The latter result agrees with electrokinetic measurements and NMR investigations in aqueous solutions [5, 10].

Besides electrokinetic measurements the determination of the dependence of the surface charge density on pH using potentiometric titration such as the determination of "ion adsorption" are common methods for the characterization of the system silica/aqueous electrolyte solution. Concerning the surface charge density, σ_0, alkali cations are often considered as indifferent ions [11]. The first systematic investigation on the influence of the kind of the alkali cations Li^+, Na^+, K^+, Cs^+ on σ_0 of porous silica was published by Tadros and Lyklema [12] for 0.1 M chloride solutions. Here an increase of the amount $|\sigma_0|$ from Li^+ to Cs^+ was found, however, noticeable only for $pH > 7$. No clear trend is perceptible for smaller pH in Fig. 5 of ref. [12]. The explanation of this result was given in terms of the size of the solvated ions connected with a reduced accessibility of micropores for greater ions. Ahmed [13] concluded from the dependence of σ_0 on the concentration of the background electrolyte KNO_3, measured on quartz powder, that there is no specific ion adsorption in this system. This controversy was argued by the same author in a later paper [14]. Under application of their double extrapolation technique, Davis et al. [15] found association constants for the system silica/K^+ corresponding to a relative strong ion binding. With the same method Janusz et al. [16] established somewhat lower association constants. Kosmulski [5] investigated the ion adsorption such as the surface charge density for porous silica in the presence of different alkali ions. For both investigations the same sequence was found as in ref. [12], but also remarkably, only for pH > 7. The investigation of the segregation of KCl and NaCl between the pore water of silica and the environmental water by Cerefolini and Boara [17] yields a stronger accumulation of K^+ in the pore water than of Na^+. The adsorption of alkali ions on silica sol particles was investigated in a wide concentration and pH range by Milonjic [18]. For small concentrations the same sequence was found as in [12] except for an exchange between K^+ and Na^+ for chloride anions. At higher concentrations, though, a change in the sequence appears.

Obviously, systematic investigations of σ_0 on silica concerning the influence of the kind of alkali cation in 1 – 1 electrolytes were performed mainly on porous samples. The interpretation of such results was done qualitatively or quantitatively on the basis of an electrical double-layer model for flat interfaces. The aim of this article is the presentation of the results of the investigation of the dependence of σ_0 on pH on spherical silica particles in chloride solutions of Li^+, Na^+, K^+, Rb^+ and Cs^+ at different concentrations, especially in the pH range smaller than 8, where the dissociation of dissolved silica species may be neglected. These data form the basis for quantitative theoretical investigations including models for a spherical electrical double layer, which are presented in part 2.

Materials and methods

AEROSIL 300 (Degussa) was outgassed at 673 K before each measurement to remove possibly adsorbed impurities. The specific surface area was determined by N_2-adsorption at 77 K with the Autossorb-1 (Quantachrome) under application of the BET-eq. [19]. A value of 266 m^2/g was found. This value is comparable with the lower limit given by the manufacturer. Potentiometric titration in comparison with a blank was used for the determination of the surface charge density in the following manner. A desired mass of alkali chloride (pa, Fluka) was dissolved in deionized water (Seralpur PRO 90 CN, Seral, conductivity < 0.1 μS/cm). After dividing this solution into two equal parts the sample was immersed in one of them. To both solutions the same amount of alkali hydroxide was added to adjust a pH between 8 and 8.5 in the sample dispersion (pH $\approx$ 10.5 in the blank). Then the solutions were flushed with Ar and thermostated at 25 °C up to the end of the titration. For pH measurements a pH meter CG 840 in combination with glass electrode N 37 A (both from Schott) and for the dosage of the HCl 0.1 N volumetric standard (Aldrich) a digital burette T80/20 (Schott) were used. First the blank was titrated. Then the sample was equilibrated. An equilibration time of 4 min between dosage and pH reading was applied.

We have restricted our investigations to a pH range between 4 and 8 because of three reasons:

i) We are interested in σ_0-pH plots for a constant ion strength. This is only valid, if the concentration of H^+ and OH^- is much smaller than the electrolyte concentration. Furthermore, this condition determines the lower limit of the electrolyte concentration. For this lower limit 0.005 mol/l was chosen. The upper limit of 0.3 mol/l for the electrolyte concentration is relatively high, therefore nearly two orders of magnitude are included.

ii) At low pH a steep rise in the volume-pH plot leads to inaccuracies in the calculation of the volume difference between the sample and the blank (see e.g. [20]).

iii) At pH > 9 the solubility of silica increases and the dissociation of dissolved species cannot be neglected. This point is discussed in detail elsewhere [21].

Results and discussion

Calculation of the surface charge density from titration data

We consider a surface charge which is counterbalanced by the ions in the electrical double layer (EDL). Furthermore we have chosen such conditions that the concentrations of the electrolyte ions are much higher than that of H^+ or OH^-. This means that the surface charge is counterbalanced essentially by electrolyte ions and the contribution of H^+ and OH^- to this process may be neglected. Now we can divide the total volume of the liquid, $v^{S,T}$, into two parts, the volume of EDL, v^{EDL}, and the volume of the bulk, $v^{S,L}$.

$$v^{S,T} = v^{EDL} + v^{S,L} \; . \tag{1}$$

Here "*S*" means the sample in distinction to the blank "*B*". Despite the concentration gradient within the EDL we can calculate an averaged ion concentration as the amount of ions, n_i, in the volume v^{EDL}.

$$c_i^{EDL} = n_i^{EDL}/v^{EDL} \tag{2}$$

such as a difference, Δc_i, between this averaged concentration and that within the bulk, $c_i^{S,L}$.

$$\Delta c_i = c_i^{EDL} - c_i^{S,L} \,. \tag{3}$$

In Eq. (2) and (3) n_i^{EDL} contains both, ions in the diffuse double layer and ions adsorbed or bonded to surface groups. This is a consequence of the fact that, in the case of background electrolyte ion binding, we cannot distinguish between these two types of ions by potentiometric pH titration and also not by adsorption measurements which consider the concentration change in the bulk. Therefore the calculated surface charge density includes not only charged species (for silica $\equiv SiO^-$ e.g.), but also complexes such as $\equiv SiOM$. The mass conservation yields

$$n_{M^+}^{S,T} = n_{EL} + n_{MOH}^{S} = n_{M^+}^{S,L} + c_{M^+}^{EDL} \cdot v^{EDL}$$

$$n_{Cl^-}^{S,T} = n_{EL} + n_{HCl}^{S} = n_{Cl^-}^{S,L} + c_{Cl^-}^{EDL} \cdot v^{EDL} \,. \tag{4}$$

Here n_i^T is the total amount of substance, "EL", "MOH" and "HCl" means the added amount of electrolyte, hydroxide and hydrochloric acid, respectively. With the specific surface area, S_{SP}, of the sample of mass, m, the Faraday constant, F_A, and the amount of charges on the surface, $\sum z_i \cdot n_i(\text{surf})$, (possibly species with bonded counterions are included as explained above), σ_0 can be calculated

$$\sigma_0 = \frac{F_A \cdot \sum z_i \cdot n_i(\text{surf})}{S_{SP} \cdot m} \tag{5}$$

and the electroneutrality for the EDL reads:

$$\sum z_i \cdot n_i(\text{surf}) = (\Delta c_{Cl^-} + \Delta c_{OH^-} - \Delta c_{M^+} - \Delta c_{H^+}) \cdot v^{EDL} \,.$$

Because of the experimental conditions, c_{Cl^-}, $c_{M^+} \gg c_{OH^-}$, c_{H^+}, it follows that Δc_{Cl^-}, $\Delta c_{M^+} \gg \Delta c_{OH^-}$, Δc_{H^+}, and the latter two may be neglected (see above). This means:

$$\sum z_i \cdot n_i(\text{surf}) = (\Delta c_{Cl^-} - \Delta c_{M^+}) \cdot v^{EDL} \,. \tag{6}$$

For the bulk we have:

$$n_{M^+}^{S,L} + n_{H^+}^{S,L} = n_{OH^-}^{S,L} + n_{Cl^-}^{S,L} \,. \tag{7}$$

Rearrangement of Eq. (1, 3, 4, 6, 7) yields (see appendix):

$$c_{H^+}^{S,L} = c_{OH^-}^{S,L} + \frac{n_{HCl}^{S} - \sum z_i \cdot n_i(\text{surf}) - n_{MOH}^{S}}{v^{S,T}} \,. \tag{8}$$

For the blank a division of the volume, v^B, into two parts is not necessary and in analogy to Eq. (7), we have:

$$c_{H^+}^{B} = c_{OH^-}^{B} + \frac{n_{HCl}^{B} - n_{MOH}^{B}}{v^B} \,. \tag{9}$$

Since we compare the two curves at equal pH, we have according to our experimental conditions $c_{H^+}^B = c_{H^+}^{S,L} = c_{H^+}$, $c_{OH^-}^B = c_{OH^-}^{S,L} = c_{OH^-}$ and $n_{MOH}^B = n_{MOH}^S = n_{MOH}$. Thus from Eqs. (8) and (9) follows:

$$n_{HCl}^{S} - n_{HCl}^{B} + (c_{OH^-} - c_{H^+}) \cdot (v^{S,T} - v^B)$$
$$= \sum z_i \cdot n_i(\text{surf}) \,. \tag{10}$$

Since the amount of HCl is the product of the added volume of volumetric standard, $v_{HCl}^{S\,or\,B}$, and the concentration of this standard, c_{HCl}, and because of

$$v^{S,T} - v^B = v_{HCl}^{S} - v_{HCl}^{B} \,, \tag{11}$$

we have from Eq. (5, 10, 11) with

$$\sigma_0 = \frac{F_A}{S_{SP} \cdot m} \cdot (c_{HCl} + c_{OH^-} - c_{H^-}) \cdot (v_{HCl}^{S} - v_{HCl}^{B}) \tag{12}$$

an equation for the calculation of σ_0. In our experiments the concentration of the volumetric standard, c_{HCl}, is much higher than c_{OH^-} and c_{H^+}. Then, Eq. (12) may be simplified to:

$$\sigma_0 = \frac{F_A \cdot c_{HCl}}{S_{SP} \cdot m} \cdot (v_{HCl}^{S} - v_{HCl}^{B}) \,. \tag{13}$$

But if such investigations are performed in other pH ranges or a volumetric standard with a lower concentration is used, Eq. (12) must be applied.

An important requirement for a quantitative interpretation of the data is a nearly constant electrolyte concentration during the titration. This may be achieved with a relative high concentration of the volumetric standard ($v_{HCl} \ll v^B \approx v^{S,T}$) and a low surface to volume ratio. On the other hand, the accuracy of the measurement decreases with decreasing surface to volume ratio. Thus, we must make a compromise. In our investigations a surface to volume ratio of approximately 1 m^2 surface in 1 cm^3 solution was used.

Surface charge density in the presence of different alkali chlorides

The surface charge density, σ_0, was determined for the five considered electrolytes at 5 concentrations. Each of these 25 σ_0-pH relations presented are mean values of at least four single measurements, with exception of RbCl at a concentration of 0.3 M. Here, only two single measurements were carried out. An average value of σ_0 as well as a residual deviation, $s(\sigma_0^m)$, were calculated.

$$s(\sigma_0^m) = \sqrt{\frac{\sum(\sigma_0 - \sigma_0^m)^2}{n \cdot (n-1)}} \,. \tag{14}$$

Here, n is the number of single measurements and σ_0^m is the mean value. The evaluation was carried out in steps of ΔpH = 0.5. Thus 9 points of every curve are included. If $s(\sigma_0)$ for four measurements was greater than 0.2 $\mu C/cm^2$

at one or more points, an additional experiment was carried out.

In this connection (see Figs. 1A and 1B) it was observed that the deviations between the single measurements decrease with increasing electrolyte concentration. One reason for such a behaviour may be the condition concerning the relation between the concentrations of electrolyte ions and H^+ and OH^- as discussed above.

Figure 2 shows the typical dependence of the surface charge density on the electrolyte concentration by way of example for CsCl. The same influence of the electrolyte concentration was found for the four other salts considered.

Figures 3A to 3E depict a comparison between σ_0 in the presence of the different alkali cations at 5 different concentrations. An increase of the amount $|\sigma_0|$ may be seen in the series

$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

with exception of the concentration of 0.01 M and 0.1 M, where the difference between the σ_0-pH plots of Li^+ and Na^+ are smaller than the experimental uncertainty of 0.2 $\mu C/cm^2$.

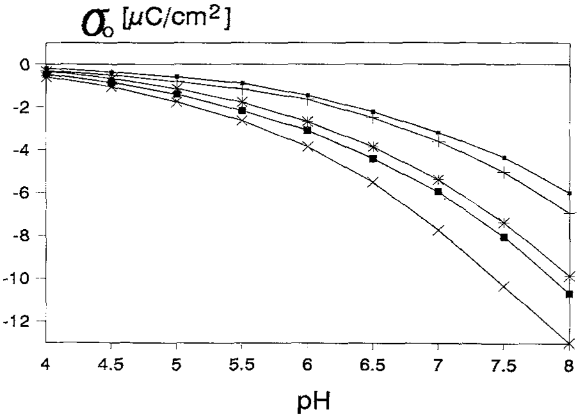


Fig. 2 Dependence of σ_0 on the concentration of CsCl: ■ 0.005 M, +0.01 M, ∗ 0.05 M, ▮ 0.1 M, ×0.3 M

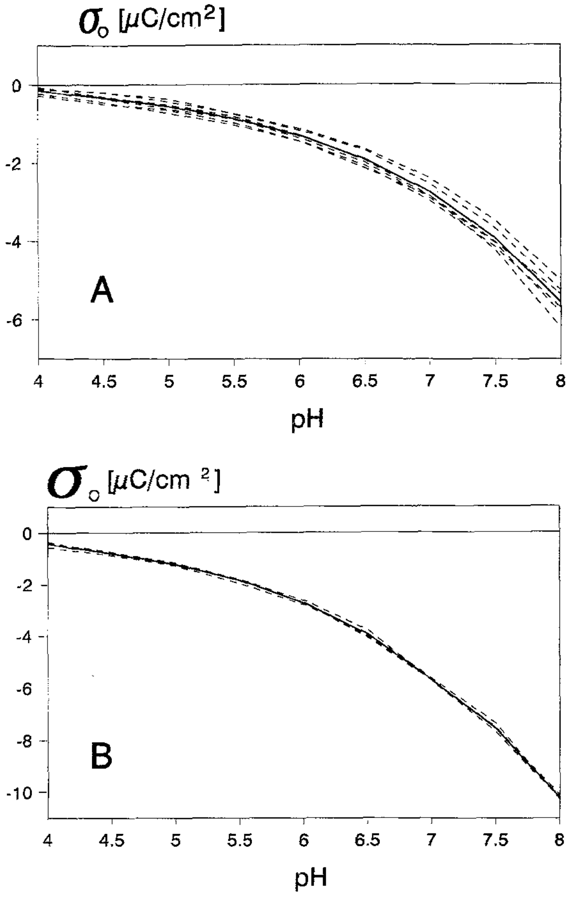
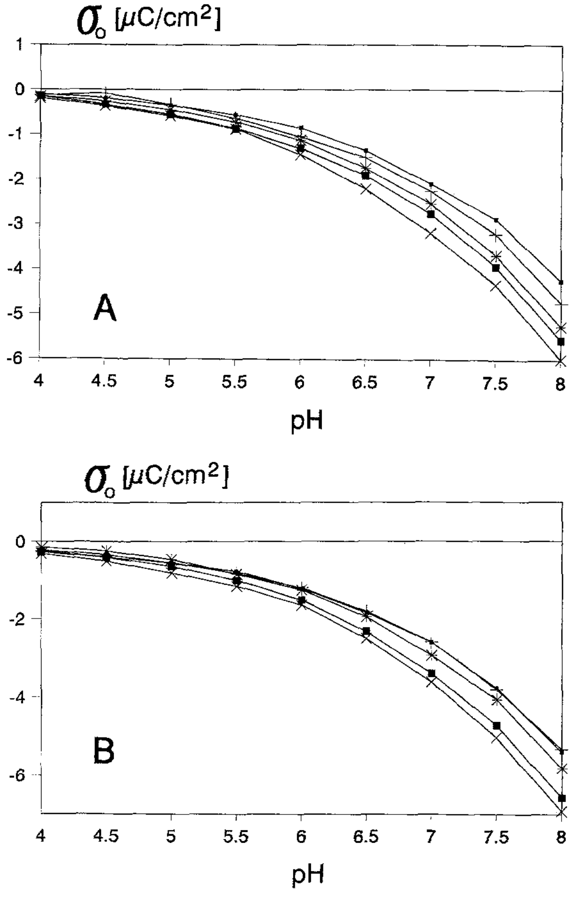


Fig. 1 On the reproducibility of single measurements. -- single measurement. — mean value; A: 0.005 M RbCl; B: 0.3 M NaCl. Note the nearly identical 4 single measurements in the case of the higher concentration

Fig. 3A, B



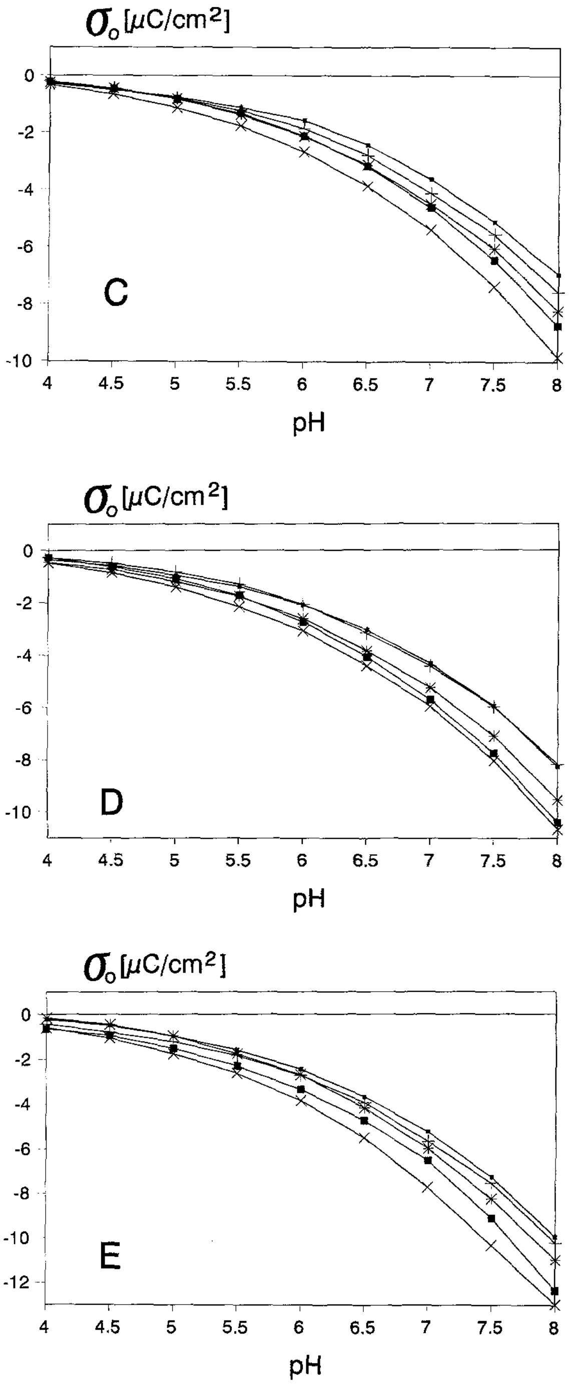


Fig. 3 σ_0 for different alkali chloride solutions; ■ LiCl, + NaCl, *KCl, ▮ RbCl, × CsCl, A: 0.005 M, B: 0.01 M, C: 0.05 M, D: 0.1 M, E: 0.3 M

Summary

In compliance with suitable experimental conditions it was possible to detect differences between the σ_0-pH plots for chloride solutions of different alkali ions in the pH range between 4 and 8, where the published data from other authors show no significant differences. The ascertained alkali sequence agrees qualitatively with the results on porous silica [5, 12]. A change in the alkali sequence as published by Milonjic [18] was not found. The measured data are a reasonable basis for the quantitative interpretation in part 2.

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Appendix

Derivation of Eq. (8)

We start the consideration with Eq. (7).

$$n^{S,L}_{M^+} + n^{S,L}_{H^+} = n^{S,L}_{OH^-} + n^{S,L}_{Cl^-} \; . \tag{7}$$

Now the amount of ions in Eq. (7) may be substituted partly or completely by their concentration.

$$c^{S,L}_{H^+} - c^{S,L}_{OH^-} = -(c^{S,L}_{M^+} - c^{S,L}_{Cl^-}) \tag{A1}$$

$$n^{S,L}_{H^+} - n^{S,L}_{OH^-} = -(c^{S,L}_{M^+} - c^{S,L}_{Cl^-}) \cdot v^{S,L} \; . \tag{A2}$$

On the other hand, $n^{S,L}_{M^+}$ and $n^{S,L}_{Cl^-}$ in Eq. (7) can be replaced under application of eq. (4):

$$\begin{aligned} n^{S,L}_{H^+} &= n^{S,L}_{OH^-} + n^{S}_{HCl} - c^{EDL}_{Cl^-} \cdot v^{EDL} \\ &\quad - n^{S}_{MOH} + c^{EDL}_{M^+} \cdot v^{EDL} \; . \end{aligned} \tag{A3}$$

Now we have with Eq. (3):

$$\begin{aligned} n^{S,L}_{H^+} &= n^{S,L}_{OH^-} + n^{S}_{HCl} - n^{S}_{MOH} - (\Delta c_{Cl^-} - \Delta c_{M^+}) \cdot v^{EDL} \\ &\quad + (c^{S,L}_{M^+} - c^{S,L}_{Cl^-}) \cdot v^{EDL} \; . \end{aligned} \tag{A4}$$

That means with Eq. (6):

$$\begin{aligned} n^{S,L}_{H^+} - n^{S,L}_{OH^-} &= n^{S}_{HCl} - n^{S}_{MOH} - \sum z_i \cdot n_i(\text{surf}) \\ &\quad + (c^{S,L}_{M^+} - c^{S,L}_{Cl^-}) \cdot v^{EDL} \; . \end{aligned} \tag{A5}$$

Inserting of Eq. (A2) into Eq. (A5) yields:

$$\begin{aligned} &-(c^{S,L}_{M^+} - c^{S,L}_{Cl^-}) \cdot (v^{S,L} + v^{EDL}) \\ &= n^{S}_{HCl} - \sum z_i \cdot n_i(\text{surf}) - n^{S}_{MOH} \; . \end{aligned} \tag{A6}$$

Because of Eq. (1), it follows now,

$$-(c^{S,L}_{M^+} - c^{S,L}_{Cl^-}) = \frac{n^{S}_{HCl} - \sum z_i \cdot n_i(\text{surf}) - n^{S}_{MOH}}{v^{S,T}} \tag{A7}$$

and after application of Eq. (A1), we have at last:

$$c^{S,L}_{H^+} = c^{S,L}_{OH^-} + \frac{n^{S}_{HCl} - \sum z_i \cdot n_i(\text{surf}) - n^{S}_{MOH}}{v^{S,T}} \; . \tag{8}$$

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