

Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 15. A Potentiometric Study of Speciation and Equilibria in the Al^{3+} - $\text{CO}_2(\text{g})$ - OH^- System

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Hedlund T., Sjöberg, S. and Öhman, L.-O., 1987. Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 15. A Potentiometric Study of Speciation and Equilibria in the Al^{3+} - $\text{CO}_2(\text{g})$ - OH^- System. - Acta Chem. Scand., Ser. A 41: 197-207.

Equilibria between aluminium(III), carbon dioxide and OH^- were studied in 0.1 M and 3.0 M NaCl, respectively, at 25 °C. The measurements were performed as emf titrations (glass electrode) within the limits $2 \leq -\log[\text{H}^+] \leq 5$, $0.0025 \text{ M} \leq [\text{Al}^{3+}] \leq 0.080 \text{ M}$ and $0.02 \text{ atm} \leq p_{\text{CO}_2} \leq 1.0 \text{ atm}$. Data were explained on the basis of formation of the hydrolytic species AlOH^{2+} , $\text{Al}_3(\text{OH})_4^{5+}$ and $\text{Al}_3\text{O}_4(\text{OH})_2^{7+}$, together with the ternary species $\text{Al}_2(\text{OH})_2\text{CO}_3^{2+}$ and $\text{Al}_3(\text{OH})_4\text{HCO}_3^{4+}$ (tentative structures). The equilibrium constants with standard deviations for both ionic strengths are reported. The medium dependence for $\text{Al}_2(\text{OH})_2\text{CO}_3^{2+}$ (-4,2,1) and $\text{Al}_3(\text{OH})_4\text{HCO}_3^{4+}$ (-5,3,1) species was explained using the equation $\log \beta_{pq}^0 + a_i I^{1/2}/(1+I^{1/2}) + b_i I$, where $\log \beta_{pq}^0$ is the formation constant in pure water and a_i and b_i are parameters of which b_i has been adjusted to present data. The following results were obtained: $(a_i, b_i) \log \beta_{4,2,1}^0 = -13.5$ (-5.110, 0.06) and $\log \beta_{5,3,1}^0 = -16.4$ (-3.066, 0.00).

The equilibrium $\text{CO}_2(\text{g}) + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+$ was studied in separate titrations, giving the result $\log(\beta_1 \pm 3\sigma) = -7.820 \pm 0.001$ and -7.619 ± 0.002 for 3.0 M and 0.1 M NaCl, respectively. Data were analysed using the least-squares program LETAGROPVRID.

In a model calculation, speciation and solubilities in the system H^+ - $\text{Al}(\text{OH})_3$ -(am)- CO_2 are demonstrated and discussed.

As a result of the marked increase in aluminium(III) mobility in watersheds affected by acid precipitation, the environmental chemistry of aluminium(III) is presently receiving much attention. Although field measurements have shown that the speciation of Al(III) in a natural water is very complex,¹ laboratory experiments seem to indicate that acute Al(III) toxicity to fish is mainly governed by the amount of inorganic Al-hydroxo species,^{2,3} i.e. the aluminium(III) hydrolysis products.

Even though the hydrolysis of Al(III) has been the subject of extensive investigations, the results have been conflicting.^{4,5} This is especially true for slightly acidic solutions, in which the formation of

polynuclear complexes dominates. Due to the extremely slow attainment of equilibria and owing to interference from transient and permanent precipitates, it has been very difficult to establish the composition and stability of these species.

The problem with transient precipitates formed upon the addition of strong base (OH^-) in a titration can be eliminated, as shown by Öhman and Forsling,⁶ by titration with a carbonate solution and equilibration with $\text{CO}_2(\text{g})$. In this way, stable and reproducible equilibria were attained within 60-90 min, provided $-\log[\text{H}^+] \leq 4.35$. Above this limit, very slow kinetics were observed.

In the present work, the same experimental ap-

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proach has been used but employing a more concentrated ionic medium, viz. 3.0 M NaCl. With this medium, a much broader range of Al(III) concentrations can be studied without violating the rule of 10% replacement of the background medium.⁷ As the reliability of a given model certainly increases with the breadth of the concentration range it is to account for, the present study is more conclusive than the study performed using 0.6 M NaCl medium.⁶ The present study also include measurements in 0.1 M NaCl ionic media, with the intention of describing the medium dependence for the different species formed.

Experimental

Chemicals and analysis. Sodium chloride (Merck *p.a.*) and sodium carbonate (Merck *p.a.*) were dried at 180°C and 300°C, respectively, and used without further purification. Dilute solutions were prepared by dissolving Na₂CO₃ in carbon dioxide-free water and were standardized against dilute hydrochloric acid.

Dilute hydrochloric acid was standardized against tris(hydroxymethyl)-aminomethane. The Al³⁺ stock solution was prepared by dissolving AlCl₃·6H₂O (Fisher *p.a.*) in dilute standardized hydrochloric acid. The Al³⁺ content was determined by two different methods: by precipitation with 8-hydroxy quinoline⁸ and by indirect titration with EDTA-Pb(NO₃)₂ using xylenol-orange as indicator. The results obtained by these two methods agreed to better than 0.2%.

Carbon dioxide, pure and in various mixtures with argon, was prepared and analyzed by the manufacturer (Alfax AB, Malmö).

Apparatus. The potentiometric titrations were performed with an automatic system for precise emf titrations.⁹ A glass electrode (Ingold type 201-NS) together with an Ag, AgCl electrode, prepared according to Brown,¹⁰ was used for emf measurements. The cell arrangement, similar to that described by Forsling *et al.*,¹¹ was immersed in an oil thermostat at 25.00 ± 0.05°C.

In order to keep the carbon dioxide pressure constant and to avoid volume reduction of the equilibrium solution, gas from the cylinder was first bubbled through 10% H₂SO₄ and pure ionic medium before it reached the equilibrium solution, which was contained in an airtight titration vessel. The gas outlet from this vessel was

placed beneath a liquid surface. During the experiments the atmospheric pressure was measured and was used, together with the vapour pressure for water (0.0309 atm at 25°C), to calculate the correct p_{CO_2} in the vessel.

Method

The measurements were carried out as a series of titrations at 25°C in constant ionic media of 3.0 M and 0.1 M NaCl. The free H⁺ concentration, h , was varied by adding carbonate solution and was determined by measuring the emf of the cell:



where ME is the glass electrode and RE is the reference half-cell Ag, AgCl|3.0/0.1 M NaCl|. The emf of this cell is given by expression (2), where E_o is a constant which is

$$E = E_o + 59.157 \log h + E_j \quad (2)$$

determined in each titration in acidic (H⁺, Al³⁺) solutions in which complex formation can be neglected ($-\log h < 3$). The liquid junction potential, E_j , is given by the expression:

$$E_j = J_{\text{ac}} \cdot h + J_{\text{alk}} \cdot K_w \cdot h^{-1} \quad (3)$$

where $J_{\text{ac}} = -15.6 \text{ mVM}^{-1}$, $J_{\text{alk}} = 7.1 \text{ mVM}^{-1}$ and $K_w = 9.504 \cdot 10^{-15} \text{ M}^2$ were used for 3.0 M NaCl, and $J_{\text{ac}} = -511.5 \text{ mVM}^{-1}$, $J_{\text{alk}} = 238.7 \text{ mVM}^{-1}$ and $K_w = 1.678 \cdot 10^{-14} \text{ M}^2$ for 0.1 M NaCl medium, respectively, according to Sjöberg *et al.*¹²

Furthermore, it was found that E_o was dependent on the Al³⁺ concentration. Thus, titrations carried out at high Al³⁺ concentrations yielded more positive E_o -values than those at low concentrations. In 3.0 M ionic medium, for which extensive dilution titrations (i.e. titrations with pure ionic medium) were performed, a correction term $J_{\text{Al}^{3+}} = 38.1 \text{ mVM}^{-1}$ (cf. Fig. 1) was applied. In 0.1 M medium, only low Al³⁺ concentrations were studied, and this E_o -dependence was neglected.

Data treatment

Equilibria in the present system comprise the three-component equilibria:

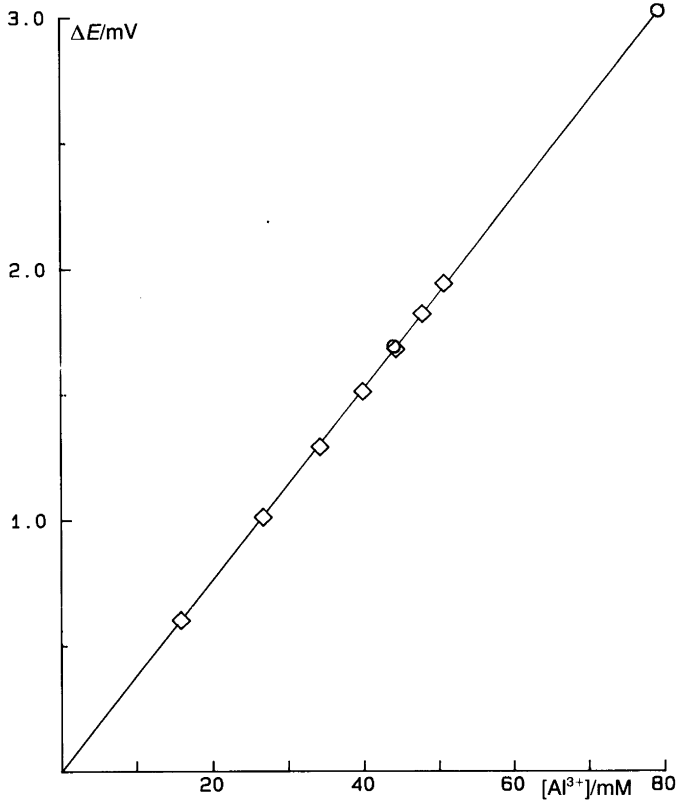
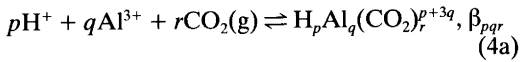
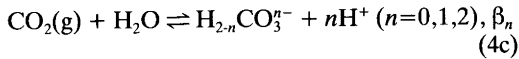
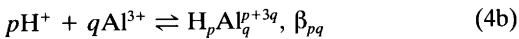


Fig. 1. The change in measured emf, E , with Al^{3+} concentration, in 3.0 M $\text{Na}(\text{Cl})$. In order to avoid hydrolysis, $-\log h$ was kept low and constant during the titration ($-\log h = 2.0$).



together with the two-component equilibria:



By applying the law of mass action, the following conditions for the total concentration are obtained:

$$H = h - \Sigma n\beta_n h^{-n} c + \Sigma \Sigma \Sigma p\beta_{pqr} h^p b^q c^r - K_w h^{-1} \quad (5a)$$

$$B = b + \Sigma \Sigma \Sigma q\beta_{pqr} h^p b^q c^r \quad (5b)$$

where $h = [\text{H}^+]$, $b = [\text{Al}^{3+}]$ and $c = p_{\text{CO}_2}$. β_{pqr} , β_{pq} and β_n are the equilibrium constants for reactions (4a), (4b) and (4c), respectively. The equilibrium

constant β_1 [reaction (4c), $n=1$] was determined in separate experiments.

To evaluate experimental data, the least-squares computer program LETAGROPVRID¹³ (version ETITR¹⁴) was applied. The error squares sum $U = \Sigma (H_{\text{calc}} - H_{\text{exp}})^2$ or $U = \Sigma (Z_{\text{calc}} - Z_{\text{exp}})^2$, where $Z = (H-h)/B$, was minimized. The LETAGROP program also gives standard deviations $\sigma(H)$, $\sigma(Z)$ and $\sigma(\log \beta_{pqr})$, defined according to Sillén.¹⁵

Data, calculation and results

Determination of β_1 . Data used to evaluate the binary H^+ - $\text{CO}_2(\text{g})$ equilibrium in 3.0 M ionic medium comprise those for 10 titrations with 101 experimental points within the pressure range 0.1 atm $\leq p_{\text{CO}_2} \leq 0.97$ atm and $-\log h \leq 7.1$. A LETAGROP calculation on these data gave: $\log(\beta_1 \pm 3\sigma) = -7.820 + 0.001$, with $\sigma(H) = 0.07$ mM.

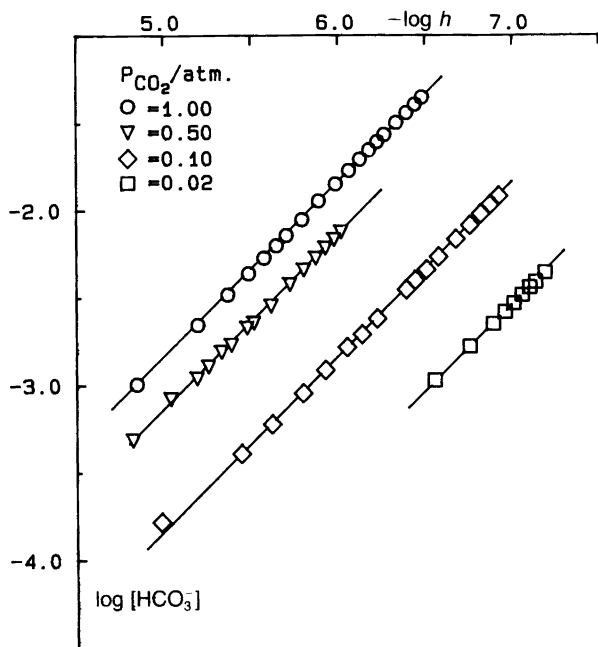


Fig. 2. A part of the binary carbon dioxide-hydrogen carbonate experimental data plotted as $\log[\text{HCO}_3^-]$ vs. $-\log h$ for different carbon dioxide pressures. The full-drawn curves have been calculated using the proposed constant [$I = 3.0 \text{ M Na(Cl)}$].

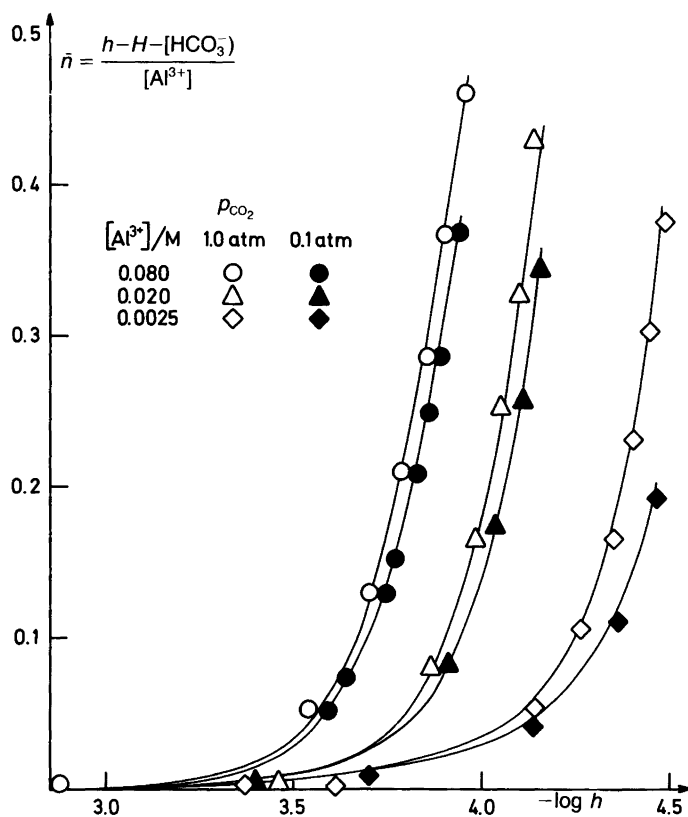


Fig. 3. Experimental data plotted as \bar{n} vs. $-\log h$. The symbols represent starting aluminium concentrations. For the sake of clarity, only a few titrations have been plotted. The full curves have been calculated using the proposed constants given in Table 2 [$I = 3.0 \text{ M Na(Cl)}$].

Data were also analysed graphically (Fig. 2), giving log $(\beta_1 \pm 3\sigma) = -7.822 \pm 0.004$.

The result for 0.1 M Na(Cl) medium (7 titrations with 71 experimental points) was: $\log(\beta_1 \pm 3\sigma) = -7.619 \pm 0.002$ and $\sigma(H) = 0.06$ mM. These values are in good agreement with those obtained by combining the data of Harned and Davis¹⁶ for the solubility of carbon dioxide and an extrapolation of the data of Harned and Bonner¹⁷ for the first ionization constant of carbonic acid: $\log \beta_1 = -7.78$ and $\log \beta_1 = -7.60$, respectively.

In the present study, no attempts were made to evaluate β_0 and β_2 .

Evaluation of three-component equilibria. In 3.0 M ionic medium, the carbon dioxide pressure p_{CO_2} , c , and the total concentration of aluminium, B , were varied within the limits $0.02 \text{ atm} \leq c \leq 0.97 \text{ atm}$ and $0.0025 \text{ M} \leq B \leq 0.080 \text{ M}$, respectively. The $\log h$ range was restricted to $-\log h \leq 4.5$, owing to slow equilibration above this limit.

The evaluation of three-component data was started by a graphical analysis, i.e. the average number of OH^- and/or HCO_3^- bound per Al^{3+} ion (\bar{n}) = $(h - H - [\text{HCO}_3^-])/B$ was plotted versus $-\log h$ for each experimental point. From this plot (Fig. 3) it can be seen that \bar{n} is slightly dependent on p_{CO_2} , indicating that ternary species

are formed to a small extent. On the other hand, the dependence on B is pronounced, owing to the formation of polynuclear hydrolytic species. The calculations were therefore started with the assumption that no ternary complexes were formed with $p_{\text{CO}_2} \leq 0.1 \text{ atm}$. A pq -analysis (systematic testing of different pq species) was performed using a data set based on 11 titrations with 119 experimental points. In this analysis, the formation constant for a large number of pq combinations was varied, one pq combination at a time, until the "best possible" (i.e. lowest error squares sum, U) fit to experimental data was obtained. According to Fig. 4, the prevailing hydrolytic complex formed (within the concentration range studied) is trinuclear, viz. $\text{Al}_3(\text{OH})_4^{5+}$, since this species gives the best fit to the experimental data.

This is in accordance with findings from several other investigations.^{6,18} However, formation of this complex cannot fully explain our experimental data. There are effects which still remain to be explained, especially at low B and close to the "instability range" at $-\log h = 4-4.5$. A pq -search for the "best possible" pair of hydrolytic complexes was therefore performed (cf. Table 1). These calculations showed that formation of the monomer $(-1,1)$, together with $(-4,3)$ best explained the experimental data. Finally, by adding the highly condensed polymer $(-32,13)$, a good fit to all experimental data was obtained [$\sigma(Z) = 0.007$; $\log \beta_{-1,1} = -5.47 \pm 0.05$; $\log \beta_{-4,3} = -13.94 \pm 0.01$ and $\log \beta_{-32,13} = -113.37 \pm 0.23$].

With $p_{\text{CO}_2} > 0.1 \text{ atm}$, the formation of ternary species must be accounted for. Preliminary calculations showed that these polynuclear species contained two and/or three aluminium ions with one carbon dioxide molecule bound. The "best" candidates were: $(-3,2,1)$, $(-4,2,1)$, $(-5,3,1)$ and $(-6,3,1)$. However, a satisfactory explanation of the data was not obtained unless a speciation scheme including two ternary species was included. A great number of pairs were tested, with the combinations $(-4,2,1) + (-5,3,1)$ or $(-3,2,1) + (-6,3,1)$ giving the best fit. It is noted that the first pair is the same as that reported by Öhman and Forsling⁶ for 0.6 M Na(Cl) medium. For that reason, the complexes $(-4,2,1)$ and $(-5,3,1)$ were included in the equilibrium model in the subsequent calculations.

With these ternary species included, a renewed calculation on data for $p_{\text{CO}_2} \leq 0.1 \text{ atm}$ was performed. This was made in order to test whether

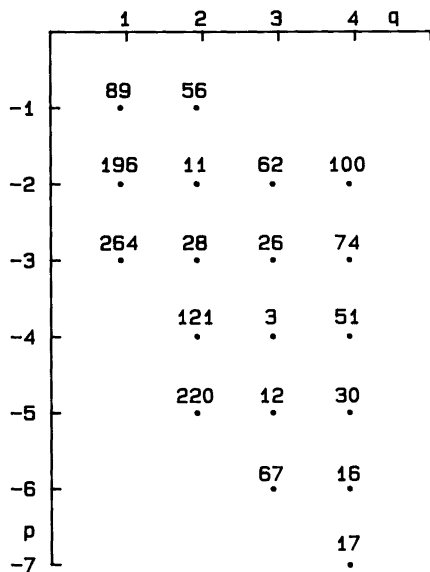


Fig. 4. Result of a pq -analysis for binary $\text{H}_p \text{Al}_q^{p+3q}$ species in titrations with $p_{\text{CO}_2} \leq 0.1 \text{ atm}$. The diagram gives $U_r(pq)$ assuming only one hydrolytic complex.

Table 1. Results of LETAGROP calculations on data with $p_{\text{CO}_2} \leq 0.1$ atm. In the calculations, pairs of hydrolytic complexes have been tested in the absence (left part) or presence (right part) of "best" ternary complexes. The formation constants are defined according to eqn. (5b) and the errors given are 3σ ($\log \beta_{\text{par}}$).

| Pair of complexes tested | No ternary complex | | with $\log \beta_{-421} = -16.58$; $\log \beta_{-521} = -18.45$ | |
|--------------------------|---|-------------|--|-------------|
| | $\log (\beta_{\text{par}} \pm 3\sigma)$ | $U/10^{-4}$ | $\log (\beta_{\text{par}} \pm 3\sigma)$ | $U/10^{-4}$ |
| (-1, 1, 0) | -5.45±0.06 | 0.61 | -5.52±0.06 | 0.43 |
| (-4, 3, 0) | -13.93±0.02 | | -13.95±0.01 | |
| (-3, 3, 0) | -10.09±0.04 | 0.89 | -10.08±0.04 | 0.94 |
| (-5, 3, 0) | -18.25±0.02 | | -18.30±0.03 | |
| (-3, 2, 0) | -11.76±0.03 | 1.33 | -11.81±0.03 | 1.41 |
| (-5, 4, 0) | -16.64±0.03 | | -16.65±0.04 | |
| (-2, 2, 0) | -7.77±0.18 | 2.30 | -7.81±0.15 | 1.48 |
| (-4, 3, 0) | -13.98±0.06 | | -14.00±0.05 | |
| (-2, 2, 0) | -7.43±0.05 | 2.38 | -7.46±0.04 | 3.65 |
| (-6, 4, 0) | -20.75±0.06 | | -20.77±0.05 | |
| (-2, 2, 0) | -7.48±0.07 | 2.69 | -7.48±0.08 | 2.69 |
| (-5, 3, 0) | -18.31±0.06 | | -18.36±0.08 | |

or not the inclusion of ternary complexes influenced the hydrolytic speciation scheme determined above. As seen in Table 1, only small changes in the formation constants for hydrolytic species were obtained.

In a final calculation, the formation constants for the species (-1,1,0), (-4,3,0), (-32,13,0), (-4,2,1) and (-5,3,1) were co-varied on the complete data set (25 titrations with 246 experimental points). The result of this calculation is

given in Table 2. An attempt was also made to include the species $\text{Al}_2(\text{OH})_2^{4+}$ and $\text{Al}(\text{OH})_2^+$, species which have been postulated.^{18,19,20} However, these calculations (cf. Table 2) showed that neither of these species could give any significant improvement of our model.

A question raised by Öhman²¹ is whether the species $\text{Al}_3(\text{OH})_4^{5+}$ represents a mean of the composition of the two species $\text{Al}_2(\text{OH})_2^{4+}$ and $\text{Al}_4(\text{OH})_6^{6+}$. He concluded that a definitive an-

Table 2. Results of some final LETAGROP calculations (3.0 and 0.1 M ionic media) with some different assumptions concerning the complexes formed.

| Binary complexes | | | | | Ternary complexes | | |
|------------------------------------|-----------------------|-----------------------|-----------------------|-------------------------|-----------------------|-----------------------|-------------|
| $\log \beta_{-1,1,0}$ | $\log \beta_{-2,2,0}$ | $\log \beta_{-4,3,0}$ | $\log \beta_{-6,4,0}$ | $\log \beta_{-32,13,0}$ | $\log \beta_{-4,2,1}$ | $\log \beta_{-5,3,1}$ | $U/10^{-4}$ |
| -5.52±0.05 | | -13.96±0.01 | | -113.35±0.13 | -16.61±0.12 | -18.39±0.07 | 1.17 |
| -5.52±0.13 | -7.57±0.05 | | -20.77±0.14 | -113.24±0.14 | -16.56±0.12 | -18.38±0.08 | 1.40 |
| -5.60±0.09 | -8.4 - -8.1 | -14.00±0.03 | | -113.34±0.16 | -16.62±0.13 | -18.34±0.10 | 1.17 |
| Proposed constants in 3.0 M medium | | | | | | | |
| -5.52±0.05 | | -13.96±0.01 | | -113.35±0.13 | -16.61±0.12 | -18.39±0.07 | |
| Proposed constants in 0.1 M medium | | | | | | | |
| -5.34 ^a | | -13.70 ^a | | -107.5 ^a | -14.95±0.17 | -17.2±0.34 | |

^aFormation constants according to Baes and Mesmer²⁰ and Brown and Sylva.²³

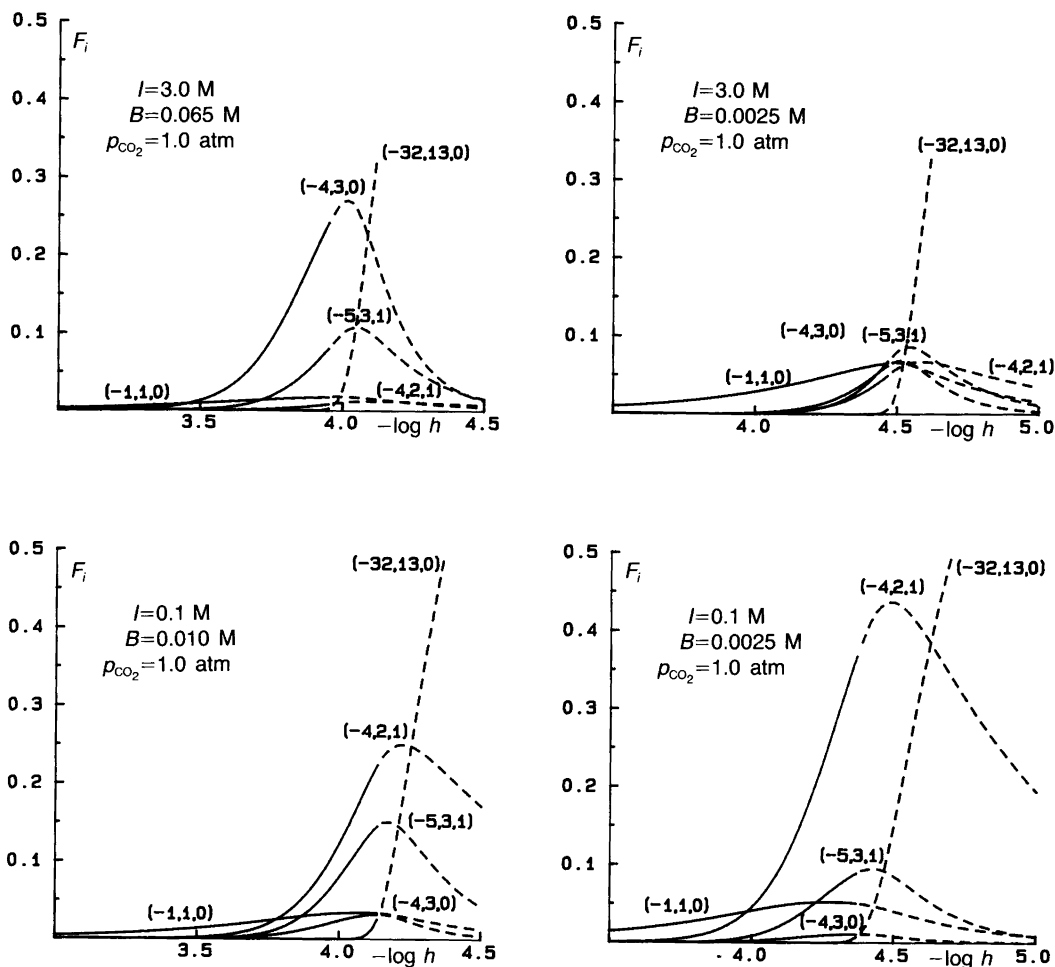


Fig. 5. Distribution diagrams [F_i vs. $(-\log h)_{B,C}$] for $I = 3.0$ M and 0.1 M Na(Cl), respectively. F_i is defined as the ratio of aluminium(III) in a given species to total aluminium(III). The calculations have been performed using the computer program SOLGASWATER²² with equilibrium constants given in Table 2. For the sake of clarity the species Al^{3+} has been omitted in the diagrams. Broken lines denote ranges where no measurements have been performed.

swer to this question was impossible to obtain from the 0.6 M Na(Cl) data, since too limited a range in B (imposed by the low ionic medium used) had been employed. In the present work, a broader range in B has been investigated; hence, a more definite answer to the question can be expected. As can be seen from Table 2, the replacement of $\text{Al}_3(\text{OH})_4^{5+}$ with $\text{Al}_2(\text{OH})_2^{4+}$ plus $\text{Al}_4(\text{OH})_6^{6+}$, results in an increase in the error squares sum, i.e. a poorer fit to the experimental data.

As final model we therefore suggest formation of the species $\text{Al}(\text{OH})_2^{2+}$, $\text{Al}_3(\text{OH})_4^{5+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$, $(-4,2,1)$ and $(-5,3,1)$, with final formation constants and standard deviations [$3\sigma(\log \beta_{pqr})$] given in Table 2.

Owing to the restricted concentration range available for investigation with 0.1 M ionic medium, an unbiased search for a speciation model cannot be made. The interpretation of experimental data for 0.1 M Na(Cl) medium was therefore made by assuming the same speciation mo-

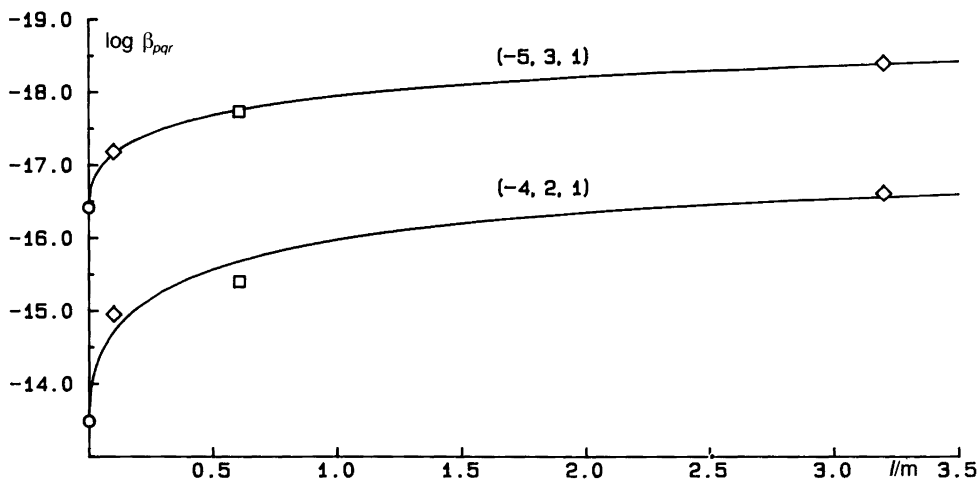


Fig. 6. The medium dependence of $\log \beta_{-421}$ and $\log \beta_{-531}$. The full-drawn curves have been calculated using eqn. (6). Symbols: (\diamond) this work, (\square) Ohman *et al.*⁶ and (\circ) the calculated $\log \beta_{pq}^0$ -value.

del as for higher ionic strength media. The following concentration ranges were studied: $2.9 \text{ mM} \leq B \leq 10.0 \text{ mM}$; $c = 1.0 \text{ atm}$ and $-\log h \leq 4.2$. A refinement of the ternary species $(-4,2,1)$ and $(-5,3,1)$ was performed, giving the results presented in Table 2.

In order to visualize the amounts of the different species, the computer program SOLGAS-WATER²² equipped with plotting procedures has been used to calculate some distribution diagrams (Fig. 5).

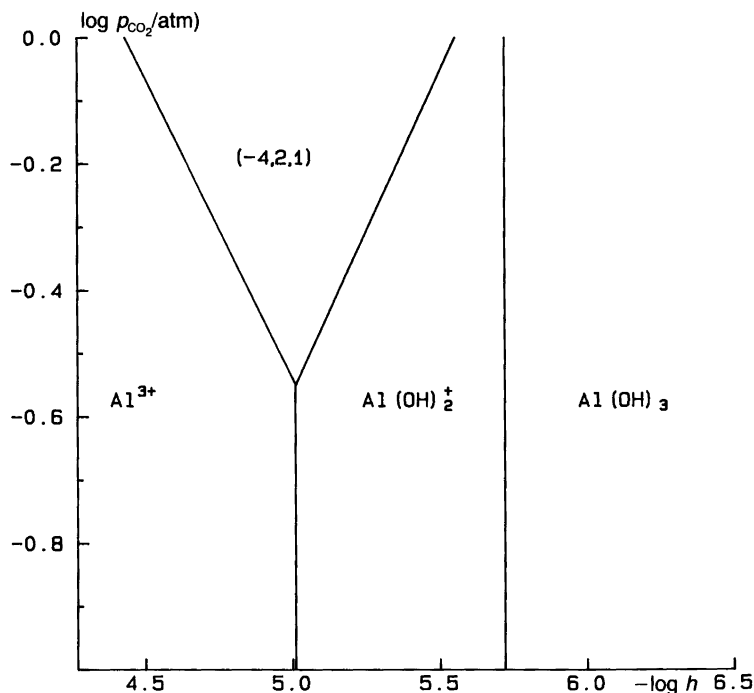


Fig. 7. Predominance area diagram showing dominant Al(III) species in equilibrium with amorphous $\text{Al}(\text{OH})_3(\text{s})$ at $I = 0.1 \text{ M NaCl}$.

The medium dependence of ternary species. According to Baes and Mesmer,²⁰ the equation:

$$\log \beta_{pqr} = \log \beta_{pqr}^{\circ} + a_i I^{1/2} / (1 + I^{1/2}) + b_i I \quad (6)$$

has proved adequate for describing the medium dependence of numerous ionization equilibria. Here, $a_i = \Delta Z_{pqr}^2 \cdot S$, where ΔZ_{pqr}^2 is the square of the charge on each species summed over the formation reaction. S denotes the Debye-Hückel limiting slope ($0.511 \text{ m}^{1/2}$ at 25°C). b_i is regarded as an adjustable parameter and reflects the sum of interaction coefficients for interaction between cations and anions in the equilibrium solution and the effects of the water activity on β_{pqr}° . $\log \beta_{pqr}^{\circ}$ and b_i were evaluated using a standard least-squares minimization program on data containing results for 3.0 M, 0.6 M (Öhman)⁶ and 0.1 M. The results of this calculation (visualized in Fig. 6) were $\log \beta_{-4,2,1}^{\circ} = -13.5$, $a_i = -5.110$, $b_i = 0.06$ and $\log \beta_{-5,3,1}^{\circ} = -16.4$, $a_i = -3.066$, $b_i = 0.00$. The extrapolation to zero ionic strength must be regarded as approximate, but it gives an idea of the stability of these complexes under natural fresh water conditions (see Discussion).

Discussion

By equilibrating hydrolyzed Al(III) solutions with a gas phase of known p_{CO_2} , the formation of binary and ternary hydroxo species of Al^{3+} was studied. With $p_{\text{CO}_2} < 0.1 \text{ atm}$, the Al-speciation scheme is characterized by the binary hydrolytic complexes AlOH^{2+} , $\text{Al}_3(\text{OH})_4^{5+}$ and $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$. This scheme is in full agreement with earlier findings by Öhman and Forsling⁶ as well as by Brown and Sylva.²³ The formation of a dimer, $\text{Al}_2(\text{OH})_2^{4+}$, postulated by Aveston¹⁸ as well as by Mesmer and Baes,¹⁹ could not be verified. Due to the very slow formation of a high molecular weight polynuclear species at $-\log h > 4$, an unbiased determination of the stoichiometry of this species was not made. Instead, a composition $(-32, 13)$ was postulated, mainly due to its detection in a solid phase.²⁰ Although the assumption that a complex found in the solid state should exist in aqueous solution is questionable, we find at present no better alternative.

At $p_{\text{CO}_2} > 0.1 \text{ atm}$, the formation of ternary hydroxo-carbonate complexes becomes significant. These were found to be polynuclear, with the compositions $\text{H}_{-4}\text{Al}_2(\text{CO}_2)^{2+}$ and $\text{H}_{-5}\text{Al}_3(\text{CO}_2)^{4+}$. The formulas $\text{Al}_2(\text{OH})_2\text{CO}_3^{2+}$ and $\text{Al}_3(\text{OH})_4\text{HCO}_3^{4+}$ or $\text{Al}_3(\text{OH})_3\text{CO}_3^{4+}$ may tentatively be assigned.

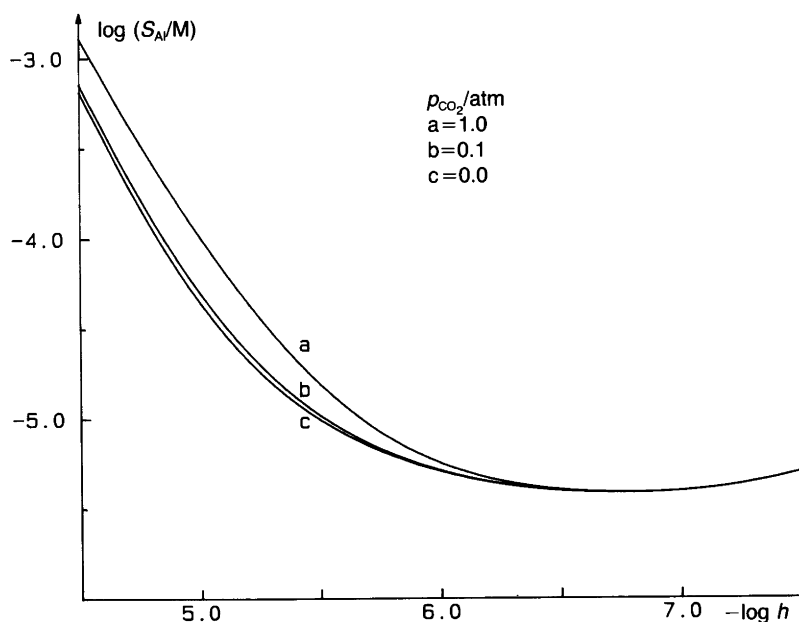


Fig. 8. The solubility of amorphous $\text{Al}(\text{OH})_3$ ($\log *K_{s0} = 10.2$) at different carbon dioxide pressures [$I = 0.1 \text{ M Na}(\text{Cl})$].

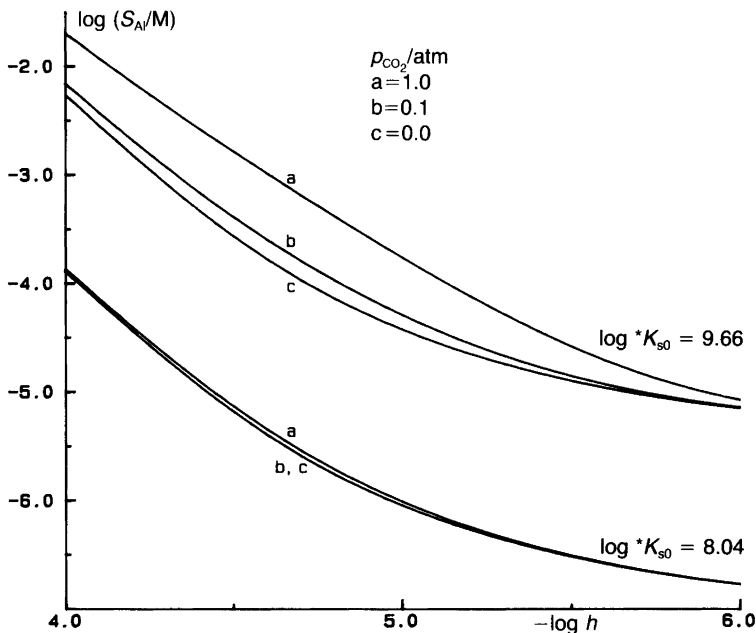


Fig. 9. The solubility of gibbsite and amorphous $\text{Al}(\text{OH})_3(\text{s})$ ($\log^* K_{s0} = 8.04$ and 9.66 , respectively²⁴) at different carbon dioxide pressures ($I = 0 \text{ M}$).

Modelling of a natural water. According to Fig. 5, the stability of the two mixed hydroxo species is enhanced by decreasing ionic strength. In 0.1 M NaCl medium the $(-4,2,1)$ -complex contributes 40 % of B , which can be compared with 10 % of B in 3.0 M NaCl medium ($B = 0.010 \text{ M}$; $p_{\text{CO}_2} = 1 \text{ atm}$). In order to visualize the significance of the aluminium carbonate complexes in natural waters, a model calculation was performed in which amorphous $\text{Al}(\text{OH})_3(\text{s})$ was considered to equilibrate with water at different carbon dioxide pressures. The dominant aqueous species (Fig. 7) and the total solubility of aluminium, S_{Al} (Fig. 8), were calculated as a function of $-\log h$. In these calculations, formation constants given in Table 2 ($I = 0.1 \text{ M}$) and $\log^* K_{s0} = 10.2$ for amorphous $\text{Al}(\text{OH})_3(\text{s})$ ²⁴ were used. As can be seen in Fig. 7, the dinuclear complex $\text{Al}_2(\text{OH})_2\text{CO}_3^{2+}$ becomes prevalent in solution at $-\log h \approx 5$, provided $p_{\text{CO}_2} \approx 10^{-0.5} \text{ atm}$. According to Fig. 8, the increase in S_{Al} at $-\log h = 5$ can be expected to be 13 % for $p_{\text{CO}_2} = 10^{-1} \text{ atm}$ and 130 % for $p_{\text{CO}_2} = 1 \text{ atm}$.

Despite the fact that we regard the zero ionic strength values for $(-4,2,1)$ and $(-5,3,1)$ as approximate, we have also performed an analogous calculation for $I = 0$ (Al-hydrolysis constants according to Baes and Mesmer²⁰). In this calculation, a comparison between the behaviour for

amorphous $\text{Al}(\text{OH})_3(\text{s})$ ($\log^* K_{s0} = 9.66$)²⁴ and crystalline gibbsite ($\log^* K_{s0} = 8.04$)²⁴ was also performed. The results of these calculations are given in Fig. 9. First of all, it can be noted that the "pure" solubility for amorphous $\text{Al}(\text{OH})_3(\text{s})$ has increased by a factor of approximately 3 compared to the solubility at $I = 0.1 \text{ M}$. Secondly, it can be seen that the influence of carbon dioxide on the solubility curve also has increased. The calculated increase in S_{Al} at $-\log h = 5$ has become 36 % at $p_{\text{CO}_2} = 10^{-1} \text{ atm}$ and 360 % at $p_{\text{CO}_2} = 1 \text{ atm}$. Finally, it can be seen that for crystalline gibbsite, no significant increase in S_{Al} can be expected even at $p_{\text{CO}_2} = 1 \text{ atm}$. Thus, it can be concluded that in soil and water regions with intensive fermentation of organic substances (giving rise to high carbon dioxide partial pressures²⁵), in contact with recently formed, reactive forms of $\text{Al}(\text{OH})_3(\text{s})$, elevated concentrations of soluble aluminium species can be expected. Such conditions probably apply to, for instance, top soils in the autumn and bottom waters of recently limed lakes.

Acknowledgement. This work forms part of a program financially supported by the Swedish Natural Science Research Council.

References

1. Driscoll, C. T. *Chemical Characterization of Some Dilute Acidified Lakes and Streams in the Adirondack Region of New York*, Thesis, Cornell University, Cornell, N. Y. 1980.
2. Baker, J. P. and Schofield, C. L. *Diss. Abstr. Int. B 41* (1981) 4384.
3. Driscoll, C. T., Baker, J. P., Bisogni, J. J. and Schofield, C. L. *Nature, (London)* 284 (1980) 161.
4. Sillén, L. G. and Martell, A. E. *Stability Constants of Metal-ion Complexes*, Spec. Publ. XVII (1964) and 25 (1971), The Chemical Society, London.
5. Högfeldt, E. *Stability Constants of Metal-ion Complexes: Part A. Inorganic Ligands*, Pergamon Press, Oxford 1982.
6. Öhman, L.-O. and Forsling, W. *Acta. Chem. Scand., Ser. A 35* (1981) 795.
7. Biedermann, G. In: Goldberg, E. D., Ed., *The Nature of Seawater*, Dahlem Konferenzen, Berlin 1975.
8. Kolthoff, M. and Sandell, E. B. *Quantitative Chemical Analysis*, Macmillan, London 1969, p. 599.
9. Ginstrup, O. *Chem. Instrum.* 4 (1973) 141.
10. Brown, A. S. *J. Am. Chem. Soc.* 56 (1934) 646.
11. Forsling, W., Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* 6 (1952) 901.
12. Sjöberg, S., Hägglund, Y., Nordin, A. and Ingri, N. *Marine Chem.* 13 (1983) 35.
13. Ingri, N. and Sillén, L. G. *Ark. Kemi* 23 (1964) 97.
14. Arnek, R., Sillén, L. G. and Wahlberg, O. *Ark. Kemi* 31 (1969) 353; Brauner, P., Sillén, L. G. and Whiteker, R. *Ark. Kemi* 31 (1969) 365.
15. Sillén, L. G. *Acta. Chem. Scand.* 16 (1969) 159; Sillén, L. G. and Warnqvist, B. *Ark. Kemi* 31 (1969) 341.
16. Harned, H. S. and Davies, R., Jr. *J. Am. Chem. Soc.* 65 (1943) 2030.
17. Harned, H. S. and Bonner, F. T. *J. Am. Chem. Soc.* 67 (1945) 1026.
18. Aveston, J. J. *J. Chem. Soc.* (1965) 4438.
19. Baes, C. F. and Mesmer, R. E. *Inorg. Chem.* 10 (1971) 2290.
20. Baes, C. F. and Mesmer, R. E. *The Hydrolysis of Cations*, Wiley, New York 1976, p. 112.
21. Öhman, L.-O. *Equilibrium Studies of Ternary Aluminium(III) Hydroxo Complexes with Ligands Related to Conditions in Natural Waters*, Thesis, University of Umeå, Umeå 1983.
22. Eriksson, G. *Anal. Chim. Acta* 112 (1979) 375.
23. Brown, P. L., Sylva, R. N., Batley, G. and Ellies, J. J. *J. Chem. Soc., Dalton Trans.* (1985) 1967.
24. Lindsay, W. L. *Chemical Equilibria in Soils*, Wiley, New York 1979, p. 36.
25. Bolt, P. L. *Soil Chemistry: Part B. Physico-chemical Models*, Elsevier, Amsterdam 1979, p. 446.

Received December 2, 1986.