

# Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 4. A Potentiometric Study of Polynuclear Aluminium(III) Hydroxo Complexes with Gallic Acid in Hydrolyzed Aluminium(III) Solutions

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Equilibria between aluminium(III), gallic acid ( $C_7H_6O_5, H_3L$ ) and  $OH^-$  were studied within the limits  $-\lg[H^+] \leq 4$ ;  $0.003 \leq B \leq 0.028$  M;  $0.0007 \leq C \leq 0.031$  M and  $0.025 \leq C/B \leq 3$  where  $B$  and  $C$  stand for the total concentrations of aluminium and gallic acid, respectively. The measurements were performed as potentiometric (glass electrode) titrations in 0.6 M NaCl at 25 °C. Besides binary hydrolytic species  $AlOH^{2+}$  and  $Al_3(OH)_4^{3+}$  and mononuclear aluminium-gallic acid complexes  $AlHL^+$  and  $AlL$ , all data could be explained with the complexes  $Al_4L_3^{3+}$  and  $Al_3(OH)_4(H_2L)^{4+}$  (tentative structures). The equilibrium constants with standard deviations are given. Data were analyzed with the least squares program LETAGROPVRID. A solid phase  $AlL \cdot 4H_2O$  (or  $Al(OH)(HL) \cdot 3H_2O$ ) was identified and an approximate solubility product of this phase was calculated.

In part 1 of this series, equilibria in the three component system  $Al^{3+} - OH^-$ -gallic acid (3,4,5-trihydroxy benzoic acid,  $H_3L$ ) were studied at 25 °C in 0.6 M NaCl medium. With  $3 \leq C/B \leq 25$  ( $B, C$  denote the total concentration of aluminium and gallic acid, respectively) data were explained with binary as well as ternary complexes. Besides the mononuclear species  $AlHL^+$ ,  $AlL$  (or  $Al(OH)HL$ ),  $AlL_2^{3-}$ , and  $AlL_3^{6-}$ , a dinuclear proton series  $Al_2(OH)_2(HL)_3^{2-} - Al_2(OH)_2L_3^{5-}$  was proposed.

For quotients  $3 \leq C/B \leq 4$  a white, noncrystalline precipitate was formed within the range  $4 \leq -\lg[H^+] \leq 5.5$ . At still lower quotients, where the hydrolysis of  $Al^{3+}$  becomes more pronounced, stable potentials were difficult to obtain after the

dissolution of the precipitate ( $-\lg[H^+] \geq 5.5$ ). This fact is probably due to the slow kinetics in hydrolyzed  $Al^{3+}$ -solutions. It was also found that additional effects, caused by ternary species other than those mentioned above, were found in slightly acidic solutions before the onset of the precipitation.

The aim of the present investigation was to interpret the complexing ability of gallic acid in these slightly acidic, hydrolyzed,  $Al^{3+}$ -solutions. The composition of the precipitate was also determined as well as an approximate value of its solubility product.

## EXPERIMENTAL

*Chemicals and analysis.* All solutions used were prepared and analyzed as described earlier.<sup>1</sup> Tropolone ( $C_7H_6O_2$ ) (Fluka, purum), used for quantitative precipitation of Al(III) in the precipitate study, was sublimed in vacuum.

*Apparatus.* The thermostat, cell arrangement and experimental details, including special precautions to protect the weakly acidic solutions from oxygen in the emf measurements, are fully described in Ref. 1.

The apparatus used to study the composition of the precipitate comprised: A thermobalance (Netzsch, type 409), to determine water content (135 °C) and Al content (800 °C), and an IR-spectrophotometer (Beckman IR 4240) to ensure that the same solid phase was formed from solutions of different compositions.

## METHOD

The titration procedures, calibrations and the assumptions made in connection with the use of the glass electrode were the same as described earlier.<sup>1</sup> Each titration was performed at a constant  $C/B$  ratio where the initial concentrations of  $B$  and  $C$  were varied within the limits  $0.003 \leq B \leq 0.028$  M and  $0.0007 \leq C \leq 0.031$  M, covering the  $C/B$  ratios: 2.6, 2, 1, 0.5, 0.3, 0.2, 0.1, 0.05 and 0.025. To test reproducibility and reversibility of equilibria, both forward (addition of  $\text{OH}^-$ ) and backward (addition of  $\text{H}^+$ ) titrations were performed. To obtain more data points in the most interesting areas some dilution experiments (titrations with pure medium solution) were also performed. Owing to the formation of precipitate ( $C/B \geq 0.3$ ) or very slow attainment of equilibria ( $C/B \leq 0.2$ ) the available  $-\lg h$  range was restricted to an upper limit of 3.8–4.2.

**Data treatment.** In order to visualize experimental results, data sets  $Z_B(\lg h)$  were calculated and some of them are given in Fig. 1.  $Z_B$  is defined as the

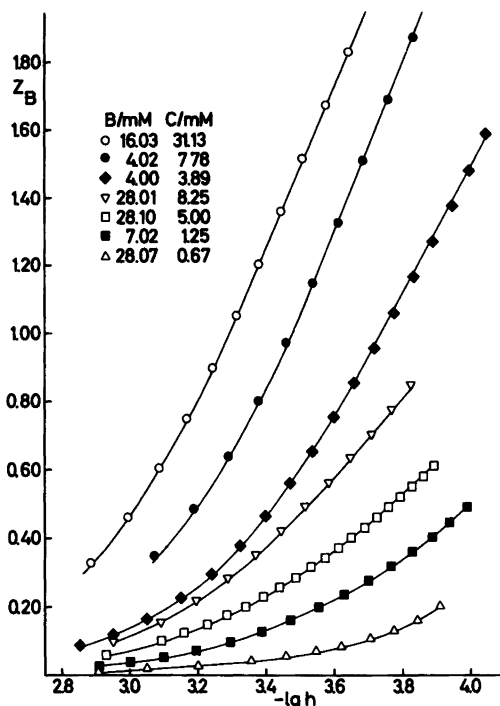
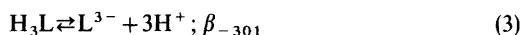
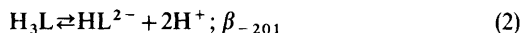
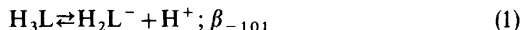


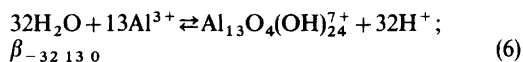
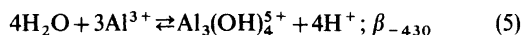
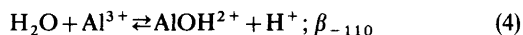
Fig. 1. A part of experimental data plotted as curves  $Z_B(-\lg h)$ , where  $Z_B = (h - H - k_w h^{-1})/B$ . All symbols represent initial concentrations. The full curves have been calculated using the set of proposed constants in Table 1.

average number of  $\text{OH}^-$  reacted per aluminium and is given by the relation  $Z_B = (h - H - k_w h^{-1})/B$ .  $H$  denotes the total concentration of protons calculated over the zero level  $\text{H}_2\text{O}$ ,  $\text{Al}^{3+}$ ,  $\text{H}_3\text{L}$ . The term  $k_w h^{-1}$ , where  $k_w$  is the ionic product of water, can be neglected in the present study. The different types of equilibria which must be considered in the present study can be divided into groups as follows:

(i) the binary gallic acid equilibria

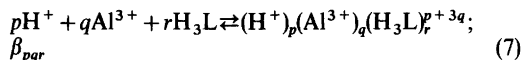


(ii) the hydrolytic equilibria of  $\text{Al}^{3+}$ , which within the actual concentration ranges of  $B$  and  $\lg h$  in this study are



Accurate values for these formation constants were evaluated from a separate study of the system  $\text{H}^+ - \text{Al}^{3+} - \text{CO}_2(\text{g})$  at  $25^\circ\text{C}$  in 0.6 M  $\text{Na}(\text{Cl})$  (Öhman and Forsling).<sup>2</sup> It can be noted that this study gave no evidence for the formation of  $\text{Al}_2(\text{OH})_2^{4+}$ .

(iii) three component equilibria of the general form



In the Part 1 investigation, formation constants for binary as well as ternary mononuclear and polynuclear complexes were determined. These constants, in addition to those under (i) and (ii), are given in Table 1. In the following calculations these constants are considered as known and no attempts will be made to vary them.

In the evaluation of the experimental data, the least squares computer program LETAGROPVRID,<sup>3</sup> version ETTR,<sup>4</sup> was applied.  $pqr$ -triplets and corresponding equilibrium constants that "best" fit the experimental data were determined by minimizing the error squares sum  $U = \sum (H_{\text{calc}} - H)^2$ . In Part 1 the minimized function was  $U = \sum ((H_{\text{calc}} - H)/C)^2$ . As in the present study,  $C$  varies between 0.0007–0.031 M, small differences in  $H_{\text{calc}} - H$  would yield large contributions to  $U$  at low  $C$  and would thus give too much weight to these data. The LETAGROP calculations also give

Table 1. Binary and ternary complexes in the three-component system  $\text{Al}^{3+} - \text{OH}^-$ -gallic acid. The formation constants are related according to the reaction  $p\text{H}^+ + q\text{Al}^{3+} + r\text{H}_3\text{L} \rightleftharpoons \text{H}_p\text{Al}_q(\text{H}_3\text{L})_r^{+3q}$ , where  $\text{H}_3\text{L}$  stands for gallic acid.

$p$	$q$	$r$	Tentative structure	$\lg(\beta_{pqr} \pm 3\sigma)$	Ref.
-1	0	1	$\text{H}_2\text{L}^-$	$-4.152 \pm 0.002$	1
-2	0	1	$\text{HL}^{2-}$	$-12.590 \pm 0.005$	1
-3	0	1	$\text{L}^{3-}$	$-23.674 \pm 0.007$	1
-1	1	0	$\text{Al}(\text{OH})^{2+}$	$-5.52 \pm 0.04$	2
-4	3	0	$\text{Al}_3(\text{OH})_4^{5+}$	$-13.57 \pm 0.02$	2
-32	13	0	$\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$	$-109.2 \pm 0.12$	2
-2	1	1	$\text{Al}(\text{HL})^+$	$-4.933 \pm 0.009$	1
-3	1	1	$\text{AlL}$ or $\text{Al}(\text{OH})(\text{HL})$	$-9.43 \pm 0.02$	1
-6	1	2	$\text{AlL}_2^{3-}$	$-21.98 \pm 0.03$	1
-9	1	3	$\text{AlL}_3^{6-}$	$-37.69 \pm 0.02$	1
-8	2	3	$\text{Al}_2(\text{OH})_2(\text{HL})_3^{3-}$	$-22.65 \pm 0.04$	1
-9	2	3	$\text{Al}_2(\text{OH})_2(\text{HL})_2\text{L}^{3-}$	$-27.81 \pm 0.07$	1
-10	2	3	$\text{Al}_2(\text{OH})_2(\text{HL})(\text{L})_2^{4-}$	$-32.87 \pm 0.03$	1
-11	2	3	$\text{Al}_2(\text{OH})_2\text{L}_3^{5-}$	$-39.56 \pm 0.05$	1
-5	3	1	$\text{Al}_3(\text{OH})_4(\text{H}_2\text{L})^{4+}$	$-12.52 \pm 0.01$	
-9	4	3	$\text{Al}_4(\text{L})_3^{3+}$	$-20.25 \pm 0.05$	This work
-3	1	1	$\text{AlL} \cdot 4\text{H}_2\text{O}(\text{s})$	$-6.2 \pm 0.5$	This work

standard deviations  $\sigma(H)$ ,  $\sigma(\beta_{pqr})$  and  $3\sigma(\log \beta_{pqr})$ . For the definitions of these errors the reader is referred to Sillén.<sup>5</sup> The computations were performed on a Cyber 172 computer.

#### DATA, CALCULATIONS AND RESULTS

The analysis of data, comprising 24 titrations with 496 experimental points, was started with a

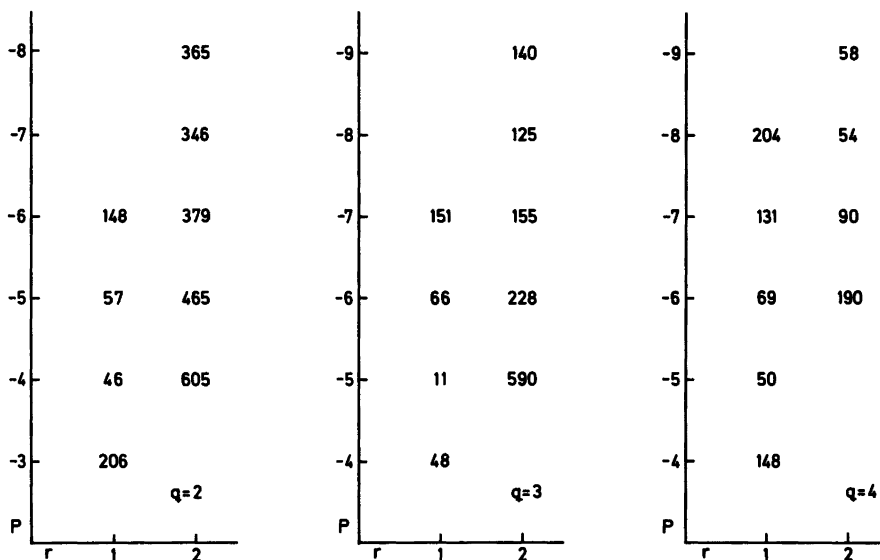


Fig. 2. Result of a  $pqr$ -analysis in the area  $C/B < 3$  and  $-\lg h \leq 4$ . The figures give the error squares sums  $U_{\text{H}}(pr)_q$  assuming one new complex. Binary and ternary complexes listed in the upper part of Table 1 have been assumed to be known. The calculations are based on 496 points giving  $U_{\text{H}}(\text{OO})_0 = 714$ .

residual calculation using the results from Refs. 1 and 2. These residuals clearly indicated that one or more additional complexes must be present. From the very strong concentration dependence it could further be concluded that the additional complexes were probably polynuclear. In order to explain the data, we tested the very simple hypothesis that only one additional complex,  $H_pAl_q(H_3L)_r^{p+3q}$ , was present. The search for the composition and the equilibrium constant for this complex was performed as a *pqr*-analysis (systematic testing of *pqr* combinations) using the LETAGROPVRID program and the criteria for best explanation was the error squares sum  $U = \Sigma(H_{\text{calc}} - H)^2$ . The result of this analysis is given in Fig. 2 and it was found that the lowest value of  $U$  was obtained for the complex  $H_{-5}Al_3(H_3L)^{4+}$  with  $\lg(\beta_{-531} \pm 3\sigma) = -12.47 \pm 0.013$ .

The fit to experimental data was very good for quotients  $C/B \leq 0.5$ ; however, at higher quotients systematic effects remained to be explained. In order to interpret this upper range we introduced another ternary complex into the model. Since the remaining residuals seemed to be strongly dependent on the constant value chosen for the complex  $H_{-5}Al_3(H_3L)^{4+}$  we found it necessary to perform this search as a covariation between  $H_{-5}Al_3(H_3L)^{4+}$  and the new  $H_pAl_q(H_3L)_r^{p+3q}$  complex. No sharp pit could be obtained for any single additional complex. However, the best fit was found assuming  $\lg(\beta_{-531} \pm 3\sigma) = -12.52 \pm 0.010$  together with  $H_{-9}Al_4(H_3L)_3^{3+}$ ;  $\lg(\beta_{-943} \pm 3\sigma) = -20.25 \pm 0.049$ , giving  $U = 3.9$  and  $\sigma(H) = 0.09 \times 10^{-3}$  M. The best tri- and pentanuclear species found were  $H_{-6}Al_3(H_3L)_2^{3+}$  and  $H_{-12}Al_5(H_3L)_4^{3+}$  giving  $U = 4.6$  and 4.1, respectively. It is interesting to note that all three complexes belong to the same series  $Al_nL_{n-1}^{3+}$ , with  $n = 3, 4$  and 5.

The conclusion we have drawn from this search is (see Discussion) that  $H_{-9}Al_4(H_3L)_3^{3+}$  is a type of average complex but that the remaining residuals are too small to permit more detailed analysis. Our final model for the complexation in the quotient range  $C/B \leq 3$  and  $-\lg h \leq 4$  is therefore:  $H_{-5}Al_3(H_3L)^{4+}$  with  $\lg(\beta_{-531} \pm 3\sigma) = -12.52 \pm 0.010$  and  $H_{-9}Al_4(H_3L)_3^{3+}$  with  $\lg(\beta_{-943} \pm 3\sigma) = -20.25 \pm 0.049$ .

*Determination of the composition of the precipitate.* The white precipitate formed in the region  $4 \leq -\lg h \leq 5.5$  for  $C/B \leq 4$  was prepared from solutions of different  $C/B$  quotients, filtered off through a Jena G4 glass filter, dried by boiling off residues of water

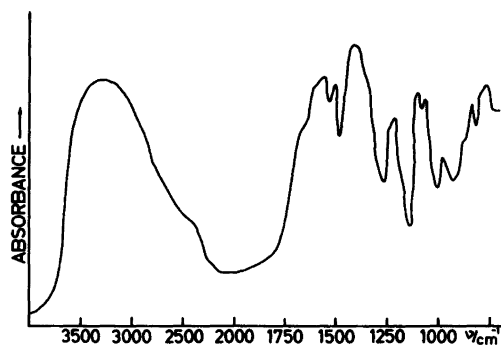


Fig. 3. IR spectrum of the solid  $H_{-3}Al(H_3L) \cdot 4H_2O$ .

in vacuum at 25 °C and examined by IR technique using KBr as pellet material. All solids gave the same spectra (Fig. 3) proving that the precipitate formed was the same independent of  $C/B$  quotient in solution. In attempts to take powder photographs of the solid, no lines were obtained and it was concluded that the precipitate was quite amorphous. To examine the Al content of the solid a thermobalance was used. A known amount was held at 800 °C for 24 h and the residue (a perfectly white powder, insoluble in conc. HCl) was assumed to be  $Al_2O_3$ . The result obtained was that the precipitate contained 11.2 % Al.

To determine the number of protons bound and the amount of gallic acid, a known amount was dissolved in a standardized hydrochloric acid,  $Al^{3+}$  was precipitated with tropolone, the solid  $Al(C_7H_5O_2)_3$  formed filtered off and a known volume of the solution titrated potentiometrically using the ordinary precautions to protect it from oxygen. The resulting titration curve was identical to an ordinary gallic acid-OH<sup>-</sup> titration curve and it was possible to determine the gallic acid content to be 61 % of the solid. From the same curve,  $H$  was determined to be  $-3 \times Al$  over our zero level. Finally, from the weight of the dried  $Al(C_7H_5O_2)_3$ , the aluminium content was checked and found to be 11.1 %, in good agreement with the thermogravimetric analysis.

The remaining part (28 %) of the solid could consist of  $Na^+$ ,  $Cl^-$  or  $H_2O$  but tests for  $Na^+$  (atomic emission) as well as for  $Cl^-$  (spot test with  $Ag^+$  after dissolution in  $HClO_4$ ) were negative. In order to determine the water content, the solid phase was analyzed thermogravimetrically, this time at 135 °C for 6 h in an atmosphere of argon. The

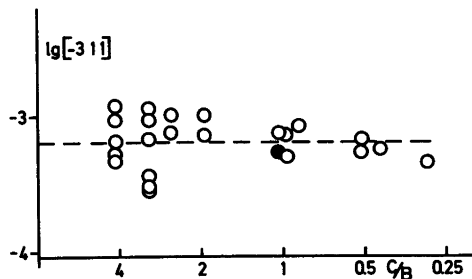
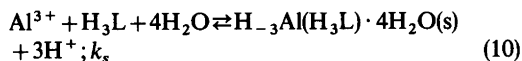


Fig. 4. Approximate solubility product of  $H_{-3}Al(H_3L) \cdot 4H_2O$  calculated as an average of the concentration of the complex  $(-3,1,1)$  in the last measured point in solution (unfilled symbols). The filled symbol represents the calculated value obtained after a 24 h equilibration time within the precipitation area.

sample lost 27 % of its weight without being discoloured afterwards. A simple stoichiometric analysis of the results obtained then gave the composition  $H_{-3}Al(H_3L) \cdot 4H_2O$  (calc. Al: 10.2 %,  $L^{3-}$ : 62.8 %,  $H_2O$ : 27.1 %).

*Approximate solubility product of  $H_{-3}Al(H_3L) \cdot 4H_2O$ .* The point of initial precipitation was clearly evident from the recorded potential. When precipitation occurred, the potential began drifting and no steady value was obtained even after several hours. This behaviour was found to be a reliable indication of the onset of precipitation provided  $C/B \geq 0.3$ . In order to determine the solubility product, defined according to the equilibria (10),



a separate titration with  $C/B=1$  was performed where the precipitate was allowed to equilibrate with the solution. During a 24 h period,  $E$  was continuously measured. No stable potential was obtained; in fact, a constant drift of about 0.05 mV per hour was found, indicating equilibria (10) to be very sluggish or some misbehaviour of the glass electrode. At the present time no efforts have been made to equilibrate the solid phase for longer periods. This probably would yield an accurate value of  $k_s$ , provided the extreme oxygen sensitivity of gallic acid, under the conditions needed for this examination, can be eliminated.

However, in an attempt to give an approximate value of  $k_s$  for freshly precipitated  $H_{-3}Al(H_3L)$ , the

concentration of the  $-3,1,1$  species ( $AIL$  or  $Al(OH)HL$ ) was calculated in the last stable point (no precipitate present) in each titration. These points (in total 23 of which 5 are from the alkaline side of the precipitate) are all  $\leq 0.1$  lg  $h$  units from the precipitation limit. In Fig. 4 the calculated values of  $[AIL]$  are plotted as a function of  $C/B$ , and as can be seen  $[AIL]$  seems to be constant within the  $C/B$  range in question, giving  $\lg k_s = -6.2 \pm 0.5$ . If it is assumed that equilibrium with the precipitate is reached within 24 h, the value  $-6.1$  in  $\lg k_s$  is obtained (filled symbol in Fig. 4).

## DISCUSSION

The present study completes the investigation of the ability of gallic acid to form complexes with the  $Al^{3+}$  ion. A compilation of proposed complexes and corresponding formation constants from this and the Part 1 investigation is given in Table 1.

In the present study evidence for the formation of ternary polynuclear complexes is given. The distribution diagrams in Fig. 5 show that the complexes with  $p,q,r$  notations  $-5,3,1$  and  $-9,4,3$  are both formed in significant amounts ( $\sim 25$  % of  $B$ ). It can also be noted that these species are formed within concentration ranges where hydrolysis of the  $Al^{3+}$  ion must be taken into consideration in the evaluation of the equilibrium model.

It has also been shown that a solid phase with the composition  $H_{-3}Al(H_3L) \cdot 4H_2O$ , is formed, and an approximate solubility product of this phase has been calculated. In Fig. 6, the approximate existence area of this solid is visualized.

Concerning the structures of the species formed, an investigation of this kind gives no direct information. Applying such aspects on the problem, however, often make the interpretation of data easier. In Ref. 1 we made comparisons with some crystal data and with other investigated  $Al^{3+}$ -organic acid systems and found it conceivable that the complexation took place between  $Al^{3+}$  and two *ortho*-coordinated phenolic groups. The same approach concerning the complex  $H_{-5}Al_3(H_3L)^{4+}$ , however, leads to very unrealistic structures. If, on the other hand, we assume that the complex is a carboxylate complex it is possible to write it as  $Al_3(OH)_4(H_2L)^{4+}$ , thus confirming the connection found earlier in several systems between the binary hydrolysis and the ternary species formed. The fact

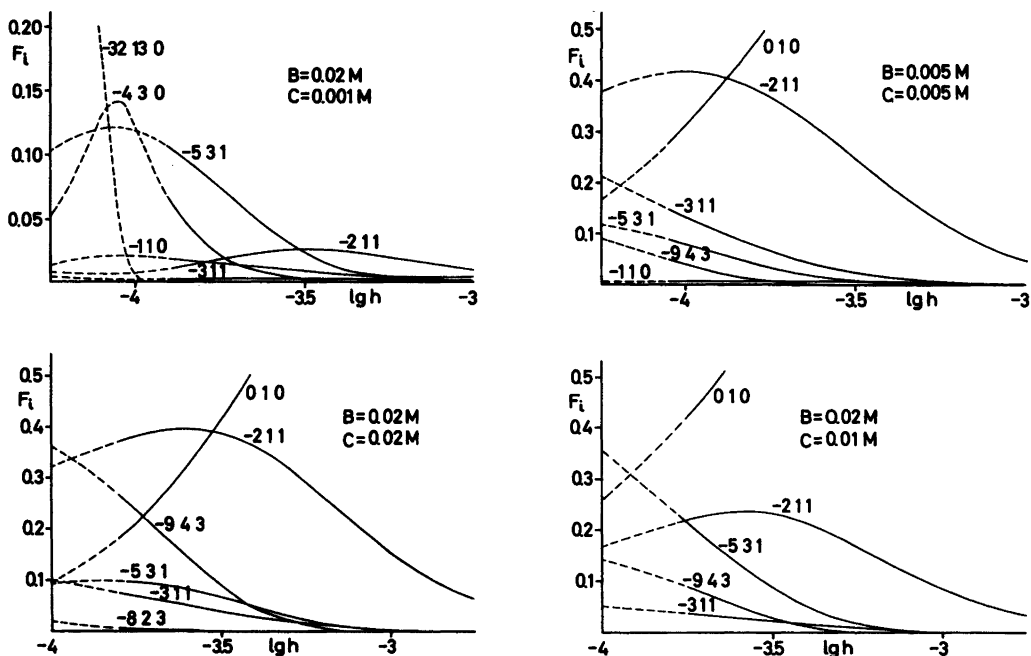


Fig. 5. Distribution diagrams  $F_i(\lg h)_{B,C}$ .  $F_i$  is defined as the ratio between aluminium(III) in a species and total aluminium(III). The calculations have been performed using the computer program SOLGASWATER<sup>6</sup> with constants given in Table 1. In order to make the figures clear the species  $\text{Al}^{3+}$  has been omitted in part of the diagrams.

that a complex of the same composition is obtained in the system  $\text{Al}^{3+} - \text{OH}^- - \text{CO}_2(\text{g})$  ( $\text{Al}_3(\text{OH})_4(\text{HCO}_3)^{4+}$ ), also provides strong support for this idea.

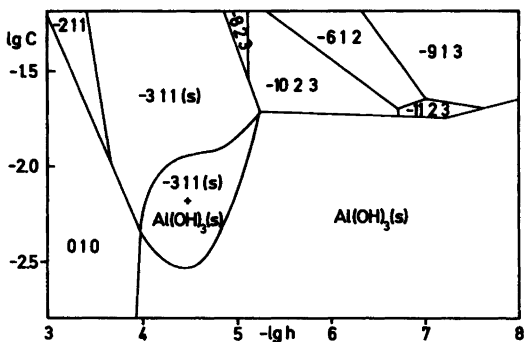


Fig. 6. Predominance area diagram for the different aluminium(III) gallic acid species. The equilibrium constants for  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_4^-$  and the solubility product for  $\text{Al}(\text{OH})_3$  are those given by Baes and Mesmer.<sup>7</sup> The calculation is performed at a total aluminium concentration of 10 mM using the computer program SOLGASWATER.<sup>6</sup>

Having *o*-diphenolic complexation at high  $C/B$  quotients and carboxylic complexation at low quotients then makes it reasonable to assume that both sites should be active in some middle quotient range. Such behaviour would then strongly promote the occurrence of chain complexes of different lengths. If we consider those tri-, tetra- and pentanuclear complexes giving the best fit in the quotient range  $0.5 \leq C/B \leq 2$ , they could all be written as  $\text{Al}_n(\text{L})_{n-1}^{3+}$ ;  $n=3, 4, 5$ . As a consequence, we have decided to regard the best fitting species,  $\text{Al}_4(\text{L})_3^{3+}$ , as a type of average complex, giving the mean length of the chains in solution.

With regard to the solid phase, we find it plausible that its building blocks are the complex  $(-3,1,1)$ , *i.e.*  $\text{AlL}$  or  $\text{Al}(\text{OH})(\text{HL})$ , found in solution. The four water molecules (or three water molecules and one hydroxyl ion) found, probably completes the oxygen octahedron around  $\text{Al}^{3+}$ . Extensive work is now in progress to prepare a single crystal of this phase for X-ray determination.

*Acknowledgements.* We thank Professor Nils Ingri for much valuable advice, for his great interest

and for all the facilities placed at our disposal. The English of the present paper has been corrected by Dr. Michael Sharp. The work forms part of a program financially supported by the Swedish Natural Science Research Council.

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Received May 8, 1981.