Surfaces of Silicates in Contact with Alkaline Aqueous Solutions II

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Adsorption measurements on α -CaSiO₃ and CaAl₂Si₂O₈ indicate that Ca²⁺ and OH⁻ adsorption stimulate each other. This is ascribed to Ca²⁺ adsorption sites being surrounded preferentially by OH⁻ adsorption sites, and OH⁻ sites being surrounded by Ca²⁺ sites. Part of the negative charge present on the CaAl₂Si₂O₈ surfaces derives from desorption of positive network fragments (Al³⁺, AlO⁺).

INTRODUCTION

In previous papers (1, 2), electrokinetic data have been reported for some calcium (alumino) silicates showing that the surfaces of these materials in contact with aqueous solutions did not show, under the conditions investigated (0.01 *N* NaOH, contact time $\leq$ 3 hr), surface hydration to an extent that would mask the difference in structure between a vitreous and a crystalline material of similar composition.

The present investigation intends to provide insight into the charging processes for two of the compounds (α -CaSiO₃ and CaAl₂Si₂O₈) whose electrokinetic properties have been described previously.

EXPERIMENTAL

Materials used were as described previously (2). The surface area of the α -CaSiO₃ sample as determined by means of an Areameter (Ströhlein) was 0.49 m² g⁻¹ and that of the CaAl₂Si₂O₈ sample was 0.40 m² g⁻¹. The CaCl₂ solution containing ⁴⁵Ca was obtained from the Radiochemical Centre, Amersham, Great Britain. The total Ca²⁺ was 1.0×10^{-3} *M* and its specific activity was 0.82 mCi ml⁻¹.

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The ethanol used was absolute (Merck, pro analysi).

METHODS

OH⁻ titrations were performed to a pH of 5. Ca²⁺ titrations were as described previously (2). ⁴⁵Ca was determined by liquid scintillation counting (3), using a Packard Tri-Carb Liquid Scintillation Spectrometer, Model 3320, and a Packard No. 6002173 emulsion ("Instagel"). Channel adjustment and amplification were chosen to give the highest efficiency and signal-to-background ratio, allowance being made for quenching by counting in two different channels. The ratio of the counts obtained in the two channels could be used, after calibration, as a measure for the counting efficiency.

The Cl⁻ was determined by potentiometric titration with 0.01 *M* AgNO₃ (electrodes were a silver wire and a calomel electrode connected through a KNO₃ salt bridge with the titration vessel and the mV meter used was the Orion digital pH measuring unit, Model 701). The potentials were plotted against the volume of the AgNO₃ solution as described by Gran (4).

Al³⁺ was determined by means of a Perkin Elmer Atomic Absorption Spectrophotometer,

model 300 (5, 6), connected to a Goerz Servogor RE 511 recorder.

Ad and Desorption Measurements

(a) *Nontracer experiments.* A sample containing accurately weighed amounts of solid (5 g) and liquid (35 ml) was magnetically stirred in a 75-ml stoppered polyethylene vessel. The liquid contained 0.01 *N* NaOH and varying amounts of CaCl₂. Magnetic stirring was adjusted to prevent sedimentation. After 150 min of *S*(olid)/*L*(iquid) contact, separation of solid and liquid was effected by centrifugation (45 min, 20 000 rpm). The upper layer of the supernatant was discarded (because some very small particles appeared to float at the air/solution interface), the rest of the supernatant was siphoned off and analyzed immediately (maximum time between separation and final titration was 25 min). A blank run showed that CO₂ influence was absent.

(b) *Tracer experiments.* A minute amount of tracer solution containing approximately 2 μ Ci was added to the liquid; the latter's radioactivity was determined before and after contact with the solid. *S/L* contact times varied from 15 min to 24 hr. Solid and liquid were separated by centrifugation (5 min, 4000 rpm), and the liquid contained in the pores of the sediment was displaced by adding 30 ml of ethanol, stirring magnetically, and centrifuging. The remaining solid was dried (15 hr at 70°C) and weighed and its radioactivity was determined.

Desorption of ⁴⁵Ca was determined by stirring the solid thus obtained in 35 ml of the liquid with a composition similar to that added first, but not containing ⁴⁵Ca, for 30 min.

RESULTS

(a) α -CaSiO₃

In Fig. 1, the charges brought to the surface per unit area by adsorption of Ca²⁺ and OH⁻ from 0.01 *N* NaOH solutions of varying CaCl₂ concentration are compared with the total charge behind the electrokinetic slipping plane.

The latter was calculated from the relation (7):

$$\sigma_{sl\ pl} = -\epsilon_r \epsilon_o \left(\frac{d\phi}{dx} \right)_{sl\ pl} \\ = - \left\{ 2kT \epsilon_r \epsilon_o \sum_i N_{i\infty} \left[\exp \left(- \frac{z_i e_o \zeta}{kT} \right) - 1 \right] \right\}^{\frac{1}{2}}$$

where σ is expressed in C m⁻² if MKSA units are used throughout (ϵ_r = dielectric constant of the medium; ϵ_o = permittivity of free space; $N_{i\infty}$ = bulk concentration of ions of type *i*; z_i = valency including sign; and e_o = charge of the proton).

The charge brought to the surface by ad or desorption of Ca²⁺ has been calculated from:

$$\sigma_{Ca^{2+}} = - 2F(V \Delta c / m s)$$

where Δc = difference in [Ca²⁺] before and after *S/L* contact; *V* = volume of the liquid; *m* = mass of solid present; *s* = surface area of solid; *F* = Faraday constant.

A similar formula was employed for σ_{OH^-} , the surface charge due to ad or desorption of OH⁻. It appears from the method of determination that dissociation of surface SiOH groups is indistinguishable from OH⁻ adsorption. Thus, the term "OH⁻ adsorption" will include in the following SiOH dissociation, whereas OH⁻ desorption includes the reverse process.

The quantities $\sigma_{Ca^{2+}}$ and σ_{OH^-} are independent of any assumption about the number of sites per unit area, but they are based on the assumption that the surface area as determined by Arcameter (essentially a BET type measurement) is the surface area which is significant for processes at the *S/L* interface. For silicates, some experimental basis for this assumption is available (8, 9).

The net surface charge within the electrokinetic slipping plane is seen to be 1–2% of $\sigma_{Ca^{2+}}$. The latter is compensated almost exclusively by OH⁻ adsorption, not by Cl⁻ adsorption even when Cl⁻ predominates in the bulk solution (as is the case in 3.10⁻² *M* CaCl₂ solution). Only at lower CaCl₂ concentrations,

FIG. 1. Charges on α -CaSiO₃. $\bigcirc$, σ_{Ca} (the charge brought to the surface by ad or desorption of Ca^{2+} per unit area); Δ , $-\sigma_{OH}$; $\times$, $\sigma_{sl\ pl}$ (the net charge between the electrokinetic slipping plane and the bulk solid); X/N_s , overall fraction of Ca^{2+} surface sites occupied.

a distinct discrepancy exists between $\sigma_{Ca^{2+}}$ and σ_{OH^-} and the charge within the electrokinetic slipping plane; this is ascribed to adsorption of Na^+ ions into the region between solid and electrokinetic slipping plane rather than to desorption of part of the silicate anions, because the latter process would expose Ca^{2+} ions, which are easily desorbed from the solid in the concentration region concerned. Thus, desorption of part of the silicate anions would just create a new surface.

For comparison of Ca^{2+} adsorption as determined from titration and from tracer experiments, see Table I.

The difference $K_a^* - K_a$ is the amount of Ca^{2+} desorbed during the adsorption step. At lower $CaCl_2$ concentrations, it corresponds to 30–60% of the Ca^{2+} ions originally present in

the outermost layer (estimated on the assumption of random passage of the surface through crystal unit cells, leading to an area per adsorption site equal to (volume per Ca^{2+} in the solid)^{1/3} and an average degree of occupation = $\frac{1}{2}$ of a site in the original surface). This means that in the original surface not all ions occupy an optimal site and that net transport to more favorable sites is made easier in the presence of an electrolyte solution, as long as the latter does not contain large concentrations of $CaCl_2$. At higher $CaCl_2$ concentrations, $K_a^* - K_a$ becomes small (even negative at $[CaCl] = 3 \cdot 10^{-2} M$, which is ascribed to experimental error). In these solutions Ca^{2+} ions adsorbed quickly after solid/liquid contact, appear to block the movement of other Ca^{2+} ions from the solid to the solution.

TABLE I
TRACER ADSORPTION OF Ca^{2+} ON
 $\alpha\text{-CaSiO}_3$ IN 0.01 *N* NaOH^a

[CaCl ₂] after adsorption (10^{-3} <i>M</i>)	K_a ($\mu\text{mole m}^{-2}$)	K_a^*
0.148	-0.34	4.3
0.695	1.84	6.0
2.611	3.52	7.4
5.607	4.31	7.4
9.459	4.46	6.0
30.241	5.32	4.0

^a Adsorption time: 150 min.

K_a = net amount of Ca^{2+} adsorbed during the adsorption process, as determined by titration.

K_a^* = total amount of Ca^{2+} adsorption during the adsorption process, as determined by tracer experiments.

(b) $\text{CaAl}_2\text{Si}_2\text{O}_8$ (Anorthite)

Fig. 2 shows data for anorthite similar to those described by Fig. 1 for $\alpha\text{-CaSiO}_3$. Its significant features are:

1. Both Ca^{2+} and OH^- adsorption on anorthite, as function of $\log [\text{CaCl}_2]$, show an increased slope at high $[\text{CaCl}_2]$, the transition being for Ca^{2+} near 5.5×10^{-3} *M* CaCl_2 . At this concentration, 33.5 Ca^{2+} ions are present on 10 nm^2 of the surface. At higher $[\text{CaCl}_2]$, the number of Ca^{2+} ions present surpasses the number of Ca^{2+} -sites (estimated to be 33 on 10 nm^2). Under these conditions, Ca^{2+} "adsorption" apparently involves the formation of hydrates either on the *S/L* interface, or totally outside of the solid.

2. Ca^{2+} and OH^- adsorption cannot account for the total charge behind the electrokinetic slipping plane; over the whole concentration range investigated there must be additional anions in the region near the solid. At positive surface charges, adsorption of Cl^- could be held responsible; however, this should be especially pronounced at high $[\text{CaCl}_2]$ where the $[\text{Cl}^-]/[\text{OH}^-]$ ratio in the solution is high, and $\sigma_{\text{Ca}^{2+}}$ is large. Fig. 2 shows this not to be the case, which excludes Cl^- adsorption as a significant contribution to the number of negative charges near the solid. At $[\text{CaCl}_2]$

$= 2.10^{-4}$ *M*, where the surface carries a negative charge, specific adsorption of Cl^- is absent as evidenced by experiments in which $[\text{Cl}^-]$ was measured before (3.85×10^{-4} *M*) and after *S/L* contact (4.02×10^{-4} *M*) (duration of *S/L* contact: 150 min). To close the charge gap, a decrease in concentration to 2.5×10^{-4} *M* would have been necessary, which lies beyond the error in the Cl^- concentrations determined ($\pm 0.3\%$). It should be remembered that specific adsorption of Cl^- is absent on SiO_2 (10), TiO_2 (11), and Fe_2O_3 (12), and that electrokinetic data indicate absence of specific adsorption of Cl^- on anorthite (2).

The lack of negative charges near or on the surface can be accounted for by desorption of positive network fragments. As such, Al^{3+} and AlO^+ can be considered. In the anorthite structure, AlO_4 tetrahedra alternate with SiO_4 tetrahedra (see Fig. 3), and from bond strength considerations a Al-O-Si bond is expected to have a greater chance of being broken at the Al-O bond than at the O-Si bond. Thus, the original surface will contain more Al^{3+} than Si^{4+} directly exposed without being covered by oxygen or hydroxyl ions. On contact with the solution, when Al^{3+} and AlO^+ pass into the solution in excess (more than equivalent amounts towards SiO_4^{4-}), the surface will be left with a negative charge. The effect remains unaltered when the Al^{3+} and AlO^+ ions, once they have left the solid, undergo reactions with OH^- forming aluminate ions, as long as the analytical procedure employed for OH^- determination does not distinguish between OH^- and aluminate ions (as was the case here, since OH^- titration was carried out to pH 5).

After 150 min of *S/L* contact with a 0.01 *N* NaOH, 2×10^{-4} *M* CaCl_2 solution 3.71 $\mu\text{mole m}^{-2}$ Al had passed into the solution. This amount can account for the charge deficiency if 22% pass into the solution as Al^{3+} and the remainder as AlO^+ , if no SiO_4^{4-} goes into solution [concerning the latter assumption, see Smirnova's (13) and Ilers (14) data]. The difference with the $\alpha\text{-CaSiO}_3$ case should be clear, where dissolution of $\text{Si}_3\text{O}_9^{6-}$ anions would expose Ca^{2+} ions to a solution poor in Ca^{2+} . In

FIG. 2. Charges on $\text{CaAl}_2\text{Si}_2\text{O}_8$. $\circ$, σ_{Oa} ; $\triangle$, $-\sigma_{\text{OH}}$; $\times$, $\sigma_{\text{sl pl.}}$.

FIG. 3. Part of the anorthite network. Shaded tetrahedra, AlO_4 ; blank tetrahedra, SiO_4 . Ca^{2+} ions are omitted. For clarity, only one layer of the continuous three-dimensional network is shown.

TABLE II
TRACER AD AND DESORPTION OF Ca^{2+}
ON $\text{CaAl}_2\text{Si}_2\text{O}_8$ IN 0.01 *N* NaOH

[CaCl_2] after adsorption (10^{-3} <i>M</i>)	Time of <i>S/L</i> contact (minutes)	K_a	K_a^* ($\mu\text{mole m}^{-2}$)	H_a	<i>g</i>
5.769	15	3.12	10.3	4.74	0.27
5.748	45	3.48	5.0	5.18	0.29
5.729	150	2.90	5.2	4.96	0.44
5.656	300	3.52	5.3	4.61	0.52
5.387	1440	8.30	26.1	4.24	0.67
0.222	150	0.02	4.2	-0.16	0.56
0.871	150	1.36	2.7	0.71	0.43
2.843	150	2.27	5.1	2.64	0.32
5.729	150	2.90	5.2	4.96	0.44
9.700	150	4.65	7.7	5.60	0.50
19.686	150	4.92	10.1	6.12	0.31
30.698	150	7.21	9.5	6.27	0.28

K_a and K_a^* have the same meaning as in Table I.

H_a = amount of Ca^{2+} adsorbed during alcohol treatment.

g = fraction of the amount of $^{45}\text{Ca}^{2+}$ present in the solid after adsorption + alcohol treatment, which cannot be removed on desorption. (Desorption time: 30 min.).

the anorthite case, part of the network remains on dissolution of Al^{3+} and AlO^+ .

Table II surveys data for the comparison of total adsorption and net adsorption. At $[\text{CaCl}_2] = 5.7 \times 10^{-3}$ *M*, the net amount of Ca^{2+} adsorbed (K_a) and the total amount of Ca^{2+} adsorbed (K_a^*) are, with the exception of the 15-min contact-time experiment, reasonably constant up to about 5 hr, but both increase ultimately. If CO_2 penetrating into the system, causing CaCO_3 precipitation, would be responsible for the final increase, $K_a^* - K_a$ should be equal to that found in experiments of shorter duration. Although the data are rather scarce, the final increase of $K_a^* - K_a$ is distinct; it indicates a process involving dissolution of part of the solid and precipitation of hydrates. At higher $[\text{CaCl}_2]$ concentrations, the adsorption data indicate a similar process even after short times (2.5 hr). On the other hand, the difference in electrokinetic properties between $\text{CaAl}_2\text{Si}_2\text{O}_8$ samples of varying degrees of surface disorder (2) indicates the absence

of significant hydrate formation after short times at lower CaCl_2 .

The fraction of $^{45}\text{Ca}^{2+}$ present in the solid after adsorption that is not recovered on desorption, tends to increase with increasing *S/L* contact time, and to decrease with increasing $[\text{CaCl}_2]$. The former effect can be understood as indicating hydrate formation, the interpretation of the latter is not clear. It should be kept in mind that the amount of $^{45}\text{Ca}^{2+}$ present in the solid is determined to a large extent by the amount adsorbed during alcohol treatment (H_a in Table II), which does not change significantly with *S/L* contact time, but increases with increasing $[\text{CaCl}_2]$.

DISCUSSION

Fig. 1 indicates absence of multilayered precipitation of $\text{Ca}(\text{OH})_2$ on $\alpha\text{-CaSiO}_3$. The adsorption of Ca^{2+} onto the surface shows a tendency towards saturation at higher $[\text{CaCl}_2]$, a multilayered $\text{Ca}(\text{OH})_2$ precipitation should increase indefinitely as soon as a certain $[\text{CaCl}_2]$ is surpassed. Similarly, from Fig. 2 we see the absence of a surface coverage by multilayered $\text{Ca}(\text{OH})_2$ for anorthite; although saturation is not observed here, and the amount of Ca^{2+} adsorbed surpasses the amount that can be accommodated in the first crystal layer, the Ca^{2+} adsorption increases in much too gradual a way for increasing $[\text{CaCl}_2]$ for $\text{Ca}(\text{OH})_2$ precipitation to be acceptable.

On the other hand, the data indicate a mutual stimulation of Ca^{2+} and OH^- adsorption for $\alpha\text{-CaSiO}_3$. That OH^- adsorption is stimulated by Ca^{2+} adsorption follows directly from the increasing OH^- adsorption with increasing $[\text{CaCl}_2]$; $[\text{OH}^-]$ is constant, and the activity coefficients (at least those of electro-neutral combinations of cations and anions) decrease in the region concerned with increasing electrolyte concentrations (15).

The stimulation of Ca^{2+} adsorption by increasing OH^- adsorption follows from a quantitative consideration. If there is equilibrium between adsorbed Ca^{2+} and Ca^{2+} in solution, the electrochemical potential of these

species must be equal. The surface will contain sites (type i), characterized by different standard chemical potentials of Ca^{2+} ions adsorbed unto them, $\mu_{i\text{ads}}^0$; the electrochemical potential of a Ca^{2+} ion adsorbed on a site of type i depends in addition on θ_i , the degree of occupation of the sites of type i , and on ψ_i , the electrical potential at the site. We assume

$$\mu_{i\text{ads}} = \mu_{i\text{ads}}^0 + RT \ln \theta_i / (1 - \theta_i) + 2F\psi_i \quad [1]$$

in which the θ_i dependency is taken into account in the usual way (16). $\mu_{i\text{ads}}^0$ will depend on the adsorption energy of Ca^{2+} ions onto the site concerned, which includes energy terms due to differences in degree of hydration of Ca^{2+} ions when adsorbed and when in solution. It is taken to be independent of the degree of occupation of neighboring sites; the influence of the latter is taken account of through ψ_i .

If the electrical potential in the bulk solution is taken to be 0, in accordance with the usual practice in colloid chemistry (17), we have

$$\mu_{i\text{ads}}^0 + RT \ln \theta_i / (1 - \theta_i) + 2F\psi_i = \mu_{\text{Ca}} + RT \ln \gamma_{\text{Ca}} m_{\text{Ca}} \quad [2]$$

where γ_{Ca} is the activity coefficient of Ca^{2+} in the solution. For convenience, the charge on the Ca^{2+} and indices T , p constant are omitted in the following, where possible. Solvation effects (17–19) are considered to be only slightly dependent on ψ_i and therefore included in $\mu_{i\text{ads}}^0$. On differentiation at constant T and p , we obtain

$$\frac{d\theta_i}{\theta_i(1 - \theta_i)} = d \ln \gamma_{\text{Ca}} + d \ln m_{\text{Ca}} - \frac{2F}{RT} d\psi_i \quad [3]$$

$$\frac{\partial \theta_i}{\partial \ln m_{\text{Ca}}} = \left[1 + \frac{\partial \ln \gamma_{\text{Ca}}}{\partial \ln m_{\text{Ca}}} - \frac{2F}{RT} \frac{\partial \psi_i}{\partial \ln m_{\text{Ca}}} \right] \theta_i(1 - \theta_i) \quad [4]$$

The experimentally accessible quantity is

$$\frac{\partial X}{\partial \ln m_{\text{Ca}}} = \sum_i N_i \frac{\partial \theta_i}{\partial \ln m_{\text{Ca}}} \quad [5]$$

where N_i = number of sites of type i per unit area; and X = number of Ca^{2+} ions present at the surface per unit area.

Combining Eqs. [4] and [5], we obtain

$$\frac{\partial X}{\partial \ln m_{\text{Ca}}} = \left[1 + \frac{\partial \ln \gamma_{\text{Ca}}}{\partial \ln m_{\text{Ca}}} - \frac{2F}{RT} \frac{\partial \psi}{\partial \ln m_{\text{Ca}}} \right] \times \sum_i N_i \theta_i(1 - \theta_i) \quad [6]$$

where an average potential increase of all adsorption sites has been introduced, defined by

$$\frac{\partial \psi}{\partial \ln m_{\text{Ca}}} = \frac{\sum_i (\partial \psi_i / \partial \ln m_{\text{Ca}}) \theta_i(1 - \theta_i) N_i}{\sum_i \theta_i(1 - \theta_i) N_i} \quad [7]$$

It follows from this definition that $\partial \psi / \partial \ln m_{\text{Ca}}$ is determined primarily by those sites where θ_i is near $\frac{1}{2}$. However, when ψ_i takes account of the degree of occupation of neighboring sites and a random distribution of sites of different types on the surface is assumed, no significant difference between $\partial \psi / \partial \ln m_{\text{Ca}}$ as defined by [7] and an unweighted average is expected. Thus, from [6]:

$$\frac{\partial \psi}{\partial \ln m_{\text{Ca}}} = \frac{RT}{2F} \left[1 + (\partial \log \gamma_{\text{Ca}} / \partial \log m_{\text{Ca}}) - (\partial X / \partial \log m_{\text{Ca}}) / 2.303 \sum_i \theta_i(1 - \theta_i) N_i \right] \quad [8]$$

Since $0 \leq \theta_i \leq 1$, $0 \leq \theta_i(1 - \theta_i) \leq \frac{1}{4}$, Therefore

$$\sum_i \theta_i(1 - \theta_i) N_i \leq \frac{1}{4} \sum_i N_i = \frac{1}{4} N_s \quad [9]$$

where N_s = total number of sites per unit area.

For $\alpha\text{-CaSiO}_3$, we estimate $N_s = 6.1 \text{ nm}^{-2}$ (see Results section). From Fig. 1, we read for $\partial X / \partial \log m_{\text{Ca}}$ in the vicinity of the IEP: $15.4 \times 10^{17} \text{ m}^{-2}$ per decade (which means on

increasing $\log m_{\text{Ca}}$ by 1). For $\partial \log \gamma_{\text{Ca}} / \partial \log m_{\text{Ca}}$ we fill in the Debye-Hückel value for the medium concerned (20), -0.0913 . Thus, from [8]:

$$\overline{\partial \psi / \partial \log m_{\text{Ca}}} \leq 14.0 \text{ mV per decade.} \quad [10]$$

This appears, at first sight, to be at variance with

$$\partial \zeta / \partial \log m_{\text{Ca}} = 26.0 \text{ mV per decade (2),} \quad [11]$$

because this would imply a negative capacity of the Stern layer. The discrepancy cannot be due to an error in the estimated value of N_s , since N_s should have much higher values in order to close the gap between [10] and [11]; these values would be acceptable only if a multilayered $\text{Ca}(\text{OH})_2$ or calcium silicate hydrate with CaO/SiO_2 molar ratio higher than 1 are formed on the CaSiO_3 .

Since arguments have been put forward against these alternatives, the discrepancy between $\overline{\partial \psi / \partial \log m_{\text{Ca}}}$ and $\partial \zeta / \partial \log m_{\text{Ca}}$ is ascribed to the systematic difference between the average potential at the Ca^{2+} adsorption sites, and the average potential of the whole wall. The former is influenced by ions adsorbed on neighboring sites. These will, for a Ca^{2+} site, be occupied preferentially by OH^- ions (or by SiO^- originating on dissociation of surface SiO_4 groups). Thus, OH^- adsorption stimulates Ca^{2+} adsorption on $\alpha\text{-CaSiO}_3$.

Similarly, on $\text{CaAl}_2\text{Si}_2\text{O}_8$, $\overline{\partial \psi / \partial \log m_{\text{Ca}}}$ for Ca^{2+} sites is calculated to be ≤ 8.0 mV per decade. In this calculation, N_s for anorthite is taken as 3.3 nm^{-2} (which is the value estimated from the dimensions of the unit cell), since in the vicinity of the IEP no adsorption of more Ca^{2+} than can be accommodated in the first layer is apparent; therefore, in view of the difference in IEP between crystalline and vitreous $\text{CaAl}_2\text{Si}_2\text{O}_8$ (2), essentially unchanged distances between Ca^{2+} adsorption sites on the surface are assumed. Anyhow, for $\text{CaAl}_2\text{Si}_2\text{O}_8$ $\partial \zeta / \partial \log m_{\text{Ca}}$ surpasses even the change in "Nernst" potential which should be valid for the wall potential if there would be no influence other than the average wall potential,

on the electrochemical potential of an adsorbed Ca^{2+} ion. Thus, such a simple model is not applicable in the case at hand.

The order of magnitude of the effect of mutual stimulation can be calculated, for $\alpha\text{-CaSiO}_3$, from the following model. Every Ca^{2+} site is granted a square $0.404 \times 0.404 \text{ nm}^2$, using the same model as was used for the estimation of N_s . The Ca^{2+} ion is thought to occupy the center of this square. The corners of these squares are thought to be available for OH^- adsorption. Additional OH^- can be situated on the top of a Ca^{2+} ion or below (the latter, for instance, as SiO^- group). The distances between Ca^{2+} and OH^- ions in the corners of the squares are 0.29 nm , and between Ca^{2+} and OH^- on top of that Ca^{2+} it is 0.24 nm . This model is both consistent with the numbers of Ca^{2+} and OH^- sites required by the data and with steric requirements.

The contributions to the potential of a Ca^{2+} ion from ions, Ca^{2+} as well as OH^- , are then summarized, assuming that the relative dielectric constant near the solid is 6, and assuming all sites to be occupied ($X/N_s = 1$), until the potential does no more change on including additional charges farther away. This gives $\Delta\psi = -0.53 \text{ V}$. Thus,

$$\frac{\partial \psi}{\partial (X/N_s)} = -0.53 \text{ V for a } \text{Ca}^{2+} \text{ site}$$

and since $\partial (X/N_s) / \partial \log m_{\text{Ca}} = 0.25$ in the vicinity of the IEP (see Fig. 1), we get $\partial \psi / \partial \log m_{\text{Ca}} = -0.13 \text{ V per decade}$. Similarly, for an OH^- site, $\partial \psi / \partial \log m_{\text{Ca}} = 0.67 \text{ V per decade}$.

There is a certain resemblance of the model of "mutual stimulation" of ions adsorbed on adjacent sites, which has been developed here, and Levine's "discrete ion" effect (21). However, there are fundamental differences: Levine calculated the influence of a random ionic environment in the adsorbed layer, whereas here a preferentially ordered surrounding of adsorbed Ca^{2+} by adsorbed OH^- is assumed, as is shown to be more realistic in our case by the fact that σ_{Ca} is compensated chiefly by OH^-

adsorption without Cl^- entering into the picture. Moreover, if we were to treat Ca^{2+} adsorption in our systems according to Levine's model, we should have to consider all ions adsorbed, Ca^{2+} as well as OH^- , as situated in one "inner Helmholtz plane" which would raise questions, however, about why Ca^{2+} ions are adsorbed at all to an amount leading to charge reversal of the surface.

A description of the simultaneous increase of Ca^{2+} and OH^- adsorption with increasing CaCl_2 as surface precipitation of $\text{Ca}(\text{OH})_2$ (19) is avoided in this paper. The use of this term would imply that the phenomena are determined by a mutual interaction between Ca^{2+} and OH^- essentially similar to that in solid $\text{Ca}(\text{OH})_2$, only stimulated by an electric field near the phase boundary. If this would be correct, the solubility product of $\text{Ca}(\text{OH})_2$ should be strongly dependent on whether conditions correspond to the point of zero charge of $\text{Ca}(\text{OH})_2$, or not, since this determines the field strength near the $\text{Ca}(\text{OH})_2$ /solution boundary. This has until now not been reported. Description of the phenomena as mutual stimulation of Ca^{2+} and OH^- adsorption, on the other hand, implies that adsorption is in all determined to an important degree by the solid silicate surface. This is considered to be more realistic in the present case; it should be remembered that the term OH^- adsorption includes here dissociation of surface SiOH groups.

Tadros and Lyklema's model (10, 22, 23) of one ionic species as primary charging unit (OH^- in the case of SiO_2), whose charge is compensated almost completely by counter ions simultaneously adsorbed (cations in the case of SiO_2) excludes superequivalent adsorption of the counter ions; moreover, the charge brought to the surface by the primary charging ion according to this model should be independent of the amount of following ions adsorbed. Since both conclusions do not apply in the cases of $\alpha\text{-CaSiO}_3$ and $\text{CaAl}_2\text{Si}_2\text{O}_8$ (see the charge reversal observed, and Figs. 1 and 2),

the model of mutual stimulation of ion adsorption is here thought to be more realistic.

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