Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 3. A Potentiometric Study of Aluminium(III) Hydrolysis and Aluminium(III) Hydroxo Carbonates in 0.6 M Na(Cl)

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Equilibria between aluminium(III), carbon dioxide and OH⁻ were studied in 0.6 M Na(Cl) medium at 25 °C. The measurements were performed as emf titrations (glass electrode) using different CO₂(g)–Ar(g) mixtures of known compositions. The ranges 1.5 ≤ -lg [H⁺] ≤ 4.3; 0.0025 M ≤ [Al³⁺] ≤ 0.02 M and 9.5 kPa ≤ PCO₂ ≤ 101 kPa were covered. Data can be explained with the binary complexes AlOH²⁺, Al₂(OH)₃⁺ and Al₃(OH)₄(OH)₂⁺ together with the ternary species Al₃(OH)₄CO₃²⁻ and Al₃(OH)₄CO₃⁺ (tentative structures). The equilibrium constants with standard deviations are given in Table 2.

The equilibrium CO₂(g) + H₂O ⇌ HCO₃⁻ + H⁺ was studied in separate titrations and lgβ₁ ± 3σ = -12.539 ± 0.001 (β₁ = 10⁻¹².539 M⁻²Pa⁻¹) was found. Data were analyzed with the least squares computer program LETAGROPV RID.

In a series of investigations in progress at this department, the ability of Si(IV) and Al(III) to form aqueous complexes with naturally occurring inorganic and organic ligands is being studied. We are working with a simplified sea water medium and our main interest is focused on the formation of ternary hydroxo complexes. From these investigations, we hope to obtain a better understanding of speciation and concentration of Si(IV) and Al(III) in natural waters. The systems so far described have been Al³⁺ – OH⁻ – gallic acid¹ and Si(OH)₄ – OH⁻.²

The aim of the present paper is to give and discuss the results obtained in the three component system Al³⁺ – OH⁻ – CO₂(g).

EXPERIMENTAL

Chemicals and analysis. Sodium carbonate (Merck p.a.) was used without purification after drying at 300°C. Dilute solutions were prepared by dissolving Na₂CO₃ in water and were standardized against dilute hydrochloric acid. Carbon dioxide, pure and in different mixtures with Ar, was prepared and analyzed by the manufacturer (ALFA AB, Malmö). Stock solutions of sodium chloride and aluminium chloride as well as the dilute hydrochloric acid and sodium hydroxide solutions were prepared and standardized as earlier.¹

Apparatus. The automatic system for precise emf titrations, the thermostat and the electrodes were described earlier.¹ During the experiments, performed in airtight vessels with gas outlet beneath a liquid surface, a stream of carbon dioxide in argon was bubbled through the solution for stirring and for maintaining a constant carbon dioxide partial pressure in the vessel. The gas, from a cylinder, was bubbled through solutions of 10 % H₂SO₄ and pure ionic medium before it came into contact with the equilibrium solution.

The atmospheric pressure was continuously measured during the experiments and used, together with the vapour pressure for water, 3.13 kPa at 25 °C, to calculate the current PCO₂ in the vessel.

METHOD

The present investigation was carried out by means of a series of titrations at 25 °C in a constant ionic medium of 0.6 M Na(Cl). The free hydrogen ion concentration, h, was varied by adding carbonate
ions and measured with a glass electrode. Calibrations and assumptions in connection with the use of the glass electrode were the same as described earlier. The initial concentration of aluminium, B, and the carbon dioxide pressure, $P_{\text{CO}_2}$, $c$, were varied within the limits $0.0025 \leq B \leq 0.02$ M, and $9.47 \text{kPa} \leq c \leq 101.4 \text{kPa}$. The available $-\log h$ range was restricted to $-\log h \leq 3.95 - 4.35$ due to very slow attainment of equilibria above this limit. Within the investigated area, stable potentials, remaining constant to $0.02 \text{mV}$ for several hours, were attained after $60 - 90 \text{ min}$. The reproducibility and reversibility of equilibria were tested by performing both forward (increasing $-\log h$) and backward (decreasing $-\log h$) titrations. The reversibility was also tested by performing dilution experiments (titrations with pure medium solution) at all $P_{\text{CO}_2}$ investigated and by changing $P_{\text{CO}_2}$ within a titration.

Data treatment. We will assume the presence of three component equilibria of the general type (1a) together with the two component equilibria (1b) and (1c).

\[
pH^+ + q\text{Al}^{3+} + r\text{CO}_2(g) = \text{H}_n\text{Al}_q(\text{CO}_2)_r^{p+3q}; \beta_{pq} \quad (1a)
\]

\[
\text{CO}_2(g) + H_2O = H_2 - \text{CO}_3^- + \text{H}^+ \quad n=0,1,2; \beta_n \quad (1b)
\]

\[
pH^+ + q\text{Al}^{3+} = \text{H}_n\text{Al}_q^{+3q}; \beta_{pq} \quad (1c)
\]

Applying the law of mass action to these equilibria gives the conditions for the total concentrations

\[
B = b + \sum_{pq} q\beta_{pq}h^pb^qc^r
\]

\[
C = \sum_n \beta_n h^{-n}c + \sum_{pq} r\beta_{pq}h^pb^qc^r
\]

\[
H = h - \sum_n n\beta_n h^{-n}c + \sum_{pq} p\beta_{pq}h^pb^qc^r - k_w h^{-1}
\]

where $h = [H^+]$, $b = [\text{Al}^{3+}]$ and $c = P_{\text{CO}_2}$. $k_w = 1.875 \times 10^{-14} \text{M}^2$ is the ionic product of water in 0.6 M NaCl.\(^2\) The summation is taken over all complexes formed where $\beta_{pq}$, $\beta_n$ and $\beta_{pq}$ are the equilibrium constants for the reactions 1a, 1b and 1c, respectively. For the binary carbon dioxide–hydrogen carbonate equilibrium ($n=1$ in reaction 1b) we will make use of the results obtained in separate experiments and these will, in the three-component

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Fig. 1. A part of binary carbon dioxide–hydrogen carbonate experimental data plotted as curves $\log [\text{HCO}_3^-]$ ($\log h$) for different carbon dioxide pressures. The full curves have been calculated using the proposed constant.

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Fig. 2. The same experimental data as in Figure 1 after division with actual carbon dioxide pressure. The figure visualizes the validity in assuming only one mononuclear equilibrium.
Fig. 3. Experimental three-component data plotted as curves $\bar{n}(\text{lg[HCO}_3^-])$ where the symbols stand for start concentrations in B. In order to make the figure clear only a few titrations have been plotted. The full curves have been calculated with the set of proposed constants given in Table 2.

analysis, be assumed to be exactly known. Previous work concerning reaction 1c is summarized and discussed by Baes and Mesmer.\(^3\) Their proposed complexes and equilibrium constants, valid in 0.6 M medium, are given in Table 2. We will, however, treat this system unbiased in our calculations. The computational problem is now to find the model (sets of $pqr$ and $pq$ with related $\beta_{pqr}$ and $\beta_{pq}$) that best can explain the experimental data.

Table 1. Results of LETAGROP calculations for some different assumptions concerning the binary hydrolytic complexes formed excluding (left part), respectively, including (right part) the dominant ternary complex. The formation constants are related according to the relation $p\text{H}^+ + q\text{Al}^{3+} + r\text{CO}_3^- \rightarrow (\text{H}_p\text{Al}_q\text{CO}_2)_r^{3+q}$. The errors given are $3\sigma(\text{lg} \beta_{pqr})$.

<table>
<thead>
<tr>
<th>Pair of complexes tested</th>
<th>No ternary complex</th>
<th>With $\text{lg} \beta_{412} = -20.27$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{lg}(\beta_{pqr} \pm 3\sigma)$</td>
<td>$U$</td>
</tr>
<tr>
<td>$(-1,1,0)$</td>
<td>$-5.37 \pm 0.04$</td>
<td>0.145</td>
</tr>
<tr>
<td>$(-4,3,0)$</td>
<td>$-13.53 \pm 0.02$</td>
<td></td>
</tr>
<tr>
<td>$(-2,2,0)$</td>
<td>$-7.46 \pm 0.07$</td>
<td>0.155</td>
</tr>
<tr>
<td>$(-3,2,0)$</td>
<td>$-11.55 \pm 0.05$</td>
<td></td>
</tr>
<tr>
<td>$(-2,2,0)$</td>
<td>$-7.25 \pm 0.03$</td>
<td>0.202</td>
</tr>
<tr>
<td>$(-4,2,0)$</td>
<td>$-16.00 \pm 0.06$</td>
<td></td>
</tr>
<tr>
<td>$(-3,2,0)$</td>
<td>$-11.44 \pm 0.04$</td>
<td>0.301</td>
</tr>
<tr>
<td>$(-3,3,0)$</td>
<td>$-9.78 \pm 0.11$</td>
<td></td>
</tr>
<tr>
<td>$(-2,2,0)$</td>
<td>$-7.33 \pm 0.08$</td>
<td>0.477</td>
</tr>
<tr>
<td>$(-4,3,0)$</td>
<td>$-13.74 \pm 0.12$</td>
<td></td>
</tr>
</tbody>
</table>

The search for the best model was made by using the least squares computer program LETAGROP-VRID \(^4\) (version ETITR \(^5\)). With this program it is possible to treat the known data set \(h, c, H\) and \(B\). As “best” model or models we will consider those giving the lowest error squares sum \(U = \sum (\bar{H}_{\text{calc}} - \bar{H}_{\text{exp}})^2\) and \(U = \sum (\bar{H}_{\text{calc}} - \bar{H}_{\text{exp}})^2\). The LETAGROP calculations also give standard deviations \(\sigma(H), \sigma(\bar{H})\), \(\sigma(\beta)\) and/or \(\sigma(\beta_{pq})\), calculated and defined according to Sillén.\(^6\) The computations were performed on a CYBER 172 computer.

**DATA, CALCULATIONS AND RESULTS**

The data used to evaluate the binary carbon dioxide—hydrogen carbonate equilibrium comprise 10 titrations with 99 experimental points within the pressure range 1.12 kPa \(\leq c \leq 101.1\) kPa and \(-\lg h \leq 6.75\). Data analysis was performed both graphically and as LETAGROP calculations. The graphical evaluation of best fit, illustrated in Fig. 1 and Fig. 2 gave \(\lg(\beta_1 \pm 3\sigma) = -12.540 \pm 0.002\). The LETAGROP analysis ended at \(\sigma(H) = 0.056\) mM and the \(\lg(\beta_1 \pm 3\sigma)\) obtained was \(-12.539 \pm 0.0011\) \((\beta_1 = 10^{-12.539} \text{M}^2\text{Pa}^{-1})\). This value is in good agreement with earlier findings, e.g. a combination of the determinations made by Dyrrsen \textit{et al.}\(^7\) and Nilsson \textit{et al.}\(^8\) yields \(\lg(\beta_1) = -12.53\). No attempts were made to evaluate \(\beta_0\) and \(\beta_2\), determinations demanding other experimental conditions than those used by us and not necessary and negligible in our three component analysis.

The first step in the mathematical analysis of the three component data was to determine, in each experimental point, the number of \(\text{OH}^-\) bound or reacted per \(\text{Al}^{3+}\)-ion, given by the relationship \(\bar{n} = (\bar{H} - k_c h^{-1} - [\text{HCO}_3^-])^{-1}\). This quantity, plotted as \(\bar{n}(\lg[\text{HCO}_3^-])\), is shown for some of the experiments in Fig. 3.

It is seen that this function depends on both \(B\) and \(p_{\text{CO}_2}\), thus indicating formation of polynuclear \(\text{H}_2\text{Al}(\text{CO}_2)^{2+34}\) complexes. As the divergence between the \(\bar{n}\)-curves for each \(B\) increases at decreasing \(p_{\text{CO}_2}\)-values, this indicates formation of polynuclear binary \(\text{H}_2\text{Al}^{2+34}\)-species. These introductory graphical considerations, consequently, left us with a system containing ternary complexes as well as binary hydrolysis complexes. In a first attempt to separate these effects, in order to obtain a less complicated computational problem, we made the assumption that the ternary complex formation could be neglected at \(c \leq 9.5\) kPa. To make this assumption even more credible, we decided to minimize the function \(U = \sum (\bar{H}_{\text{calc}} - \bar{H}_{\text{exp}})^2\) as this would favour high concentrations and consequently high \(B/c\). On this material, comprising 9 titrations with 111 experimental points, we then performed a \(pq\)-analysis (systematic testing of different \(pq\)-complexes) with the simple hypothesis that only one complex \(\text{H}_2\text{Al}^{2+34}\) was present. The results of this analysis are given in Fig. 4 and it can be seen that the complex \(\text{Al}_2(\text{OH})_3^{3+}\) with \(\lg(\beta_{-320}) = -11.30 \pm 0.02\) gave the “best” fit (that means, the lowest error squares sum \(U = \sum (\bar{H}_{\text{calc}} - \bar{H}_{\text{exp}})^2\)). However, as the complex left considerable deviations in \(\Delta H = \bar{H}_{\text{calc}} - \bar{H}_{\text{exp}}\), we decided to examine the assumption that this complex was a kind of average complex of two or more complexes. A number of alternative pairs were therefore tested and the best five combinations are given in the left part of Table 1. With the best pair, comprising the complexes \(\text{AlOH}^{2+}\) and \(\text{Al}_5(\text{OH})^{6+}\), we obtained a good fit, and decided to regard these as known, with equilibrium constants given in Table 1, in the search for ternary species.

This search, made on a representative part of data (in all 8 titrations with 80 exp. points including all \(p_{\text{CO}_2}\)), was performed as a \(pq\)-analysis in the same manner as described above. As is seen from Fig. 5, a sharp peak was obtained for the complex \((-4.2, 1)\) with \(\lg(\beta_{-421} \pm 3\sigma) = -20.27 \pm 0.011\), giving \(\sigma(H) = 0.061\) mM. With this ternary complex, we now returned to the first data set \(p_{\text{CO}_2} = 9.5\) kPa) and renewed the calculations for the five “best”

Fig. 4. LETAGROP-search for binary \(\text{H}_2\text{Al}^{2+34}\) species on titrations with \(p_{\text{CO}_2} = 9.5\) kPa. The diagram gives \(U_{pq}(pq)\) assuming only one hydrolysis complex. The calculations are based on 111 experimental points giving \(U_{pq}(00) = 45.7\).
The results, given in the right part of Table 1, show that the pair AlOH\(^{2+}\) and Al\(_3\)(OH)\(_4\)\(^{2+}\) still gives the best fit, with an agreement with experimental data even better than in the first calculation.

As the equilibrium constant values only changed moderately, we found no need for renewing the ternary pqr-analysis but performed a covariation of all three equilibrium constants on the whole data material, comprising 25 titrations with 286 experimental points. This calculation ended at \(\sigma(H) = 0.064 \text{ mM} \) indicating a good fit.

However, a graphical representation of the model compared with experimental data plotted as \(n([\text{HCO}_3^-])\) indicated a relatively poor fit at low \(B\)-values. The explanation for this is that minimizing \(\Delta H\) in the LETAGROP calculations disfavors data sets with low \(B\)-values as \(\Delta \frac{\Delta H}{B}\). As a consequence, we found it necessary to modify our LETAGROP version so that we were able to minimize the function \(U = \sum (\bar{n}_{\text{calc}} - \bar{n}_{\text{exp}})^2\). It then turned out, when we tried to add another ternary complex to the model, that a better fit to the experimental data was obtained if either a complex \((-5,3,1)\) or a complex \((-7,4,1)\) was included.

Finally, we performed some calculations where we have tried to include those hydrolysis complexes \((\text{Al}_3\text{OH})_4^{2+}\), \(\text{Al}_3\text{O}_4\text{(OH)}_4^{2+}\) suggested by Baes and Mesmer\(^3\) but which are absent in our model. The result of these calculations are given in Table 2 and it is seen that while \(\text{Al}_3\text{O}_4\text{(OH)}_4^{2+}\) is accepted with a moderate error, \(\text{Al}_3\text{OH}_4^{2+}\) gives no significant contribution to the model. It is also clear that when \(\text{Al}_3\text{O}_4\text{(OH)}_4^{2+}\) is included in our model, the complex \((-5,3,1)\) fits better to experimental data than \((-7,4,1)\). As a final model, we therefore suggest the species \(\text{AlOH}^{2+}\), \(\text{Al}_3\text{OH}_4^{2+}\), \(\text{Al}_3\text{O}_4\text{(OH)}_4^{2+}\), \((-4,2,1)^2\) and \((-5,3,1)^4\) and the final formation constants with standard deviations (3\(\sigma\)) are given in Table 2.

In order to visualize the amounts of the different species, we have used the computer program SOLGASWATER\(^8\) equipped with plotting procedures, to calculate some distribution diagrams. These are given in Fig. 6.

DISCUSSION

The present investigation has clearly indicated the formation of ternary hydrolytic species in hydrolyzed aluminium solutions in equilibrium with
carbon dioxide of quite high partial pressures (50-100 kPa). The ternary complexes occur in rather large amounts ($\leq 25\%$ of the total aluminium concentration) and the dominating ternary species has the composition $(H^+)_{-x}(Al^{3+})_{2}CO_2$. It is, of course, not possible to establish the structures of the species from Emf-data, but as the compositions of the complexes are obtained, more or less possible structures may be predicted. Concerning $(H^+)_{-x}(Al^{3+})_{2}CO_2$, we find it credible that this species actually should be written $Al_3(OH)_{2}CO_3^-$ having the structure

![Structure diagram]

This speculation is based on the fact that there are several solid phases with similar coordination around aluminium (Dawsonite NaAl(CO$_3$)$_2$(OH)$_2$)$_{10}$ Dundasite PbAl$_2$(CO$_3$)$_2$(OH)$_4\cdot$H$_2$O$_{11}$) and, in addition, that the same coordination is found in complexes with other metal(III) ions such as Rh(III) and Cr(III)$_{12}$. Concerning the minor ternary species with the composition $(H^+)_{-x}(Al^{3+})_{3}CO_2$ we believe that it may be written $Al_3(OH)_{2}HCO_3^+$ thus establishing the often found connection between the binary hydrolysis and the ternary species formed. Besides, attempts to build a complex $Al_3(OH)_{2}CO_3^+$ give rise to unrealistic structures.

The fact that the standard deviations of the equilibrium constants are low [$3\sigma(\lg \beta_{pp}) \leq 0.06$] makes it possible to regard the proposed complexes as well determined. Furthermore, by bubbling CO$_2$(g) with different partial pressures into the equilibrium solutions, two free concentrations ($h$ and $c$) are measured and this improves the reliability in the evaluation of the complex model.

The binary aluminium hydrolysis dominates in equilibrium solutions with low $p_{CO_2}$. Although this system usually is known to be very sluggish, we found that the "addition" of even small amounts of carbon dioxide had a remarkable stabilizing effect on the system. The only probable reason for this effect is, that the carbon dioxide hydrogen carbonate system acts as a $pH$-buffer system preventing local excesses of base (with formation of large polymeric species and $Al(OH)_3$ as a consequence) at the moment of base addition. We believe that this is a general observation and that the technique could be useful in other systems as well. The drawback with it is, of course, that a third component must be included in the data analysis.

The low-molecular weight hydrolytic species needed to explain experimental data were $Al(OH)_2^+$ and $Al_3(OH)_4^{2+}$, while the often proposed complex.
Al$_3$(OH)$_5^{3+}$ was not found, meaning that upon introducing this complex to the data material no better fit was obtained. On the other hand, addition of the species Al$_{13}$O$_4$(OH)$_{24}^{7+}$ to the model made the error squares sum lower and a value of the equilibrium constant was determined. As the titrations were interrupted owing to slow equilibria, when Al$_{13}$O$_4$(OH)$_{24}^{7+}$ was formed in greater amounts, the equilibrium constant of this complex is to be regarded as approximate. However, the earlier proposed value (recalculated to 0.6 M medium) could not be adapted to experimental data and seems to be several powers of ten too large. The equilibrium constants of AIOH$_2^{2+}$ and Al$_3$(OH)$_5^{3+}$ are in good agreement with earlier values in the literature.

A model calculation has shown that the ternary hydrolytic species are of little geochemical importance in the sense that the solubility of aluminosilicates with respect to Al is increased very little at those pH (4–8); $P_{CO_2}$ ($\leq$ 5 kPa) and alkalinites ($\leq$0.005 M) occurring in nature.

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