Surfaces of Silicates in Aqueous Alkaline Solutions I

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The ζ-potential measurements reported indicate that the surface layers of CaAl₂Si₂O₈₉, Ca₂MgSi₂O₆₉, and Ca₂Al₂SiO₇ in aqueous 0.01 N NaOH solutions have a structure reminiscent of the bulk structure of these materials. With Ca₂MgSi₂O₆₉, surface desorption of SiO₄⁻ occurs leading to a net positive surface charge. Aluminate ions are adsorbed on the surfaces of α-CaSiO₃ and CaAl₂Si₂O₈₉, increasing the number of Ca²⁺ adsorption sites; Cl⁻ is not specifically adsorbed by CaAl₂Si₂O₉.

INTRODUCTION

The surfaces of silicates in contact with aqueous solutions lend themselves less easily to colloid chemical experiments than the mercury/aqueous electrolyte or AgJ/aqueous electrolyte interface. The latter interfaces cannot act as models in all respects for the silicate/aqueous electrolyte interface, however, because: (a) a variety of ions, including H₃O⁺ and OH⁻, can be potential-determining in the case of silicates (see, e.g., (1), and (b) silicates may be subject to reactions with water, leading to a hydrated or swollen layer on their surface.

Such a layer is known to exist on some types of glasses (2, 3) and on SiO₂ (4). The temptation arises then to regard all silicate surfaces in contact with aqueous solutions as covered by a hydrated layer whose structure bears only a remote relationship to the bulk structure of the solid. However, some time ago it was reported (5) that there is a difference in electrokinetic properties between crystalline and vitreous CaSiO₃, or crystalline CaSiO₃ after intensive grinding, which could be attributed to Ca²⁺ ions being picked up from the surrounding solution less easily by (or released more easily from) sites in a disordered surface

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than by sites specially adapted to Ca²⁺ ions such as those expected on a crystalline Ca²⁺ containing species. If this interpretation is correct, it excludes the existence of a hydrated layer of any appreciable depth, at least for the compounds and under the conditions investigated, since such a layer would certainly mask any difference between crystalline and vitreous material of the same chemical composition.

Although observations on some silicates in dimethylsulfoxide have reported a similar trend (6), the experimental evidence is still none too abundant: The solid phases investigated were limited to the silicates of divalent cations (Ca²⁺, Cd²⁺, Zn²⁺), and in aqueous solutions the effect itself was rather small (though of the magnitude that might be expected on the basis of a simplified theory).

The present investigation intends to extend the range of solids, including Na⁺-containing species. The latter is important because formation of a hydrated layer on glasses is thought to be initiated by an exchange of Na⁺ from the solid against H⁺ or H₂O⁺ from the solution (4, 7). The present paper surveys electrokinetic properties of these compounds. For two of the solids investigated (α-CaSiO₃ and anorthite), data have been obtained on the
mechanism of charge transfer to the solid surface; these will be described separately.

Throughout this paper, the term “surface hydration” will refer to the formation of a hydrate layer on the surface of at least some molecular diameters depth. Thus, a single layer of OH\(^-\) ions on the outermost surface will not be included in the term.

**EXPERIMENTAL**

(a) **Materials.** Starting materials for syntheses were CaCO\(_3\), BaCO\(_3\), Na\(_2\)CO\(_3\), MgO, and SiO\(_2\) Merck “pro analysi,” and Al\(_2\)O\(_3\), Analar.

Glasses were prepared by melting a mixture of calculated quantities of these materials in a platinum dish. They did not show any discrete X-ray reflections, which the exception of the Ca\(_2\)MgSi\(_2\)O\(_7\) glass, which showed, even after quenching in water, weak reflections corresponding to lattice spacings \(d\) of 0.287 and 0.309 nm, respectively.

Anhydrous crystalline solids were in most cases prepared by sintering, until the X-ray diffraction diagram agreed with given data in (8). Special precautions were necessary in preparing BaAl\(_2\)Si\(_2\)O\(_8\) since BaO attacks platinum. In this case, the starting materials were mixed to a paste with benzene; this paste was pressed into cylinders which remained intact on careful heating. During sintering, a number of cylinders were placed on top of each other to minimize contact with the platinum; the material from the bottom cylinder was rejected.

The åkermanite sample showed, in addition to X-ray reflections agreeing with (8), weak reflections for \(d\) of 0.331 and 0.297 nm, respectively.

In one case (Ca\(_2\)Al\(_3\)SiO\(_7\)) devitrification of a glass of the same composition was employed as a method of preparing a crystalline compound. Devitrification was effected through heating at 1100°C for 12 hr.

After synthesis, glasses and crystalline compounds were ground in an agate ball mill; the crystalline compounds are then referred to as “intensively ground” (ig). Crystals with a “slightly disordered surface structure” (sdss) were prepared from ig samples by heating again to temperatures where sintering occurs to a slight extent only, i.e., to restore the damage that intensive grinding may have caused to the surface structure. As an example, data are mentioned for one of the CaAl\(_2\)Si\(_2\)O\(_8\) (anorthite) samples. The ingredients were melted together at 1600°C, ground in a ball mill; sintered for 5 hr at 1480°C, again ground in a ball mill; and sintered for 6 hr at 1300°C and 12 hr at 1100°C, after which the sample could be turned into a powder by cautions treatment in a mortar. Gehlenite hydrate (Ca\(_2\)Al\(_3\)SiO\(_7\)-8H\(_2\)O) was prepared by Dörre's method (9).

Solutions were prepared from twice distilled water and Merck “pro analysi” chemicals. A 0.01 M NaAlO\(_2\) stock solution was obtained by dissolving 269.8 mg Al tape (Merck, 99.99%) in a slight excess of NaOH and diluting to 1 l; ultimate solutions containing aluminate were prepared by mixing the stock solutions with 0.1 M NaOH solutions and diluting to the desired value.

(b) **Methods.** Electroosmosis was performed using conventional apparatus (5), at a temperature of 25 ± 0.5°C. Diaphragms were prepared as follows: 7 g of the solid was dispersed in 30 ml of the solution concerned and the supernatant was decanted. This was repeated eight times. Ultimately, 50 ml of the solution was employed by free sedimentation in the turn of the U-tube of the electroosmosis apparatus. Part of the last supernatant was used for filling the apparatus, and another part was used for the analysis. The total time between first contact of the solid with electrolyte solution and the last electroosmosis experiment was 2.5–3 hr.

To prevent differences in wettability of the capillaries, a small drop of a surfactant [Hicol (Rotterdam), RBS 25] was placed in the meniscus in the capillaries (by means of a micrometer syringe) after the apparatus had been assembled.
The pH and electrical conductivity were determined in the final supernatant using conventional apparatus. Ca$^{2+}$ and Ba$^{2+}$ were titrated complexometrically (10), Al$^{3+}$ was determined spectrophotometrically, either according to (11) or (12)–(14).

From the results, $\zeta$-potentials were calculated in the usual way, and IEP's were found by assuming a linear $\zeta$-log $[\text{Ca}^{2+}]$ relationship in the vicinity of the IEP; this linear relation was calculated from the data by the method of least squares.

RESULTS AND DISCUSSION

(a) IEP's of the various solids. The results (see Table I) can be summarized in the following statements:

1. Compounds containing Ca$^{2+}$ (Ca$_3$Al$_2$Si$_2$O$_8$, Ca$_2$MgSi$_2$O$_7$, Ca$_2$Al$_2$SiO$_7$) behave qualitatively according to the predictions of the theory (5), showing a shift of the IEP towards higher CaCl$_2$-concentration with increasing disorder of the surface structure (Fig. 1). Thus, the surface structure still retains some of the character of the bulk structure after about 3 hr of contact with an aqueous 0.01 N NaOH solution. A hydrated layer of any appreciable depth is thus excluded.

2. Results obtained for anorthite with CaCl$_2$ and Ca(ClO$_4$)$_2$ solutions, respectively, do not show any difference (Fig. 2), indicating the absence of specific adsorption of Cl$^-$, in accordance with other data for SiO$_2$ (15, 16).

3. Åkermanite acquires a positive surface charge when brought into contact with a 0.01 N NaOH solution originally containing no CaCl$_2$. Since some Ca$^{2+}$ is found in the liquid after contact, part of the silicate network (which in the compound concerned consists of [MgSi$_2$O$_7$]$^{4-}$ layers) must dissolve; the only other alternative, specific adsorption of Na$^+$, is discarded at least to an extent leading to a positive surface.

4. This network decomposition on åkermanite is thought to comprise the passing into solution of Si$_2$O$_5$$^{2-}$ ions (see Fig. 3) since the Mg–O bonds form weak spots in the network. Thus, a surface Mg–O–Si bond runs a great chance of being disrupted between Mg and O. Some OH$^-$ may be adsorbed instead, forming MgOH groups. If the surface is to become positive by the process concerned, less OH$^-$ than would be equivalent to Si$_2$O$_5$$^{2-}$ should be adsorbed.

5. The network decomposition is more pronounced with åkermanite than with gehlenite (which has a similar crystal structure containing [Al$_2$SiO$_4$]$^{4-}$ layers), as seen by comparison of the IEP's. This is consistent with statement 4, since Al–O bonds are stronger.
# TABLE I

**ISOELECTRIC POINTS FOR THE VARIOUS COMPOUNDS INVESTIGATED ([NaOH] = 0.01 N)**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Modification</th>
<th>Type of surface</th>
<th>Electrolyte</th>
<th>Concentration at IEP (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaSiO₅</td>
<td>α</td>
<td>sdss</td>
<td>CaCl₂</td>
<td>2.8 × 10⁻³</td>
</tr>
<tr>
<td>Ca₂Al₂Si₄O₉</td>
<td>Anorthite</td>
<td>sdss</td>
<td>CaCl₂</td>
<td>1.5–2.0 × 10⁻³</td>
</tr>
<tr>
<td></td>
<td>Anorthite</td>
<td>ig</td>
<td>CaCl₂</td>
<td>3.0 × 10⁻³</td>
</tr>
<tr>
<td></td>
<td>Vitreous</td>
<td>—</td>
<td>CaCl₂</td>
<td>3.7 × 10⁻³</td>
</tr>
<tr>
<td></td>
<td>Anorthite</td>
<td>sdss</td>
<td>Ca(ClO₄)₂</td>
<td>1.9 × 10⁻³</td>
</tr>
<tr>
<td></td>
<td>Anorthite</td>
<td>sdss</td>
<td>BaCl₂</td>
<td>2.9 × 10⁻³</td>
</tr>
<tr>
<td>BaAl₂Si₄O₉</td>
<td>Celsiane</td>
<td>sdss</td>
<td>CaCl₂</td>
<td>2.1 × 10⁻³</td>
</tr>
<tr>
<td></td>
<td>Vitreous</td>
<td>—</td>
<td>CaCl₂</td>
<td>3.3 × 10⁻³</td>
</tr>
<tr>
<td></td>
<td>Celsiane</td>
<td>sdss</td>
<td>BaCl₂</td>
<td>2.0 × 10⁻³</td>
</tr>
<tr>
<td>NaAlSi₅O₈</td>
<td>Albite (high)</td>
<td>sdss</td>
<td>CaCl₂</td>
<td>3.5 × 10⁻³</td>
</tr>
<tr>
<td></td>
<td>Vitreous</td>
<td>—</td>
<td>CaCl₂</td>
<td>3.7 × 10⁻³</td>
</tr>
<tr>
<td>Ca₂Al₃SiO₇</td>
<td>Gehlenite</td>
<td>sdss</td>
<td>CaCl₂</td>
<td>0.8–1.0 × 10⁻³</td>
</tr>
<tr>
<td></td>
<td>Gehlenite</td>
<td>ig</td>
<td>CaCl₂</td>
<td>1.0 × 10⁻³</td>
</tr>
<tr>
<td></td>
<td>Gehlenite</td>
<td>devitrified glass</td>
<td>CaCl₂</td>
<td>1.5 × 10⁻³</td>
</tr>
<tr>
<td></td>
<td>Vitreous</td>
<td>—</td>
<td>CaCl₂</td>
<td>2.4 × 10⁻³</td>
</tr>
<tr>
<td>Ca₂Al₃SiO₇·8H₂O</td>
<td>Gehlenite hydrate</td>
<td>—</td>
<td>CaCl₂</td>
<td>0.6 × 10⁻³</td>
</tr>
<tr>
<td>Ca₂MgSi₅O₇</td>
<td>Åkermanite</td>
<td>sdss</td>
<td>CaCl₂</td>
<td>0.15 × 10⁻³</td>
</tr>
<tr>
<td></td>
<td>Vitreous</td>
<td>—</td>
<td>CaCl₂</td>
<td>1.5 × 10⁻³</td>
</tr>
<tr>
<td>Al₄Si₂O₁₃</td>
<td>Mullite</td>
<td>sdss</td>
<td>CaCl₂</td>
<td>2.8 × 10⁻³</td>
</tr>
<tr>
<td></td>
<td>Mullite</td>
<td>ig</td>
<td>CaCl₂</td>
<td>2.4 × 10⁻³</td>
</tr>
</tbody>
</table>

* sdss = slightly disordered surface structure; ig = intensively ground.
* Different samples.
* Extrapolated value, since on bringing Ca₂MgSi₅O₇ into contact with 0.01 N solution of NaOH containing no CaCl₂, a [Ca²⁺] = 2.10⁻⁴ M and a ζ = + 2.5 mV are observed.

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**Fig. 2.** Electrokinetic data on anorthite, in 0.01 N NaOH, with: ☐, CaCl₂; ☐, BaCl₂; ☐, Ca(ClO₄)₂.

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Fig. 3. Part of the akermanite structure, seen on top of the \([\text{MgSi}_2\text{O}_5]^4^−\) layer. ⋄, Ca\(^{2+}\); ⋄, Mg\(^{2+}\); Si\(^{4+}\) (not shown), at the center of the tetrahedra not filled by Mg\(^{2+}\). Oxygen is situated at the corners of the tetrahedra. A Si\(_2\)O\(_7\)^{−} unit, that may become desorbed, is separated by thin dashed lines.

than Mg–O bonds. However, surface hydration on gehlenite cannot be excluded.

6. Dissolution of part of the network may occur with other solids also. Its primary effect is the creation of a new surface on the anhydrous solid. A secondary effect may be precipitation of calcium silicate hydrates and calcium aluminate hydrates effecting: (a) changes in the concentrations in the solution (which are, however, checked by analyses); and (b) creation of hydrate surfaces, which should be equal for materials of the same composition and a different degree of surface disorder, and thus, are ruled out as dominant features, at least for the Ca\(^{2+}\) containing solids, by statement 1.

7. There is a difference in IEP between vitreous Ca\(_2\)Al\(_2\)SiO\(_7\) and Ca\(_2\)Al\(_2\)SiO\(_7\)·8H\(_2\)O, but not between gehlenite and Ca\(_2\)Al\(_2\)SiO\(_7\)·8H\(_2\)O. This could be ascribed either to gehlenite hydrating faster than vitreous Ca\(_2\)Al\(_2\)SiO\(_7\) [which would disagree with some data (17, 18) but would agree with other data (19)] or to a fortuitous coincidence of the IEP’s of gehlenite and gehlenite hydrate (no surface hydration of any extent occurring in gehlenite).

8. Compounds containing no divalent ions (albite, mullite) do not show any significant influence of surface disorder on the IEP. In the case of albite, this may be due to formation of a hydrated surface layer; however, vitreous CaAl\(_2\)SiO\(_5\), NaAlSi\(_2\)O\(_5\) and BaAl\(_2\)Si\(_2\)O\(_6\) have their IEP’s close together, indicating a similar surface without surface hydration to any extent in all cases in view of the differences in IEP between crystalline and vitreous CaAl\(_2\)SiO\(_5\) and BaAl\(_2\)Si\(_2\)O\(_6\). On mullite, no crystalline hydration product was formed in 5 days to an extent detectable by X rays (5%). However, even in this case, a hydrated surface layer is not completely ruled out since it may be amorphous or the layer initially formed might retard its continued formation.

If surface hydration is thought to be absent, the absence of influence of surface disorder on the IEP in the case of NaAlSi\(_2\)O\(_5\) and mullite should be attributed to a lack of specificity of the adsorption sites towards Ca\(^{2+}\) in the well-ordered compound.

9. BaAl\(_2\)Si\(_2\)O\(_8\) is as easily charged by Ca\(^{2+}\) as by Ba\(^{2+}\) ions, but CaAl\(_2\)Si\(_2\)O\(_8\) is less easily charged by Ba\(^{2+}\) than by Ca\(^{2+}\). This is analogous to the results obtained on α and β-CaSi\(_2\)O\(_4\) (5) and can be explained as follows. Interstices in the [Al\(_2\)Si\(_2\)O\(_8\)^{−}]\(_n\) network in the Ba\(^{2+}\) compound are large enough to accommo-
SILICATES IN ALKALINE SOLUTIONS

date Ba\(^{2+}\) as well as Ca\(^{2+}\), but those in the Ca\(^{2+}\) compound cannot accommodate Ba\(^{2+}\). This difference excludes Ca(OH)\(_2\) or Ba(OH)\(_2\) layer formation on the surfaces of the solid, as suggested by James and Healy (20).

(b) Influence of aluminate ions on the \(\zeta\)-potential. It is well-known (21, 22) that aluminium-containing ions can exert a profound influence on \(\zeta\)-potentials, leading in some cases to a charge reversal. To check whether aluminate ions dissolved from the solids investigated exert an influence on the IEP, some electroosmosis experiments were performed with solutions containing deliberately added amounts of aluminate ions at constant NaOH and CaCl\(_2\) concentrations. Solid phases in these experiments were \(\alpha\)-CaSiO\(_3\) and anorthite, which were investigated both at positive and at negative surface charges.

The results obtained with \(\alpha\)-CaSiO\(_3\) are shown in Fig. 4. The effect of the aluminate concentration on the \(\zeta\)-potential appears to be small, but leads in all cases to an increase in the absolute value of the \(\zeta\)-potential, especially at positive surface charges. Similar observations were obtained with anorthite.

At low CaCl\(_2\) concentrations, aluminate ions are seen to be adsorbed on the surface, which is already negative. They may be attracted by nonelectrostatic forces (23) and by positive sites on a surface with net negative charge, and thus, increase the surface charge.

At high CaCl\(_2\) concentrations, the surface charge is increased again, because the adsorption of aluminate ions has increased the number of sites available for the Ca\(^{2+}\) ions. Alternatively, CaAl(OH)\(_3\) complexes may be formed in solution and be adsorbed by nonelectrostatic forces by the positively charged surface; however, the fact that the aluminate influence is more distinct at positive surface charges can be understood better by the former alternative (adsorption of aluminate ions by both electrostatic and nonelectrostatic forces).

The IEP is not noticeably changed by the presence of aluminate ions, since the positive and negative \(\zeta\)-potentials move by their presence in opposite directions. Moreover, in all experiments without deliberately added aluminate ions, their concentration was lower than \(5 \times 10^{-6} \text{ M}\) in the final decantate; thus, their influence may be neglected.

CONCLUSIONS

CaAl\(_2\)Si\(_2\)O\(_8\), Ca\(_2\)MgSi\(_2\)O\(_7\), and Ca\(_2\)Al\(_2\)SiO\(_7\) are not hydrated in aqueous 0.01 \(N\) NaOH solution within 3 hr to an extent that might mask the surface structure. Precipitation of Ca(OH)\(_2\) or Ba(OH)\(_2\) on the surfaces does not

![Fig. 4. Influence of aluminate ions on the \(\zeta\)-potential at constant [NaOH] and [CaCl\(_2\)]. Solid phase: \(\alpha\)-CaSiO\(_3\). +, 0.01 \(N\) NaOH +0.01 \(M\) CaCl\(_2\); \(\Box\), 0.01 \(N\) NaOH +0.0005 \(M\) CaCl\(_2\).](image)

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occur under the conditions prevailing in the present investigation. Aluminate ions are adsorbed on the surfaces of α-CaSiO₃ and Ca₆Al₂Si₂O₈ and they increase the number of Ca²⁺ sites. Cl⁻ is not specifically adsorbed by Ca₆Al₂Si₂O₈.

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